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## Quantification of Hydrogen Cyanide in Fire Effluent

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### Abstract:

Hydrogen Cyanide (HCN) is often the most toxicologically significant component in fire effluents from nitrogen-containing materials. Unlike the other major asphyxiant, carbon monoxide, sensors for continuous HCN quantification, at and above dangerous concentrations, are not commercially available. This paper investigates the analysis of fire effluent captured in bubbler solutions, by colorimetric quantification of HCN 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 one year. Alkaline bubbler solutions, through which the fire effluent has passed, showed consistent cyanide concentrations, for samples stored between 5°C and 35°C, for up to 31 days after sampling. The effect of other common ions likely to be present in fire effluent solution samples ( $\text{CO}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ ) was investigated for their potential interference. The most significant interference was sulphite which reduced the apparent cyanide concentration by 13% at 10 mg L<sup>-1</sup>  $\text{SO}_3^{2-}$  concentration.

### 1. 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 lead to incapacitation, due to respiratory tract and eye irritation, followed by asphyxiation as the major cause of death and injury [1], [2], [3], [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], [8], [9] [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], [12], [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 foams [19], 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 ( $0.1 \text{ mol L}^{-1}$ ) trapping HCN as cyanide ( $\text{CN}^-$ ) 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], [24], [25], [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 19701 [27] 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 specialized 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 19702 [29] 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 contains overlapping peaks and requires 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 hydrogen cyanide 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], [32], [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 cyanide (a), collected in the bubbler, being oxidized 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  $\lambda = 638 \text{ nm}$  [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 optimized 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.

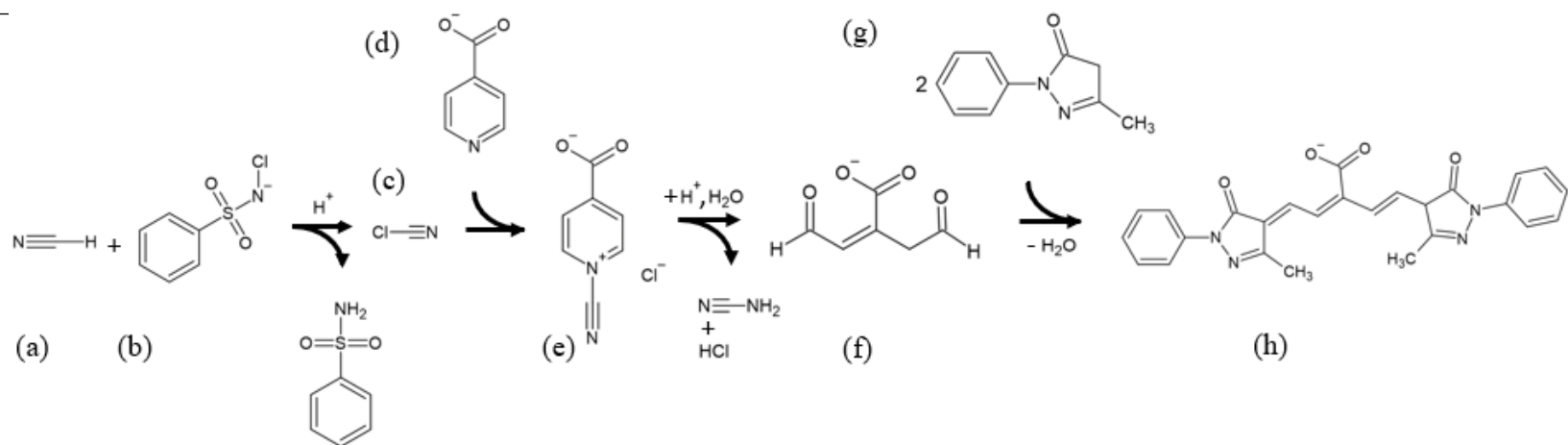
## 2. Material and Methods

### 2.1 Sample preparation

**Cyanide standard solutions** A 500 mg L<sup>-1</sup> stock cyanide solution as CN<sup>-</sup> 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<sup>-1</sup>, 0.8 mg L<sup>-1</sup>, 2.0 mg L<sup>-1</sup>, 5.0 mg L<sup>-1</sup> and 8.0 mg L<sup>-1</sup> by dilution of an intermediate cyanide solution of 20 mg L<sup>-1</sup> (10 mL of stock cyanide solution made up to made up to 250 mL with 0.1 mol L<sup>-1</sup> 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<sup>-1</sup> cyanide and one of five potentially interfering ions. To simulate fire gases containing CO<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub>, NO, and NO<sub>2</sub>, respectively, sodium salts of CO<sub>3</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> (Sigma Aldrich, analytical grades) were added to obtain ion concentrations of 1.0 mg L<sup>-1</sup> and 10 mg L<sup>-1</sup> as the ion in solution. A total of 20 cross-sensitivity solutions were prepared as two sets of the 1 and 10 mg L<sup>-1</sup> 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 maximize absorption, but avoid blockage by soot), containing 150 mL of 0.1 mol L<sup>-1</sup> NaOH at an effluent sampling volume rate of 1 L min<sup>-1</sup> (flow verified using a PFM71-F01-F flow sensor, SMC, Japan) for three to five minutes, and the total volume of sampled effluent was recorded. After immediate testing, approximately 4 hours 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.



**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.

## 2.2 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<sup>-1</sup> NaOH adjusted to pH = 7.0 by 1 mol L<sup>-1</sup> hydrochloric acid (HCl)) and made up to 250 mL with distilled water); phosphate buffer, 19.8 g sodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>) to 300 mL distilled water, adjusted to pH = 7.2 with potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub> 200 g L<sup>-1</sup>), and made up to 500 mL with distilled water). **Reagents A and B** were prepared freshly on each test day.

## 2.3 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 mm 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<sup>-1</sup> NaOH was employed as a blank, and standards were included in all analyses. Subsequently, the gas phase hydrogen cyanide concentration of fire atmosphere can be calculated in g L<sup>-1</sup> of effluent according to §5.4.1.9 of ISO 19701.

Absorbance ( $\lambda = 638$  nm), in 10 mm and 40 mm cuvettes of five standard cyanide solutions (0.3, 0.8, 2.0, 5.0 and 8.0 mg L<sup>-1</sup>) was determined regularly during the storage period of one 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<sup>-1</sup> cyanide standard was collected on five separate occasions at two wavelengths corresponding to the red and blue colours (543 nm and 638 nm, using 10 mm cuvette) for 90 min in total. Temperature dependence was tested by reacting an 8.0 mg L<sup>-1</sup> 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 nm and 638 nm for 90 min.

## 3. Results

### 3.1 Repeatability

Table 1 lists average absorbance, absolute, and relative (%) standard deviations (SD) from repeatability tests in two different cuvettes (10 mm and 40 mm) on the same UV-visible spectrophotometers for the five stored standard cyanide solutions, determined over a period of one 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<sup>-1</sup> 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 [CN<sup>-</sup>] concentrations (28 min after addition of **reagent B**).

Table 1. Repeatability test over 12 months (reaction temperature 21°C). Absorbance (A) of the standard cyanide solutions for 40 mm and 10 mm cuvettes with standard deviation (SD).

Absorbance ± SD (%)		
[CN <sup>-</sup> ] / mg L <sup>-1</sup>	40mm 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*	0.806 ± 0.024 (3 %)
8.0	NA*	1.207 ± 0.060 (5 %)

\*The 40 mm cuvette does not give linear absorbance above 2.0 mg L<sup>-1</sup> [CN<sup>-</sup>] but provides greater sensitivity at [CN<sup>-</sup>] < 2.0 mg L<sup>-1</sup>.



Fig. 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 mol L<sup>-1</sup> NaOH), and standard cyanide solutions.

Figure 2 shows the linearity of the absorbance of the polymethine dye product as a function of cyanide concentration over the range 0.3 to 8 mg L<sup>-1</sup>, using the repeatability data presented in Table 1.

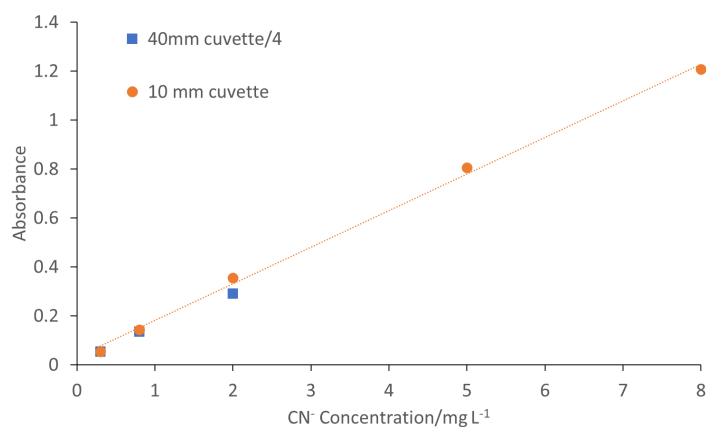


Fig. 2. Variation of Absorbance with CN<sup>-</sup> concentration



### 3.2 Time/temperature dependence of colorimetric reaction

Fig. 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<sup>-1</sup> standard cyanide solution measured at two wavelengths (543 nm and 638 nm) expressed as a fraction of maximum value.

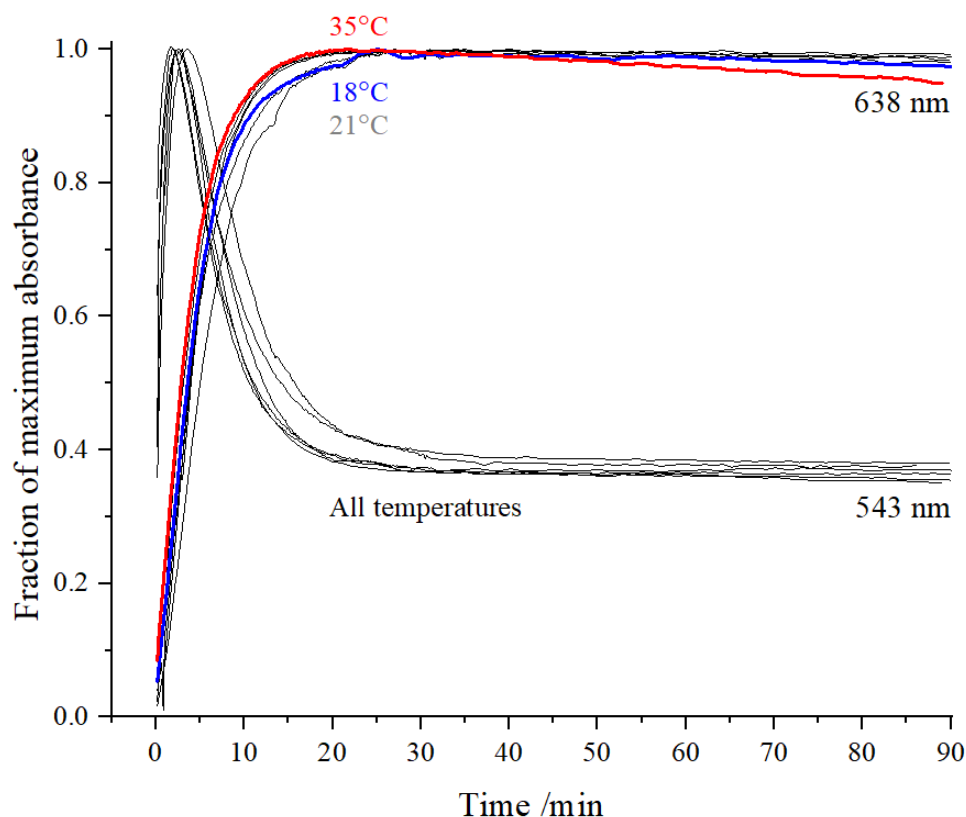


Fig. 3. Temperature dependence of colorimetric reaction plotted as absorbance at 543 nm and 638 nm versus time after addition of **reagent B** (18°C, 21°C and 35°C), as a function of maximum absorbance. Line colours for 638 nm curves show reagent storage temperature.

Regardless of the reagent temperature, Fig. 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, 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 minutes (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.

### 3.3 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 hours 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.

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

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

### 3.4 Cross-sensitivity

Fig. 4 summarizes the effects of analysing a 2.0 mg L<sup>-1</sup> cyanide solution when CO<sub>3</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, or NO<sub>3</sub><sup>-</sup> were added at concentrations of 1 mg L<sup>-1</sup> or 10 mg L<sup>-1</sup> (Fig. 4A and 4B, 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<sup>-1</sup>, Fig. 4A shows that carbonate and sulphate have negligible effect on the quantification of cyanide (2.0 mg L<sup>-1</sup>). At 1 mg L<sup>-1</sup> sulphite reduced the apparent concentration of cyanide by approximately 0.25 mg L<sup>-1</sup> (9.5 to 12.5 %), and both nitrite and nitrate reduced the apparent concentration of cyanide by approximately 0.20 mg L<sup>-1</sup> (7 to 8 %). Increasing the interfering ion concentrations to 10 mg L<sup>-1</sup>, Fig. 4B, 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<sup>-1</sup>, 7.5 to 13 %). Surprisingly, sulphite displays the largest reduction in the apparent concentration of cyanide on the day of measurement (about -0.50 mg L<sup>-1</sup>, 26 to 28 %), which came closer to the actual concentration after 24 hours (about -0.25 mg L<sup>-1</sup>, 13 %). On no occasion did the addition of these ions result in an increase in the measured cyanide concentration.

## 4. Discussion

### 4.1 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 Fig. 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 [33], [35], [40]. Interestingly, Fig. 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], [41].

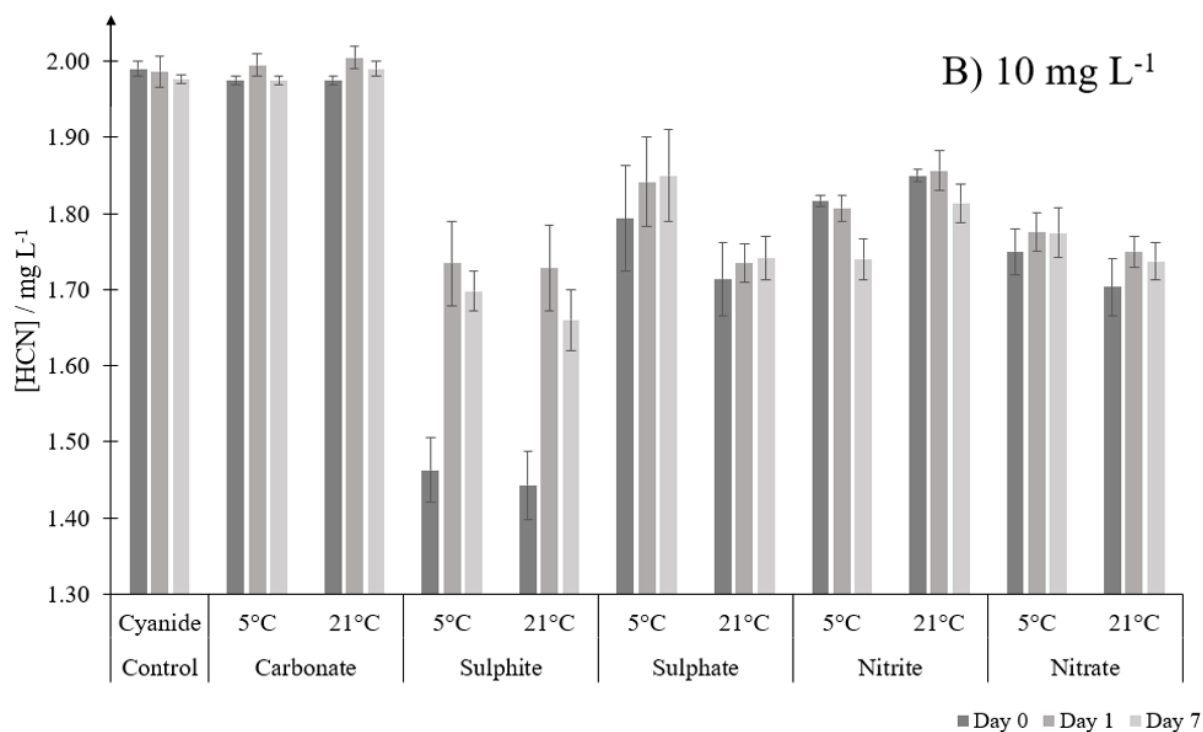
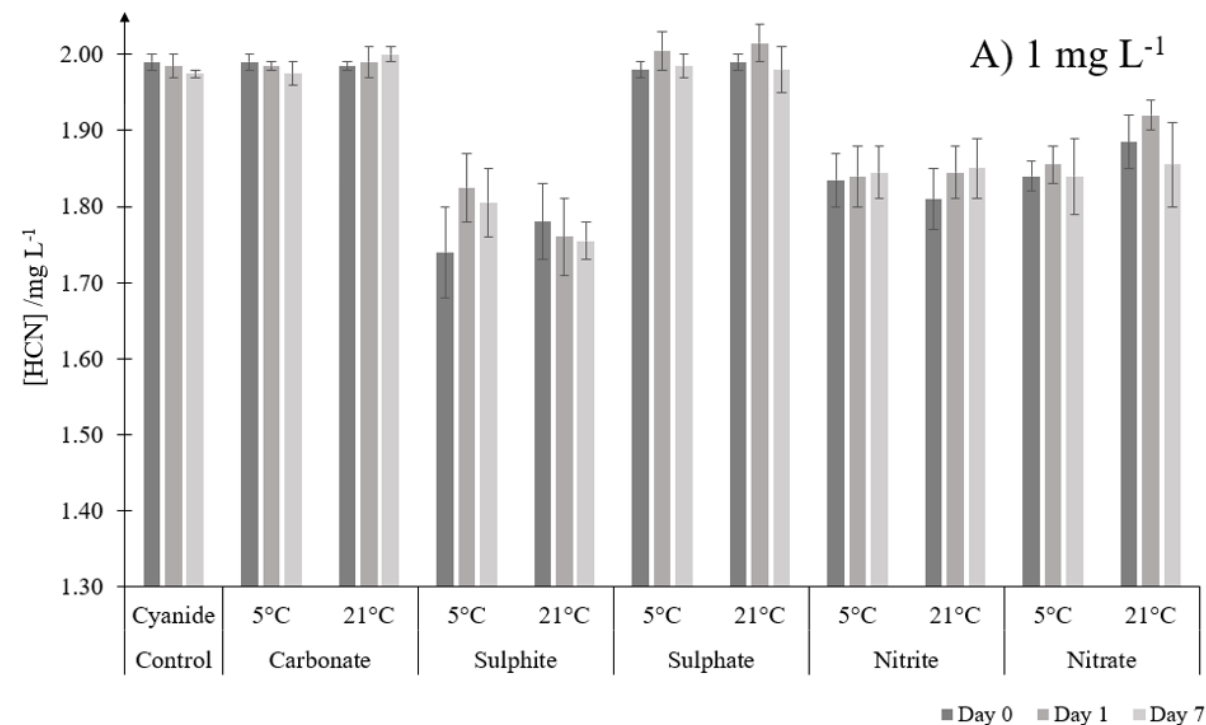


Fig. 4. Cross-sensitivity tests on a  $2.0 \text{ mg L}^{-1}$  cyanide concentration. Potentially interfering ion concentrations of  $1 \text{ mg L}^{-1}$  (A) and  $10 \text{ mg L}^{-1}$  (B) after 0, 1 and 7 days for samples stored at  $5^\circ\text{C}$  and  $21^\circ\text{C}$ , respectively. Note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

Within the chosen analytical window, table 1 summarizes the repeatability of quantifying standard cyanide solutions. For cyanide concentrations above  $2 \text{ mg L}^{-1}$ , uncertainty is around 3 % if a 10 mm cuvette is used. For concentrations less than  $2 \text{ mg L}^{-1}$ , a 40 mm cuvette will result in similar uncertainty (below 4 %). Hence, below  $2 \text{ mg L}^{-1}$ , a 40 mm cuvette is preferable, but in practice both cuvettes are used during data collection. Further, it has been shown in Section 3.1 that standard cyanide solutions are stable after storage in a refrigerator over a period of one year. This is in contrast to the requirements to prepare fresh standards daily in ISO 19701 [27] and elsewhere [42]. From the results in Figs. 2 and 3 and table 1, the colour development in Fig. 1 appears to be a reliable indicator of cyanide concentration. Consequently, the 70 min analytical window allows for batch analysis of samples.

#### 4.2 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 ( $\text{pK}_a = 9.31$  [43]), is trapped in its anionic form [22]. ISO 19701 states that the effluent shall be drawn through a fritted bubbler tube containing 20 mL  $0.01 \text{ mol L}^{-1}$  NaOH solution at a flow rate of  $0.4 \text{ L min}^{-1}$  for 4 to 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  $\text{CO}_2$  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  $0.1 \text{ mol L}^{-1}$  NaOH at  $1 \text{ L min}^{-1}$  over 3 to 5 min. Further, 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  $0.01 \text{ mol L}^{-1}$  of NaOH, the absorbing solution contains  $0.0002 \text{ mol OH}^-$ . Sampling effluent containing 100 ppm HCN for 5 min at  $0.4 \text{ L min}^{-1}$  results in 2 L of effluent being sampled into solution, thus containing  $0.0002 \text{ L HCN}$  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 %  $\text{CO}_2$ , this results in  $0.25 \text{ L CO}_2$ , or approximately 0.01 mol, which would neutralise all the  $\text{OH}^-$  ions in the bubbler. (In aqueous solution,  $\text{CO}_2$  exists in equilibrium with carbonic acid ( $\text{H}_2\text{CO}_3$ ) for which  $\text{pK}_{a1} = 6.37$  and  $\text{pK}_{a2} = 10.32$ . As the first  $\text{pK}_a$  is significantly lower than that of HCN, dissociation of carbonic acid would reprotonate the HCN, allowing trapped  $\text{CN}^-$  to escape from the bubbler solution, or neutralise the alkalinity so the slightly soluble HCN gas was not trapped). Therefore, using  $0.1 \text{ mol L}^{-1}$  NaOH ensures sufficient alkalinity for trapping HCN gas, and allows greater effluent volumes to be collected, minimising dead volumes in tubes etc. 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  $0.1 \text{ mol L}^{-1}$  NaOH bubbler solution is that its greater alkalinity will stabilise the  $\text{CN}^-$  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<sup>-1</sup> NaOH and 0.1 mol L<sup>-1</sup> NaOH was not investigated directly in the current work.

### 4.3 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<sup>-1</sup> 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 [44]. Additionally, Fig. 4 shows that the measured apparent concentration of cyanide is independent of storage temperatures (5 °C, 21°C) and storage over 0 to 7 days. Hence, fire effluent solutions collected in 0.1 mol L<sup>-1</sup> 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.

### 4.4 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<sub>2</sub>, O<sub>2</sub>, NO, or NO<sub>2</sub> in alkaline solution [43], [45]. The resultant cyanate may slowly decompose to form carbonate ions (negative interference) [46]. 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<sub>x</sub>S<sup>2-</sup> (with formation of thiocyanate, SCN<sup>-</sup>), elemental sulphur S<sub>8</sub>, (second order ring opening reaction resulting in formation of thiocyanate), and thiosulphate S<sub>2</sub>O<sub>3</sub><sup>2-</sup> (with formation of sulphite (SO<sub>3</sub><sup>2-</sup>) and thiocyanate) [43], [47], [48]. 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 [49]. However, in fire atmospheres these sulphur compounds (i.e., S<sub>x</sub>S<sup>2-</sup>, S<sub>8</sub>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, SCN<sup>-</sup>) are rarely found even when burning sulphur-containing materials, as the released SO<sub>2</sub> and SO<sub>3</sub> gases dissolve in alkaline aqueous solution to form sulphite (SO<sub>3</sub><sup>2-</sup>) and sulphate (SO<sub>4</sub><sup>2-</sup>) ions [50].

Early interference studies from Epstein, showed no interferences from carbonates, borates, chlorides, ammonium/sodium salts, cyanate, oxalate, ferri/ferrocyanides and sulphates. Further, 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 [51].

However, in this work cross-sensitivity mainly arises from the presence of sulphite ( $1 \text{ mg L}^{-1}$ , Fig. 4A). At  $10 \text{ mg L}^{-1}$  the losses increase to 26 to 28 % when tested immediately but decreased to 13 % after 24 hours (Fig. 4B). Even though sulphite ions are reported to react with cyanogen chloride [52], [53], 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  $\text{CO}_2$  in fire gas could acidify the absorbing solution sufficiently to prevent trapping of hydrogen cyanide. The combination of optimized sampling conditions and the data in Fig. 4 indicate that, apart from the effect on trapping by the absorbing solution, carbonate (and bicarbonate) have negligible effect on the analysis.

Well-ventilated fire conditions, where high concentrations of  $\text{NO}_x$  are formed, generally produce low HCN concentrations [54], [55]. Fig. 4 shows losses in cyanide quantification range from about 7 % at  $1 \text{ mg L}^{-1}$  to about 13 % at  $10 \text{ mg L}^{-1}$ , possibly due to oxidation of cyanide [56]. Hence, interferences from  $\text{NO}_x$  products could result in 7 to 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  $\text{NO}_x$  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  $\text{S}_x\text{S}^{2-}$ ,  $\text{S}_8$ ,  $\text{S}_2\text{O}_3^{2-}$ , and  $\text{SCN}^-$  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 to 13 % was observed from  $\text{SO}_3^{2-}$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$  present at  $1 \text{ mg L}^{-1}$  and  $\text{SO}_4^{2-}$  at  $10 \text{ mg L}^{-1}$ , but negligible effect of  $\text{CO}_3^{2-}$  even if present at  $10 \text{ mg L}^{-1}$  in the fire effluent solution.

## 5. Conclusions

An optimized 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  $21^\circ\text{C}$  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  $18^\circ\text{C}$  to  $35^\circ\text{C}$  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 mm or 40 mm, the latter preferred for quantifying  $2 \text{ mg L}^{-1}$  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  $10 \text{ mg L}^{-1}$  of  $\text{CO}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$  ions to  $2 \text{ mg L}^{-1}$  cyanide solutions, storing at  $21^\circ\text{C}$  for a week and analysing.

The work demonstrates the enhanced stability and repeatability of the analysis. An optimized 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.

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### CRedit

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