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## The latest developments in quantifying cyanide and hydrogen cyanide

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## ABSTRACT

Cyanides are highly poisonous in small quantities, yet are used in a variety of applications on a daily basis amounting to a global annual usage of around 1.1 million tonnes. With the usage of cyanides not decelerating, it is imperative for analytical chemists to devise methods of detection to ensure safe usage and working conditions, and to determine concentrations in the blood of patients who may have been over-exposed to cyanides or in the breath of sufferers from cystic fibrosis who contract HCN-producing bacterial infections. This review introduces the synthesis and the occurrence of cyanides before disseminating several examples of recent analytical protocols tailored towards the detection of cyanides within a range of media.

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## 1. Introduction

Hydrogen cyanide, also commonly referred to as prussic acid, hydrocyanic acid and formic ammonide, is a triatomic linear molecule that exists primarily as HCN, although its highly unstable tautomer, HNC, is known to exist particularly within the interstellar medium where its abundance is similar to HCN [1]. HCN is infamous as a highly poisonous room-temperature liquid with a lethal dose, LD<sub>50</sub>, reportedly being in the range of 150–173 ppm (178–206 ppmv) *via* inhalation for a 30-min exposure time [2,3]; but, it can also cause fatalities upon contact with skin or through ingestion. Irrespective of the administration route, concentrations over

1 ppm (1.2 ppmv) in any form are generally considered to be toxic [4]. Despite the health and safety concerns surrounding HCN, it is the simplest source of the cyanide ion, CN<sup>-</sup>, which is utilized in the synthesis of a plethora of commonly used compounds [5] and polymers [6], and in noble metal mining [7], medicine [8] and pest control [9]; there are many more uses for cyanide – a more comprehensive list of uses is described in a review by Mudder and Botz [7].

## 1.1. Production and natural occurrence

As of today, cyanide usage equates to an annual mass of approximately 1.1 million tonnes [10]. This extremely large amount of cyanide utilized industrially per annum is indicative of the extensive commercial demand. The majority of industrially synthesized HCN is utilized for the manufacture of Perspex and nylon [11], and is produced from one of three common industrially utilized HCN

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production processes. These are the Andrussov process, the Degussa process, and the SOHIO process. All three processes synthesize HCN from ammonia in various ways, as highlighted by Cummings [11]. Current research into improving the production methods focuses primarily upon changing the catalyst in the reaction. As with most industrial catalysts, the aim for researchers is to reduce cost and weight whilst improving yield; routes for HCN synthesis are beyond the scope of this review, but interested readers are referred to Dietz III et al. [12].

HCN is a naturally occurring molecule, albeit in very low abundances. Cyanogenic species are present in common foodstuffs, such as apples, mangoes and rapeseed [13]. It is widely accepted that cyanogenic species are present within plants as a defense mechanism against herbivores [13]; larger mammalian species, such as human beings, are unlikely to be affected by the low levels of HCN present within such foodstuffs. HCN is also used as a defense mechanism by insects and some animals. Certain types of millipede are also known to secrete HCN [14] whilst under attack from suspected perpetrators. Trace amounts of HCN are also exhaled by human beings; primitive investigations in the late 1980s hypothesized that HCN was produced in the airways of human beings as concentrations in breath far superseded the levels found in blood [15]. There is a review [16] for readers interested in the metabolism and the breakdown products of cyanides.

## 1.2. Academic and commercial interest

Cyanide is of interest to analytical chemists due to its profound acute and chronic toxicity which can lead to blood, cardiovascular, and nervous system disorders [2]. High acute levels of exposure can even cause death, usually by suffocation. Cyanide restricts the functionality of an enzyme in mitochondria called cytochrome c oxidase [17], which is responsible for the metabolism of oxygen from blood in the electron transport chain process, which creates the majority of the ATP produced through respiration [18]. While HCN concentrations are generally low and naturally it occurs in almost infinitesimally small amounts (at least, not enough to affect human beings), it is nonetheless prevalent in specific circumstances. For example, HCN is abundant in fire smoke [19], particularly if plastic is being combusted. Consequently, sufferers of acute smoke inhalation may harbor elevated levels of HCN in the blood for prolonged periods after an incident [20,21] and should be monitored to uncover progress of bodily repair. Also, cyanide concentrations are reported to increase after mortality [22]. Also, in the mining industry, cyanides are utilized abundantly to create noble-metal salts. Any gaseous HCN must be closely monitored to avoid suffocation in these mines. Additionally, the lungs of cystic fibrosis (CF) sufferers accommodate HCN-producing bacteria due to the composition of the patient's mucus being specifically favorable for such types of bacteria [23], leading to attempts to design gas sensors to monitor HCN in exhaled breath.

As a consequence of the hazards associated with cyanides, it is imperative that strategies are devised to detect cyanides.

## 2. Analytical detection strategies

A concise overview of reported analytical methods until 2004 is presented in the literature by Lindsay et al. [20]. Their review covers a vast array of analytical techniques, including colorimetry, gas chromatography (GC), and electrochemistry for the detection of cyanides in blood. Typically, when analyzing concentrations of a target analyte in the blood, the extraction method is as important as the analytical technique. The review by Lindsay et al. summarizes all the extraction methods available {which include microdiffusion [24], acidification [25], derivatization [26], and headspace [27]} for the sample-treatment process [20]. Another

review regarding cyanide detection focuses upon organic optical sensors only [28].

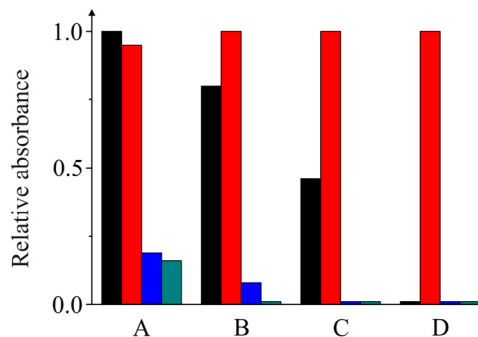
A more extensive review was written by Ma and Dasgupta [29] and covers a broad spectrum of analytical techniques for the detection of cyanides. The methods described in their review include optical sensors [30], GC [31,32], quartz-crystal microbalance (QCM) [33], mass spectrometry (MS) [31] and electrochemical detection (ECD) [34].

This review aims to provide readers with a more up-to-date selection of analytical detection strategies that could be utilized and/or developed into useful cyanide-detection platforms. Since 2009, research has focused primarily upon chromogenic optical sensors [28], fluorescence spectroscopy [35], MS [36], GC [37], QCM [38–40] and ECD [41,42]. We outline and discuss some of these techniques in this review.

### 2.1. Naked-eye detection – chromogenic sensors

Chromogenic sensors are chemical sensors that are tailored to change color when a molecule reacts with a specific analyte. Thus, in the case of chromogenic HCN sensors, a color change is observed by the naked eye when HCN reacts with the sensor. In the case of the basic  $\text{CN}^-$  ion, an interaction with a target molecule invokes hydrogen bonding or proton exchange [43]. Though not used prominently with HCN (far more commonly with solution-based cyanides), there have been some successful efforts to create such sensors.

Literature reports describe laboratory-synthesized molecules, such as 4-(4-nitrobenzylideneamine)-2,6-diphenylphenol, as highly specific anionic chromogenic sensors for the detection of a small range of anions ( $\text{F}^-$ ,  $\text{CN}^-$ , and  $\text{H}_2\text{PO}_4^-$  and  $\text{CH}_3\text{COO}^-$  in smaller intensities) [43]. Marini et al. reacted tetra-*n*-butylammonium salts of nine different anions in acetonitrile with the starting precursor to reveal a color change from a pale yellow to a deep royal blue that appears as a result of the deprotonation of 4-(4-nitrobenzylideneamine)-2,6-diphenylphenol due to the presence of strongly electronegative anions [43]. The intensity of the color change is measured via UV/Vis spectrophotometry, where a  $\lambda_{\text{max}}$  is recorded in the visible light region at 592 nm, which is typical of the deprotonated product. Interestingly, though this system detects a few different anions, the specificity of this system towards  $\text{CN}^-$  can be further tailored by changing the relative basicity of the anionic species by introducing small percentages of water into the solvent. A water percentage (in acetonitrile) of just 2.4% (v/v) obliterates the observed  $\lambda_{\text{max}}$  for all but the  $\text{CN}^-$  species, and occurs as a result of the relative basicity of the anions (except for  $\text{CN}^-$ ) decreasing, as depicted graphically in Fig. 1 [43]. Thus, through diligent tailoring of the chemical system



**Fig. 1.** Relative absorbance for: (black)  $\text{F}^-$ ; (red)  $\text{CN}^-$ ; (blue)  $\text{CH}_3\text{COO}^-$ ; and (green)  $\text{H}_2\text{PO}_4^-$  added to solutions of 4-(4-nitrobenzylideneamine)-2,6-diphenylphenol in acetonitrile with: (A) 0% water; (B) 0.5% water; (C) 1.2% water; and, (D) 2.4% water. {Redrawn from [43] with permission from Arkat USA}.

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