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Selective determination of cyanides by gas diffusion-stopped flow-sequential injection analysis and an on-line standard addition approach

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ABSTRACT

A highly selective sequential injection (SI) method for the automated determination of weak-acid-dissociable cyanides is reported. The analytical procedure is based on the on-line reaction of the analyte with ninhydrin in carbonate medium to form a coloured product (λ_{max} = 510 nm). Cyanides are removed from sample matrix by acidification through a gas-diffusion step incorporated in the SI manifold. The effect of instrumental and chemical variables was studied. By adopting an on-line standard addition protocol, the sensitivity of the proposed method was enhanced drastically, without affecting the determination range. The assay was validated in terms of linearity (up to 200 $\mu g\,L^{-1}$), limit of detection ($c_L = 2.5\ \mu g\,L^{-1}$), limit of quantitation ($c_Q = 7.5\ \mu g\,L^{-1}$), precision ($s_r < 2.5\%$ at 100 $\mu g\,L^{-1}$) and selectivity. High tolerance against critical species such as sulfides and thiocyanates was achieved. The applicability of the method was demonstrated by analyzing tap and mineral water samples at levels below the limits established by international E.U. and U.S. organizations. The percent recoveries were satisfactory in all cases, ranging between 94.2 and 103.6%.

1. Introduction

Cyanides comprise a wide range of compounds of varying degrees of chemical complexity, all of which contain a CN moiety, to which humans are exposed in gas, liquid, and solid form from a broad range of natural and anthropogenic sources. While many chemical forms of cyanide are used in industrial application or are present in the environment, the cyanide anion is the primary toxic agent, regardless of origin. Non-point sources of cyanide released to water can result from runoff from cyanide-containing anti-caking salts used on roads, migration from landfills, and agricultural and atmospheric fallout and washout. Point sources of releases to water include discharges from gold mining plants, wastewater treatment works, iron and steel production, and organic chemical industries [1]. From a toxicological point of view, cyanide is an irreversible inhibitor of the enzyme cytochrome *C* oxidase. The binding of cyanide to this cytochrome prevents transport of electrons from cytochrome *C* oxidase to oxygen. As a result, the electron transport chain is disrupted, meaning that the cell can no longer aerobically produce ATP for energy. Tissues that mainly depend on aerobic respiration, such as the central nervous system and the heart, are particularly affected [2].

The regulations on the use and allowed levels established by international authorities are updated continuously as new knowledge becomes available. Typical examples regarding drinking water include the following: The highest concentration of cyanide allowed in drinking water by the US EPA (Environmental Protection Agency) is 200 $\mu g\,L^{-1}$ [3]. The directive 1998/83 of the European Union on the quality of drinking water sets an even lower limit of 50 $\mu g\,L^{-1}$ [4], while the maximum amount of cyanides allowed in mineral waters according to directive 2003/40/E.U. is 70 $\mu g\,L^{-1}$ [5].

Spectrophotometry is the most “classic” and widely applied technique among official methods for the determination of cyanides in environmental samples, offering a quantitation limit of 5 $\mu g\,L^{-1}$ (EPA 9014-1) [6]. The method is based on conversion of the analyte to cyanogen chloride by chloramine-T followed by reaction with the pyridine (or alternatively isonicotinic acid [7] or γ-picoline [8])–barbituric acid system. Alternatively, flow injection (FI)-amperometry using a silver working electrode (OIA-1677) offers a working range of 2 $\mu g\,L^{-1}$ to 5 $mg\,L^{-1}$ [9], while potentiometry based on cyanide selective electrodes is less sensitive [10]. A serious drawback of the above-mentioned official methods is interference caused by sulfides. Typical approaches for selectivity enhancement include precipitation of sulfides by lead acetate followed by immediate filtration [11] and/or off-line distillation [12]. On the other hand, published studies during the last five years reporting the determination of cyanides cover almost all aspects of modern instrumental analysis (the values in parentheses corre-

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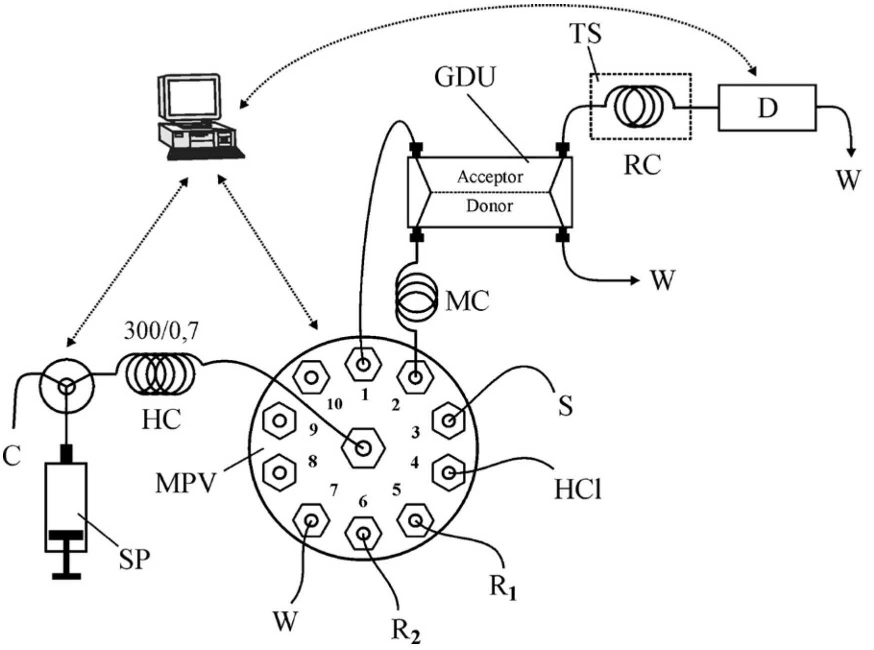

Fig. 1. Schematic depiction of the SI setup: C: water as carrier; SP: syringe pump (V = 1000 μL); HC: holding coil (V = 700 μL); MPV: multi-position valve; S: sample; HCl: 1.0 mol L^{-1} HCl solution; R_1: ninhydrin (5 mg mL^{-1}); R_2: acceptor (w(carbonate) = 1% + 200 μg L^{-1} CN^{-}); W: waste; MC: mixing coil (60 cm/0.5 mm i.d.); GDU: gas-diffusion unit; TS: thermostat; RC: reaction coil (60 cm/0.5 mm i.d.); D: spectrophotometric detector (λ_{max} = 510 nm).

spond to the reported detection limits of the methods): capillary electrophoresis (CE) after single-drop microextraction (2 μg L^{-1}) [13]; chemiluminescence (0.1 μg L^{-1}) [14]; indirect flame atomic absorption spectrometry (FAAS) using silver (60 μg L^{-1}) [15] or cadmium columns (200 μg L^{-1}) [16]; FI fluorimetry (20 μg L^{-1}) [17]; gas chromatography (GC) with either electron capture (ECD) (0.57 μg L^{-1}) [18] or mass spectrometric (MS) detection after solid phase microextraction (6 μg L^{-1}) [19]; ion chromatography with pulsed amperometric detection using standard (2 μg L^{-1}) [20] or disposable silver electrodes (1 μg L^{-1}) [21]; piezoelectric quartz crystal sensors using gold (2.7 μg L^{-1}) [22] or silver (2.2 μg L^{-1}) [23]; potentiometry using modified carbon paste electrodes (390 μg L^{-1}) [24]; surface modified CdSe quantum dots as luminescent probes (2.9 μg L^{-1}) [25]; amperometric (104 μg L^{-1}) [26] and optical sensors (63 mg L^{-1}) [27]; indirect adsorptive stripping voltammetry at a mercury electrode (0.26 μg L^{-1}) [28]; batch spectrophotometry based on the Berthelot reaction (30 μg L^{-1}) [29] or a revised phenolphthalein method (5 μg L^{-1}) [30]; FI spectrophotometry using aquacyanocobyrinic acid heptamethyl ester (20 μg L^{-1}) [31]; chemometrics based on partial least squares regression (8.7 μg L^{-1}) [32].

Sequential injection (SI) is considered to be the 2nd generation of flow injection analysis. In general it is based on the sequential aspiration of discrete zones of reagents and samples via a selection valve in a holding coil [33]. By reversing the pump flow the aspirated zones are propelled towards either the detector or other manifold components such as mini-columns, gas-diffusion units or even chromatographic columns based on monolithic materials [34]. SI offers significant advantages in terms of precise computer control, practically single-channeled manifolds, robustness and low reagents and sample consumption, finding numerous applications in all areas of analytical science [35–39].

Since the first report of coupling gas diffusion (GD) to FI [40], numerous reports have proven the advantages of such a “marriage” mainly in terms of selectivity, sampling throughput and preconcentration capabilities. On the other hand, there are relatively few studies on SI-GD, reporting determinations of ammonia [41–43], free chlorine [44], sulphide [45], sulphur dioxide [46] and dissolved carbon [47].

The present study reports a novel spectrophotometric assay for the determination of cyanides using SI-GD. The method is based on the on-line formation of gaseous HCN, passage through the hydrophobic membrane of the GD unit and subsequent reaction with ninhydrin in alkaline medium under strictly controlled conditions. This novel reaction has been reported recently in batch mode by two independent research groups [48–51] and using FI by Santelli et al. [52]. The developed analytical scheme offers significant advantages: fully automated procedures through computer controlled handling; high selectivity especially against sulfides and thiocyanates that are common interferents in many methods including official ones [6,9,10]; adequate sensitivity for the determination of the analyte in environmental samples with detection limits lower [15–17,19,24,26,27,29–32], or comparable [13,20–23,25] to recently reported procedures. The most sensitive methods in terms of detection limits are chemiluminescence-based – although without applications to real samples – [14], GC-ECD which involves an unattractive time consuming reaction step of the analyte with chloramine-T followed by extraction with n-hexane [18] and voltammetry that required several pre-treatment steps in order to avoid interferences from metals and fouling of the electrode due to absorption of organic matter [28]. Additionally, these procedures in many cases employ sophisticated and expensive instrumentation such as capillary electrophoresis [13] or GC–MS [19], are indirect using unattractive packed columns coupled to FAAS [15,16] or require chromatographic separation prior to detection [20,21] even when only cyanides were determined [21]. In terms of sample preparation and sampling rate, single-drop-microextraction prior to CE requires a 15 min extraction period [13], time consuming off-line distillation is often employed for selectivity enhancement [29,31], while a piezoelectric based approach can achieve a detection limit of 2.7 μg L^{-1} only after 60 min analysis time [22]. The applicability of the proposed assay was demonstrated by successfully analyzing mineral and tap water samples.