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Determination of total cyanide in soil by isotope dilution GC/MS following pentafluorobenzyl derivatization

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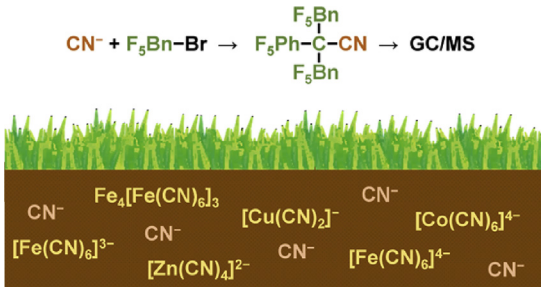
HIGHLIGHTS

- A cost-effective, fast and simple method for determination of total cyanide in soil is presented.
- A new micro-distillation strategy was developed overcoming the problems of a conventional distillation.
- Negative chemical ionization-mass spectrometer has been exploited to obtain a high sensitivity and specificity.
- High accuracy was attained for the analysis of certified reference materials with quadruple isotope dilution technique.

GRAPHICAL ABSTRACT



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ABSTRACT

The high toxicity of cyanide, along with its widespread industrial use, has fuelled interest in the development of analytical methods for its determination in complex matrices. In this study, we propose a novel approach for the measurement of total cyanide in soil samples based on single-step derivatization with pentafluorobenzyl bromide ($F_5Bn–Br$) followed by quantitation with gas chromatography mass spectrometry in negative chemical ionization mode.

The reaction between CN^- and $F_5Bn–Br$ resulted in the identification of several derivatives such as $F_5Bn–CN$, $(F_5Bn)(F_5Ph)CH–CN$, and $(F_5Bn)_2(F_5Ph)C–CN$. The relative proportion between such compounds was dependent on experimental conditions. When a 100 μL aliquot of an alkaline-aqueous extract was reacted with 700 μL of 1.3% $F_5Bn–Br$ in acetone, the tri-alkylated derivative was the most abundant. In such conditions a detection limit of 0.5 ng/g of CN^- was attained.

Soil samples were initially spiked with an alkaline solution of $K^{13}C^{15}N$ internal standard and suspended in 7.5% aqueous NaOH. Determination of total cyanide was achieved by digestion of the alkaline extract with H_3PO_4 to produce HCN which was then trapped in 0.1% NaOH in a sealed double vial system, followed by reaction with $F_5Bn–Br$. Isotope dilution calibration was chosen for quantitation, and the validity of the novel method was demonstrated by analysis of soil Certified Reference Materials (CRMs) and by spike recovery tests.

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1. Introduction

Hydrogen cyanide and its salts are well known powerful toxic agents for living organisms. Chronic exposure to cyanide can lead to liver and kidney damage, permanent paralysis, nervous lesions, hypothyroidism, and miscarriages [1]. Despite the potential hazard, cyanide is widely used for gold mining, where 90,000 tons of cyanide are employed every year in the USA for heap leaching extraction of gold from ore [2]. Furthermore, sites of former manufacturing gas plants or coke ovens – which are widespread in the industrialised world – are often contaminated by cyanide [3]. For these reasons, cyanide monitoring in soil has been of interest since the beginning of the 20th century [4]. The determination of cyanide in soil helps to assure national food safety and supports the development of soil specific and crop-specific remedies for contaminated sites. Since the availability of soil for cultivation and farming is affected by potential contamination with cyanide, several countries have established guidelines for its maximum allowable concentration. These regulations (Table 1) take into consideration the chemical form of the cyanide and the intended use of the soil. Cyanide may be present in soil in several chemical forms such as (*i*) ionic cyanide salts (NaCN, KCN) weakly adsorbed onto soil particles at pH > 9.2, (*ii*) weak metal-cyanide complexes (such as $[Zn(CN)_4]^{2-}$ and [$[Cd(CN)_3]^-$), (iii) moderately strong metal-cyanide complexes (such as $[Cu(CN)_2]^-$ and $[Ag(CN)_2]^-$), (*iv*) strong metal-cyanide complexes (such as $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{4-}$, $[Au(CN)_2]^-$, and $[Hg(CN)_4]^{2-}$) and (*v*) Prussian Blue, $Fe_4[Fe(CN)_6]_3$ [3]. There is no a unanimous definition for metal cyanide complexes, but as a general rule we can consider the compounds having a logK between 10 and 20 as weak complexes, between 20 and 30 moderately strong complexes and over 30 as strong complexes [5].

Since these metal complexes have different stability toward hydrolysis, their toxicity varies from one compound to another and depends upon environmental conditions. In this regard, speciation of cyanide compounds plays an important role in understanding mobility, toxicity and fate of cyanide in soil [6]. For example, Fe(III) cyanide complexes – which have been associated with low environmental risk [7] – may decompose under solar light to the toxic free cyanide form [8]. Furthermore, changes in the physico-chemical properties of the soil may result in the remobilization of adsorbed cyanide complexes leading to migration in groundwater or the atmosphere [6]. Therefore, attention should be given to the quantification of total cyanide in soil monitoring schemes.

The U.S. EPA developed several methods for cyanide determination, including titration [9], spectrophotometry [9], potentiometry with cyanide-selective electrodes [10] and flow injection with amperometric detection [11]. These methods can achieve detection limits that are sufficient for most regulatory needs (2–5 μg/L), but are complex, time-consuming, and require the manipulation of 20–40 g of sample, from which large amounts of hydrogen cyanide can be released. Furthermore, spectrophotometric methods are not entirely compatible with high-alkaline solutions and are prone to matrix interferences from oxidizers and sulfur-bearing compounds [12]. Detection with cyanide-selective electrodes is severely affected by heavy matrices [12]. Ion chromatography with amperometric and conductometric detection has been proposed for the determination of cyanide [13]. However, fouling problems are reported with DC amperometric probes, whereas conductivity detection is rarely used due to the intrinsic nonlinear response with cyanide [12].

The use of mass spectrometry (MS) can overcome most of the issues related to the selectivity and specificity of the classic approaches and has the advantage of allowing the use of isotopically labelled internal standards for high-precision quantitation. Mass spectrometry has been proposed in conjunction with high performance liquid chromatography (HPLC) [14–18] and also with gas chromatography (GC) [4], mainly for biological applications and for the determination of free cyanide. Both approaches require derivatization of cyanide before analysis. GC–MS appears most efficient because of the enormous abilities of high-resolution capillary column together with high selective detection system. The simplest chemistry proposed for GC entails acidification of the sample followed by headspace analysis of HCN [19]. Hydrogen cyanide, however, has poor retention on common GC columns and its low molar mass limits the performance of MS detection. To overcome the disadvantages, CN should be derived to a high-mass molecule, which can be detected in an excellent mass range by GC–MS. Pentafluorobenzyl bromide ($F_5Bn–Br$) is a commercial and well-known alkylating agent for GC analysis of inorganic anions and allows for the conversion of cyanide into a derivative suitable for GC/MS [20]. Compared with the derivatization strategies proposed in the literature, the alkylation by PFBBr is a straightforward and rapid procedure, without liquid-liquid extraction of the analyte.

In this study, we present the general reactivity model for the $CN^-/F_5Bn–Br$ system and discuss the experimental parameters that

Table 1
Selected international quality guidelines for total cyanide in soil.

Country	Soil use				Ref.
	Natural area (mg/kg)	Agricultural (mg/kg)	Residential (mg/kg)	Commercial/Industrial (mg/kg)	
Argentina	n.a.	5	50	500	[21]
Australia	1000	n.a.	500	2500	[22]
Austria	n.a.	5	5	n.a.	[23]
Belgium	5		5	12	[24]
British Columbia (Canada)	n.a.	5	50	500	[41]
Czech Republic	n.a.	5		n.a.	[26]
Denmark	n.a.	n.a.	500	n.a.	[27]
Estonia	n.a.	n.a.	50	500	[42]
Finland	n.a.	n.a.	50	n.a.	[29]
Germany	50	n.a.	50	100	[30]
Lithuania	n.a.	n.a.	5	n.a.	[32]
Netherlands	n.a.	n.a.	50	n.a.	[33]
Poland	5	5	n.a.	40	[36]
South Africa	n.a.	n.a.	1200	10000	[37]
Tanzania	n.a.	10	10	n.a.	[43]
Thailand	n.a.	11	11	35	[38]
Turkey	n.a.	n.a.	5	n.a.	[39]
Korea	n.a.	2	2	120	[40]