Talanta 77 (2009) 1620–1626

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Amperometric determination of cyanides at the low ppb level by automated preconcentration based on gas diffusion coupled to sequential injection analysis

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ARTICLE INFO

Article history:
Received 1 July 2008
Received in revised form
18 September 2008
Accepted 29 September 2008
Available online 1 November 2008

Keywords:
Cyanide
Gas diffusion
Sequential injection
Amperometric detection
Water samples

ABSTRACT

A simple, sensitive method for determining free cyanides is described. The assay is based on automated gas diffusion of the analyte using sequential injection analysis (SIA) coupled to amperometric detection on a silver working electrode. The effects of varying several parameters affecting the analytical procedure (including the flow rates of the donor and acceptor streams, the concentrations of the reagents and the sample volumes) were studied. The validity and quality of the method were also assessed, by examining its linearity, limits of detection and quantitation, precision, selectivity to potentially interfering substances. Its sensitivity can be enhanced by applying a simple preconcentration step, following which limits of detection were found to be 0.05–0.12 $\mu g\,L^{-1}$. Application of the proposed assay to the analysis of tap, mineral and table water samples spiked at concentrations ranging from 1 to 10 $\mu g\,L^{-1}$ CN^-, yielded satisfactory recoveries (88–112%).

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1. Introduction

Hydrogen cyanide and its simple sodium and potassium salts are among the most rapidly acting poisons affecting the central nervous system (CNS) of both animals and humans. Cyanides are both human-made and naturally occurring substances, which are released to the environment from industrial sources and car emissions [1] in addition to being present in plants of several species as cyanogenic glycosides and produced by certain bacteria, fungi, and algae.

Hydrogen cyanide is rapidly absorbed by the gastrointestinal and respiratory tracts, while in solution and possibly the concentrated vapor, it can be absorbed directly through the intact skin [2]. It exerts its toxic effects by forming a complex with the Fe(III) of mitochondrial cytochrome oxidase, thereby preventing use of oxygen by cells [3]. The most specific symptom in acute cyanide poisoning is the bright red color of venous blood, which provides evidence of the inability of the tissues to use oxygen [4].

Recommendations and regulations regarding its use and permitted levels are updated periodically as more information becomes available. Typical examples include the following [5]. The highest concentration of cyanide allowed in drinking water by the US EPA (Environmental Protection Agency) is 200 $\mu g\,L^{-1}$ or 0.2 ppm. Limits are also set for amounts of hydrogen cyanide in stored foods that have been treated with cyanide to control pests (e.g. 50 ppm for citrus fruits by the US EPA) and in workplace air (11 $mg\,m^{-3}$ averaged over an 8-h workday and 40-h workweek by the US Occupational Safety and Health Administration [1].

Official methods for determining cyanides in environmental samples are mainly based on spectrophotometric [6], potentiometric [7] and amperometric detections [8]. Typical spectrophotometric assays involve converting the analyte to cyanogen chloride by chloramine-T and subsequent reaction with pyridine and barbituric acid. The applicable range is 5–500 $\mu g\,L^{-1}$ [6]. Off-line distillation is employed for total cyanide determinations [9]. Substances that can cause substantial increases in measurements of cyanides include thiocyanates, therefore approaches have been proposed for the simultaneous determination of both of these classes of analytes [10–14]. Alternatives to the pyridine–barbituric acid system include the isonicotinic acid–barbituric acid [15] and γ-picoline–barbituric acid [16] methods. Potentiometry [7] using

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doi:10.1016/j.talanta.2008.09.058

cyanide-selective electrodes enables the determination of free CN^- in various samples at concentrations exceeding 50 μg L^{-1}. In addition to taking precautions to avoid potential problems caused by known interfering species, such as sulfides and hydrogen ions, special care should be taken to maintain precise temperature control. Cyanide ion-selective electrodes (CN-ISEs) have also been successfully incorporated into automated flow injection (FI) systems [17–19], improving the sensitivity and sampling rates of analyses. Finally, amperometric detection using a silver working electrode incorporated in a FI system [8] offers a wide determination range, of 2 μg L^{-1} to 5 mg L^{-1}, with a limit of detection (LOD) of 0.5 μg L^{-1}.

FI coupled to gas diffusion (GD) has proven to be a popular and effective approach for the determination of cyanides, exploiting the formation of gaseous HCN in acidic media [20–28]. Reported assays have been carried out using: spectrophotometric detection [20–22], with LODs in the range of 0.025–100 μg L^{-1}; fluorimetry [23–25], with generally lower LODs in the range of 0.4–0.5 μg L^{-1}; and electrochemical detection [26–28], offering LODs in the range of 0.2–26 μg L^{-1}. The sampling throughputs per hour of these FI–GD setups range between 4 [29] and 60 [22]. From a selectivity perspective, sulfide ions seem to be the major interfering species in FI–GD determinations of cyanides [22,26–28]. Apart from the well-established pre-treatment protocol using lead salts [6–8], attempts have been made to overcome this problem by using oxidants in the donor stream to oxidise sulfides to sulfates [22,26]. However, precipitation of MnO_2 in the flow system when using $KMnO_4$ and the generation of increased signals from the detector due to the conversion of SCN^- to HCN limit their applicability.

Sequential injection (SI) analysis—the second generation of FI techniques—has been developed as an advantageous alternative to traditional FI [30]. SI has unique sample handling potential due to the combined use of a multi-position valve and a bi-directional propulsion system. SI has also been effectively coupled to gas diffusion, combining the advantages of both techniques. SI–GD determinations of ammonia [29,31,32], free chlorine [33], sulfide [34], sulfur dioxide [35], dissolved carbon [36] and urea [37] have been reported recently. However, to the best of our knowledge, no SI–GD method has been previously reported for the determination of cyanides.

The present study reports the first development and application of a SI–GD method for determining trace free cyanides. Cyanides were converted on-line to HCN by acidification followed by diffusion through the hydrophobic PTFE membrane of a GD unit incorporated in the SI manifold. The analyte was detected amperometrically in the alkaline acceptor stream using an Ag working electrode avoiding the need for complex reactions prior to measurement. Due to the static nature of the acceptor stream enrichment of the analyte and therefore increased sensitivity was achieved by repetitive preconcentration cycles. The detection limits offered by the proposed method are better or comparable to those of the most sensitive methods reported to date [8,19,23,24,28] and far below limits set by international standards and regulations. The applicability of the method was evaluated by analyzing several tap, mineral and table water samples.

2. Experimental

2.1. Apparatus

A schematic diagram of the SI–GD configuration is outlined in Fig. 1. The FIALab 3000 system (FIALab Instruments, WA, USA) consisted of a Cavro 1000 μL syringe pump (Tecan, Switzerland) and a Cheminert® six-port selection valve (Valco VICI, Houston, USA). The SI analyzer was controlled by the FIALab software. The volume of the holding coil (HC) was 700 μL. PTFE tubing (0.5 mm i.d.) was used throughout including connections, holding, reaction and delay coils.

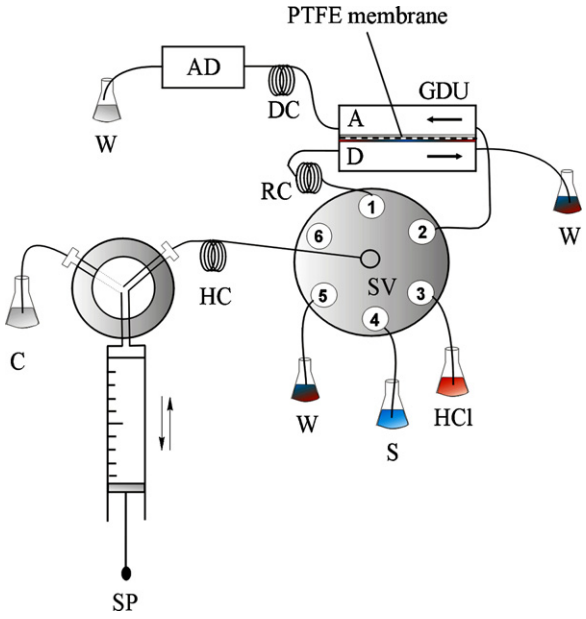

Fig. 1. Schematic diagram of the SIA–GD instrumentation, where C = carrier (0.2 mol L^{-1} NaOH), SP = syringe pump (V = 1000 μL), HC = holding coil (700 μL), SV = selection valve, S = sample, HCl = HCl solution at 0.5 mol L^{-1}, RC = reaction coil (60 cm/0.5 mm i.d.), DC = dilution coil (60 cm/0.5 mm i.d.), W = waste, A = acceptor, D = donor, GDU = gas-diffusion unit, AD = amperometric detector. For further details see Section 2.1.

The flow-through amperometric cell of a Cyanide Solution® 3000 Analyzer (Alpkem®, O.I. Analytical, College Station, TX, USA) comprised an Ag working electrode and a Pt counter electrode. The reference electrode (Ag/AgCl) was separated from the flowing stream by an ion-exchange Nafion membrane. The detector was operated at a potential of 0.0 V. The resulting current (pA) was monitored by the WinFLOW™ software (O.I. Analytical) and was graphically represented as a peak. The amperometric detector was equilibrated at the beginning of each working day for at least 30 min by continuous propulsion of a NaOH solution (0.2 mol L^{-1}) at a flow rate of 0.9 mL min^{-1} using a peristaltic pump (Gilson Minipuls3, Villiers-le-Bel, France). Typical, weekly maintenance of the detector included polishing of the active surface of the working electrode using alumina and refilling of the reference solution. On daily usage, the flow-cell was stored filled with a NaOH solution. De-ionized water was used for longer storage periods.

A Chemifold™ Type V gas diffusion unit (Tecator, Sweden) was employed throughout this work. The dimensions of the gas-diffusion groove were 72 mm × 2 mm. PTFE gas-diffusion membranes were also provided by Tecator and were typically replaced on weekly basis.

2.2. Chemicals and solutions

KCN, NaOH and HCl were all of analytical grade and provided by Merck (Darmstadt, Germany). All other reagents used for assessing the effects of potentially interfering substances were purchased from Sigma–Aldrich or Merck and were also of analytical grade. Water was purified by a Milli-Q system (Millipore, Bedford, MA, USA) and used for preparing all solutions.

Stock CN^- solutions (γ-CN^- = 1000 μg mL^{-1}) were prepared in 0.1 mol L^{-1} NaOH, kept refrigerated at 4 °C for a week, and then replaced. Working standards were prepared by diluting the stock solution as appropriate in 0.01 mol L^{-1} NaOH.

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