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Headspace single-drop microextraction and cuvetteless microspectrophotometry for the selective determination of free and total cyanide involving reaction with ninhydrin

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ABSTRACT

Headspace single-drop microextraction has been used for the determination of cyanide with ninhydrin in combination with fibre-optic-based cuvetteless microspectrophotometry which accommodates sample volume of 1 μL placed between the two ends of optical fibres, and has been found to avoid salient drawbacks of batch methods. This method involved hydrocyanic acid formation in a closed vial, and simultaneous extraction and reaction with 2 μL drop of ninhydrin in carbonate medium suspended at the tip of a microsyringe needle held in the headspace of the acidified sample solution. The method was linear in range 0.025–0.5 mg L^{-1} of cyanide. The headspace reaction was free from the interference of substances, e.g., thiocyanate, hydrazine sulphate, hydroxylammonium chloride and ascorbic acid. Sulphide was masked by cadmium sulphate, nitrite by sulphamic acid, sulphite by *N*-ethylmaleimide, and halogens by ascorbic acid. The limit of detection was found to be 4.3 μg L^{-1} of cyanide which was comparable to existing most sensitive methods for cyanide. However, the present method is far more simple. The method was applied to acid-labile and metal cyanides complexes by treatment with sulphide when metal sulphides were precipitated setting cyanide ion free, and to iron(II) and (III) cyanide complexes by their decomposition with mercury(II), the mercury(II) cyanide formed was then determined. These pre-treatment methods avoided cumbersome pre-separation of cyanide by methods such as distillation or gas diffusion. The overall recovery of cyanide in diverse samples was 97% with RSD of 3.9%.

1. Introduction

Cyanide is known for its propensity to bind iron in cytochrome oxidase inhibiting the mitochondrial electron-transport chain and resulting in hypoxia. Consequently, cyanide is extremely toxic and even relatively small amounts of this species are lethal to humans [1]. The World Health Organization has set the maximum contaminant level of 70 μg L^{-1} of cyanide in drinking water [2]. The industrial activities that are responsible for cyanide generation and release into the environment include electroplating, metallurgy, electronic manufacturing, ore leaching, and production of nitriles, nylon and acrylic plastics. Motor vehicle exhaust and fire fumes, therapeutic treatment with sodium nitrosyl-pentacyanoferrate(III) (nitroprusside), pyrolysis of polymers that contain nitrogen, inhalation of tobacco smoke are some other sources of cyanide exposure. Dietary sources such as cassava roots, lima beans and bamboo shoots contain cyanogenic glycosides [3] which produce hydrocyanic acid (hydrogen cyanide) enzymatically after cell rupture. Cyanide has also been identified as a chemical terrorism agent. Besides cyanide and hydrocyanic acid, toxicologically important are also cyanide complexes of zinc(II), cadmium(II), copper(II), nickel(II), mercury(II) and silver(I), labelled as weak acid-dissociable (WAD) complexes, some of which can easily release cyanide in acidic medium, and iron(II) and (III) complexes which are relatively more stable but can be decomposed by sunlight.

Several analytical methods have been reported for the determination of cyanide in diverse sample matrices and relying on a range of experimental protocols and detection techniques. Most of these strategies, however, suffer from some disadvantages of requiring large sample sizes, long analysis times, multi-step procedures with cumbersome sample pre-treatments, high detection limits or use of sophisticated instrumentation which need special operational skill. Many of them also suffer the deleterious interference of other ions and substances which are commonly found in the environmental samples. While free cyanide can be directly determined by a wide variety of methods, such as headspace gas chromatography for hydrocyanic acid [4], sample preparation by distillation of acidified sample and collection of hydrocyanic acid in alkaline solution for analysis is frequently used for metal–cyanide complexes [5]. Iron(II) and (III) complexes which are normally found in petroleum

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refinery effluents have been reported as stubborn examples [6]. Simultaneous clean-up, pre-concentration and derivatization by headspace single-drop microextraction (SDME) [7] or hollow-fibre protected liquid-phase microextraction of hydrocyanic acid [8] and capillary electrophoresis (CE) with UV detection of the derivative tetracyanonickel(II) has been used for cyanide determination in biological samples; the acceptor phase of nickel(II) chloride, ammonium hydroxide and sodium carbonate played a critical role [8], and hydrogen sulphide interfered with the determination due to the precipitation of nickel(II) sulphide. The headspace gas chromatography and atomic emission detection for hydrocyanic acid [9] was unaffected by the presence of hydrogen sulphide, and gave about 15% higher results than the ion-selective electrode (ISE) method ostensibly due to the loss of hydrocyanic acid during the distillation step in ISE method to remove sulphide [10]. Thiocyanate was found to interfere in the determination of cyanide in blood by headspace gas chromatography with nitrogen–phosphorus detection [11]. Ethylenediamine together with dithizone was used for WAD cyanide complexes to liberate cyanide by a ligand displacement mechanism [12], which was determined by headspace formation of tetracyanonickel(II) and its CE [7]. A flow injection method for WAD cyanide complexes allowed skipping of separation step for interference by using a combination of thin-layer electroplated silver chalcogenide ion-selective membranes and electrochemical pre-treatment for release of bound cyanide [13]. Solid-phase reactors packed with cadmium carbonate [14], zinc carbonate [15] or silver carbonate [16] were placed in a single line flow injection-flame atomic absorption spectrometry system, when a metal cyanide complex was released on cyanide injection, and has been used for indirect determination of free cyanide. Many ions, though do not interfere, may deplete the solid reagents.

Separation of cyanide from its WAD complexes by gas diffusion, and flow injection derivatization with o-phthalaldehyde (OPA) and glycine to give a highly fluorescent product, which was measured [17], avoided many of the problems of widely used batch spectrophotometric method based on the Konig reaction [18]. The effect of several species on OPA and glycine reaction was also studied [19], only sulphide interfered when present in large amounts. Determination of free and total cyanide (sum of free and metal-complexed cyanide) was based on focused microwave irradiation of sample to distil hydrocyanic acid, which was collected in alkaline solution and analyzed by flow injection spectrophotometry utilizing the Aldridge reaction [20]. This method was much faster (10–20 min) and convenient than the traditional distillation methods (about 1 h). Hexacyanoferrate(II) and (III) (ferrocyanide and ferricyanide, respectively) required the presence of EDTA during distillation, and produced cyanide recoveries over 90%. Thiocyanate did not interfere, however, elevated levels of nitrate caused liberation of some cyanide due to oxidation of thiocyanate under the prevailing rigorous distillation conditions. Cyanide catalyzes the oxidation of phenolphthalin (colourless) by copper(II) in basic solution giving pink phenolphthalein, which can be measured spectrophotometrically [21]. It was necessary to measure the colour after a pre-determined period of time or to use 'a stabilizing agent,' that reduced copper(II), to quench the reaction. This problem was perhaps best avoided by conducting the reaction in flow injection mode where the reaction mixture was presented before the detector at exactly and reproducibly the same time [22]. Hexacyanoferrate(III), being oxidizing agent, also responded to the same colour reaction in the phenolphthalin method.

Cyanide and thiocyanate formed a coloured ternary complex with copper(II)-2,2′-dipyridyl-2-quinolylhydrazone that was extracted into chloroform in a flow injection manifold [23]; thiocyanate alone was determined after masking cyanide with formaldehyde. The azo dye, 2-methoxy-4-(4′-nitrophenylazo)aniline-*N*,*N*-bis(3′-propanoic acid), complexed with copper(II) giving a colour change from red to yellow; cyanide withdrew copper(II) from the complex and reversed the colour change [24]. Both copper(II) complex methods suffered from the interference of sulphide. Aquacyanocobester, which has a corrin ring with cobalt(III) in its centre and two axial substituents, a cyano group and a water molecule, showed replacement of coordinated water on reaction with cyanide leading to the colour change from orange to violet, which was measured [25,26]. This reagent is particularly free from the interference of thiocyanate and sulphide. Besides these metal complexes, some organic compounds have also been used as chromogenic reagents for cyanide. Coloured species were formed by the nucleophilic addition of cyanide to the imine group of 6-hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)-one [27] or to the indoline fragment of the oxazines, formed by fusion of benzo-oxazine ring to an indoline moiety [28,29], the colour was measured spectrophotometrically. All these organic reagents are commercially unavailable, and the methods reported using them are applicable only to free cyanide. These methods seem to be unaffected by thiocyanate, which has too slow reaction with the electrophilic cyclic structures, but the interference of sulphide is unknown. Recently reported are thiourea based chemosensors which respond to both cyanide and fluoride [30].

Ninhydrin (2,2-dihydroxy-1,3-indanedione) is commercially available reagent and has been used for cyanide, a method that was adapted from the detection of amino acids [31]. Indeed, cyanide gave a colour reaction with ninhydrin, which was the reason for high blank in amino acids analysis, and formed the basis of cyanide determination by batch spectrophotometry published by two independent research groups [32–34]. In sodium carbonate medium cyanide formed a red colour on reaction with ninhydrin, but it turned to blue in alkaline medium [32]. The method was rapid, simple and sensitive, and formed the basis of automated flow injection [35] and sequential injection spectrophotometry [36]. Though the mechanism of ninhydrin and cyanide reaction was elucidated earlier [37], the subsequent proposals showed disharmony [32,38]. Similarly, selectivity against sulphide was claimed [32,33], there were conflicting reports on the interference of thiocyanate and many metal ions. To attain selectivity, cyanide (as hydrocyanic acid) was removed from sample matrix by gas diffusion and determined using ninhydrin by a stopped flow-sequential injection analysis [39]. The features of diverse analytical methods for cyanide are presented in Table 1.

In the present work, the inherent shortcomings of analytical methods for cyanide involving ninhydrin have been circumvented by using headspace SDME and cuvetteless fibre-optics-based microspectrophotometry. SDME customarily results in high enrichment factor due to a large ratio (V_{aq}/V_o) of the volume of aqueous sample (V_{aq}) to that of organic phase (V_o) [40], and this new technique has of late been used in conjunction with NanoDrop® microspectrophotometer, which is equipped to accommodate sample volumes as small as 1 μL for absorbance measurement with high accuracy and reproducibility [41–47]. In the proposed method hydrocyanic acid that was liberated from free and acid-labile cyanides was extracted into an aqueous drop of ninhydrin held in the headspace, when the red colour developed was measured at 530 nm using NanoDrop® microspectrophotometer. Headspace extraction/reaction avoided the interferences of a number of reducing ions/substances which interfered in batch or flow injection methods, and eliminated the need for gas diffusion to achieve selectivity. Another advancement was determination of cyanide in its salts/complexes with mercury(II), silver(I), nickel(II) and copper(I), which are reported to give poor recovery for cyanide [12], by the addition of sodium sulphide when more stable metal sulphides were formed setting free cyanide ion; the excess sulphide was masked with cadmium(II). Finally, the method was extended