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Quick detection and quantification of iron-cyanide complexes using fourier transform infrared spectroscopy☆

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ABSTRACT

The continuous release of persistent iron-cyanide (Fe-CN) complexes from various industrial sources poses a high hazard to the environment and indicates the necessity to analyze a considerable amount of samples. Conventional flow injection analysis (FIA) is a time and cost consuming method for cyanide (CN) determination. Thus, a rapid and economic alternative needs to be developed to quantify the Fe-CN complexes. 52 soil samples were collected at a former Manufactured Gas Plant (MGP) site in order to determine the feasibility of diffuse reflectance infrared Fourier spectroscopy (DRIFTS). Soil analysis revealed CN concentrations in a range from 8 to 14.809 mg kg^{-1}, where 97% was in the solid form ($Fe_4[Fe(CN)_6]_3$), which is characterized by a single symmetrical CN band in the range 2092–2084 cm^{-1}. The partial least squares (PLS) calibration-validation model revealed IR response to CN_{tot} which exceeds 2306 mg kg^{-1} (limit of detection, LOD). Leave-one-out cross-validation (LOO-CV) was performed on soil samples, which contained low CN_{tot} (<900 mg kg^{-1}). This improved the sensitivity of the model by reducing the LOD to 154 mg kg^{-1}. Finally, the LOO-CV conducted on the samples with $CN_{tot} > 900$ mg kg^{-1} resulted in LOD equal to 3751 mg kg^{-1}. It was found that FTIR spectroscopy provides the information concerning different CN species in the soil samples. Additionally, it is suitable for quantifying Fe-CN species in matrixes with $CN_{tot} > 154$ mg kg^{-1}. Thus, FTIR spectroscopy, in combination with the statistical approach applied here seems to be a feasible and quick method for screening of contaminated sites.

1. Introduction

The gas manufacturing and purification processes yielded contaminated residues (including petroleum hydrocarbons, polycyclic aromatic hydrocarbons, cyanides, etc.) that were spread in the vicinities or used as a filling material (Dzombak et al., 2006). Soils and groundwater on the sites of former Manufactured Gas Plants (MGPs) are contaminated with various complex iron-cyanides (Fe-CN), mainly present in the form of Prussian Blue (ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$) and its dissolution products hexacyanoferrat (II) $[Fe(CN)_6]^{4-}$ and (III) $[Fe(CN)_6]^{3-}$ (Kjeldsen, 1998; Sut, 2014). The total number of former MGPs amounts to 1064 in Germany, according to Mansfeldt (2003), of which 63 facilities are located in the state of Brandenburg. 12 MGP sites in Brandenburg have been reclaimed. Road salt with a concentration of 100 mg $Fe(CN)_6$ kg^{-1} is used on German streets resulting in an annual input of 75–425 mg cyanide to the road soil environment (Gschwendtner et al., 2016). This issue becomes even more significant due to ongoing gas purification processes in China or Poland and worldwide intensive and continuous release of Fe-CN complexes from other industries (mining, electroplating, deicing road salts etc.).

Contaminated sites create a significant risk to human health, by poisoning drinking water, soil, air and as a consequence food. A detailed soil monitoring, including identification of “hot spots” is needed at the aforementioned sites, because of the high hazard potential for the environment and the significant risk to human health emanating from Fe-CN contaminations. At the present time quantitative determination of iron-cyanide concentration in soil usually requires a time consuming two step process: digestion of the sample (e.g., micro distillation system) and its analytical detection performed, e.g., by automated spectrophotometrical flow injection analysis (FIA) (Sut et al., 2012).

On the other hand, spectroscopic techniques have become very popular and widely used in industry due to the rapid and non-

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List of abbreviations

ATR	Attenuated Total Reflectance
b	slope of the line (gradient)
CN	cyanide
DRIFTS	diffuse reflectance infrared Fourier spectroscopy
DW	Dry weight
Fe-CN	iron-cyanide
FIA	flow injection analysis
FTIR	Fourier transform infrared spectroscopy
MGP	Manufactured Gas Plant
MIR	medium infrared range
LOD	limit of detection
LOO-CV	Leave-one-out cross-validation
OM	organic matter
P	probability value
PCA	principal component analysis
PLS	partial least squares
R^2	correlation coefficient
RMSEP	root mean square error of prediction
SE	standard error
$s_{y.x}$	standard deviation

destructive analysis of bulk material. It requires minimal sample preparations, and can simultaneously analyze various soil parameters based on one single spectrum. Fourier transform infrared spectroscopy (FTIR) exploits the fact that different chemical functional groups absorb at specific wavenumbers in the medium infrared range (MIR, 4000–400 cm^{-1}) (Movasaghi et al., 2008). Therefore, FTIR spectra analysis of soil samples provides information on functional groups and molecular structures that can be useful for the identification of specific compounds (Giordano et al., 2001).

FTIR spectroscopy has been successfully applied to characterize Fe-CN complexes in soils, due to its strong C≡N stretching vibration in the range of 2200–2000 cm^{-1} (Proffit et al., 2001; Jannusch et al., 2002; Rennert et al., 2007; Sut et al., 2012). According to Rennert et al. (2007) various molecular environments of the CN group can be distinguished by the wavenumber of the CN stretching vibration ν(CN) due to its change upon complexation with different metal atoms. For example, the wavenumber of free CN occurs at 2080 cm^{-1}, whereas vibrations of the compound characteristic for the MGP sites ($Fe_4[Fe(CN)_6]_3$) appear at 2092, 2087 or 2084 cm^{-1} (Nakamoto, 2002; Scholz et al., 2001) and its dissolution products complexed with potassium $K_4[Fe^{II}(CN)_6]^{4-}$ at 2044 cm^{-1} and $K_3[Fe^{III}(CN)_6]^{3-}$ at 2117 cm^{-1} (Rennert et al., 2007) or $Fe^{III}[(CN)_6]^{3-}$ adsorbed on goethite at 2026 cm^{-1} (Rennert et al., 2005). As proven above, FTIR spectroscopy is a successful tool in rapid analysis and identification of Fe-CN compounds in the soil. However, there is lack of information concerning the application of FTIR spectroscopy for the quantification of Fe-CN complexes in soil. Most of the studies concerning this method focus on the ability of IR to provide structural and compositional information concerning the soil sample. For example, the study conducted by Oumabady Alias Cannane et al. (2013) in South India mainly applies clay mineral analysis. Henrique de Santana et al. (2006) evaluated the effect of heating on clay and soil structure and adsorption using FTIR spectroscopy. Furthermore, this technique was used to investigate the organic carbon speciation in soils (Solomon et al., 2005). Study conducted by Pérez-Rodríguez et al. (2016) indicated the feasibility of spectroscopic data in combination with partial least square (PLS) statistics to predict mercury concentrations in peat soil. It is believed that FTIR can be a promising tool to predict the Fe-CN compounds concentration in the affected soils, taking under consideration, the successful application of IR spectroscopy to identify complexed CN in soil and the feasibility of this method to quantify environmental pollutants.

Currently, soil remediation is of vital importance (Lim et al., 2016) but laboratory methods to determine Fe-CN concentrations in soil samples are usually time consuming, Thus developing and improving rapid and nondestructive methods to measure soil contaminants is crucial in order to determine potential environmental hazards. In this study we aim to generate a protocol for a quick and cheap quantitative cyanide analysis in soil using FTIR by i) identifying the CN compounds in contaminated soil samples from a former MGP site in Cottbus; ii) using a multivariate calibration model (PLS, principal component analysis PCA) to predict the Fe-CN concentration in the soil samples and iii) decipher the limits of detection for this method.

2. Methods

2.1. Study site

For this study the samples were collected at the former MGP in Cottbus Germany (Fig. 1) (51°45,161′ N; 14°18,529′ E). Top soil is composed of sand containing coal, slag, gas purification wastes and organic matter (up to 0.5 m deep). The deeper soil (0.5–7.0 m) has a sandy texture (texture classes according to German classification system). At the depth of approximately 1 m a layer of coherent structured soil occurs, which unevenly covers the whole investigation field (up to 2 m deep). The soil pH varies between 3.2 and 7.7 (Sut, 2014).

2.2. Sampling and sample preparation

The soil samples ($n = 52$) were collected up to 190 cm depth using a hand driller. Subsequently the fresh samples were homogenized and the total and water soluble cyanide concentration was determined using FIA Compact (Medizin-und Labortechnik Engineering GmbH, Dresden, Germany). Injection Analyzer refers to the standard for determination of total and free cyanide (DIN EN ISO, 2012). For CN_{tot} 20 g of collected soil samples were extracted in 200 ml 1 M sodium hydroxide (1:10, w/v) for 12 h in an end-over-end shaker at 16 rpm. The extracts were centrifuged for 10 min at 3.000 rpm in order to force settling of soil particles. Subsequently, 5 ml of extracts were digested in an acidic environment using a micro distillation system (Sut et al., 2012). The micro dist system refers to the method of the Hach Company (Loveland, CO, USA), US QuikChem Method 10-204-00-1-X approved by the USEPA (2008).

Water soluble cyanide was determined by extracting 20 g of the soil sample in 50 ml of distilled water (2:5 w/v relation) for 1 h with an end-over-end shaker at 16 rpm. Subsequently, water extracts were introduced in a centrifuge at 3.000 rpm for 20 min and 20–30 ml were filtered through 0.45 µm syringe filters. Following procedures were consistent with the method used for the CN_{tot} analysis. The detection limit for both extractions is 0.02 mgl^{-1} of cyanide in analyte.

For the spectroscopic analysis, soil samples ($n = 52$) were homogenized, air dried, sieved (<2 mm) and ground, using an agate mortar.

2.3. Spectroscopic analysis and model development

The spectroscopic analysis of the soil samples ($n = 52$) was performed using FTIR spectrometer (Bruker, Tensor 27, HTS-XT,