Preparation of ^{15}N-labeled Potassium Ferrocyanide for Tracer Studies

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Abstract

Isotopic labels are widely used to trace the fate and cycling of common environmental contaminants. Many of the labeled materials are not available commercially and, depending on the complexity of the substance, the label and the enrichment level, custom syntheses are costly. A simple, straightforward, and cost effective method for the preparation of a highly enriched, ^{15}N-labeled potassium ferrocyanide ($K_4[Fe(C^{15}N)_6]*3H_2O$) has been developed to meet the requirements of related tracer experiments and minimize their costs. In this case, the ^{15}N label was used to quantify iron cyanide detoxification (biodegradation and/or transformation) within soil-plant-systems. ^{15}N-labeled potassium cyanide ($KC^{15}N$) and a ferrous iron salt have been used for the synthesis. Extensive qualitative and quantitative analyses showed a product, entirely identical in its functional and elemental components to commercial non-labeled $K_4[Fe(CN)_6]*3H_2O$ and in its ^{15}N enrichment to the $KC^{15}N$ used for its synthesis. To investigate their behavior and fate in various environmental compartments, other labeled iron or metal cyanide complexes might be synthesized in analogous manner.

Keywords: contaminant, enrichment, fate, iron cyanide, isotopic label, synthesis

1. Introduction

Iron cyanide contamination in the environment is primarily of anthropogenic origin. One of the greatest iron cyanide sources are the sites of former manufactured gas plants and coke ovens, existing in a high number (>8700) in Europe and the United States (Wehrer, Rennert, Mansfeldt & Totsche 2011). Due to their high stability and complex behavior, iron cyanides might both be very persistent (Meeussen, Keizer, van Riemsdijk & de Haan 1992) or migrate from one environmental compartment to another (Meeussen, van Riemsdijk & van der Zee 1995; Theis, Young, Huang & Knutsen 1994) and pose serious wildlife and human health risks by releasing toxic free cyanide (Kjeldsen 1999). To better understand and predict the complex behavior of contaminants, isotopic tracers have increasingly been applied in the past decades, including in studies on biodegradation and detoxification of simple and complexed cyanide species within plant tissue (Ebbs, Bushey, Poston, Kosma, Samiotakis & Dzombak 2003; Ebbs, Piccinin, Goodger, Kolev, Woodrow & Baker 2008; Ebbs, Kosma, Nielson, Machingura, Baker & Woodrow 2010; Ebel, Evangelou & Schaeffer 2007; Samiotakis & Ebbs 2004). Yet, labeled complexed (including iron) cyanides are not commercially available and custom label costs are rather high, which might cause extensive study limitations. Therefore, a novel procedure has been developed for the synthesis of potassium ferrocyanide ($K_4[Fe(CN)_6]$), incorporating the stable ^{15}N isotope of nitrogen. There exist a few $K_4[Fe(CN)_6]$ synthesis methods described so far, incorporating a ^{57}Fe complex label and intended for Mössbauer spectroscopy studies (Jaskula & Petlicki 1978; Ganguli, Das & Bhattacharya 1998). However, including a ^{57}Fe label in the complex requires several preparation steps, special laboratory conditions, and consumables. The synthesis method described in this paper is simple, straightforward, effective and can be conducted under standard laboratory conditions. Qualitative and quantitative analyses of the product showed that it is entirely identical in its functional and elemental components and ^{15}N enrichment to commercial products. This is the first summary of such a synthesis procedure. It saves time and costs, thus facilitating further research on the fate of iron (complex) cyanides in the environment. Particularly the low costs and the high yield allow for the application of the product in large scale studies or even directly under real field conditions. Both have so far not been possible.
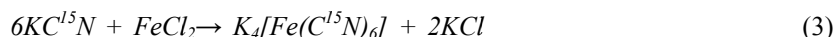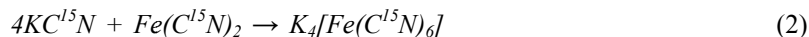
2. Materials and Methods

2.1 Chemicals

All chemicals used for the preparation of the labeled potassium ferrocyanide were of reagent grade with >98% chemical purity.

2.2 Preparation Procedure

Potassium ferrocyanide can be prepared from a solution of a ferrous iron salt and potassium cyanide (Jander & Blasius, 2006). The ^{15}N-labeled potassium ferrocyanide was synthesized using ^{15}N-labeled potassium cyanide ($KC^{15}N$, Sigma Aldrich, Germany). The overall reaction (equation 3) proceeds in two steps as in equation 1 and 2 below (modified from Holleman & Wiberg, 1995):

$$2KC^{15}N + FeCl_2 \rightarrow Fe(C^{15}N)_2\downarrow + 2KCl \tag{1}$$

$$4KC^{15}N + Fe(C^{15}N)_2 \rightarrow K_4[Fe(C^{15}N)_6] \tag{2}$$

$$6KC^{15}N + FeCl_2 \rightarrow K_4[Fe(C^{15}N)_6] + 2KCl \tag{3}$$

As obvious from Figure 1, the setup and the equipment used for the synthesis are rather simple (a heated stirring plate, reaction vessel and a dropping funnel). A 0.1 mol L^{-1} solution of iron chloride ($FeCl_2*4H_2O$, Sigma Aldrich, Germany) in deionized water was slowly added with a dropping funnel and under constant stirring to a hot deionized water solution of excess $KC^{15}N$ (0.9 mol L^{-1}). The $KC^{15}N$ solution was constantly heated in a water bath (Figure 1). A precipitate of rust-brown iron II cyanide ($Fe(C^{15}N)_2$) forms initially (equation 2) and readily dissolves in surplus $KC^{15}N$, resulting in a clear yellow solution of ^{15}N-labeled potassium ferrocyanide ($K_4[Fe(C^{15}N)_6]$) and potassium chloride (KCl, equation 3).
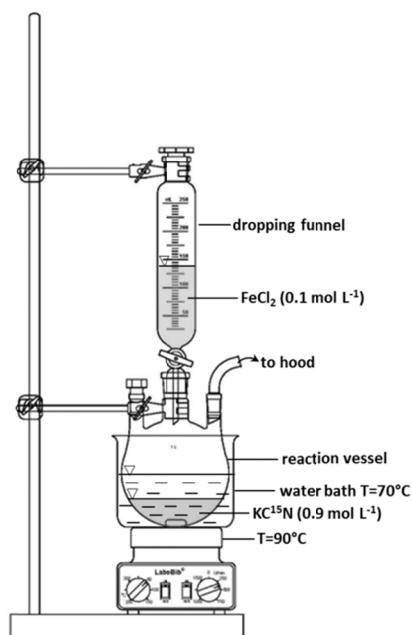

Figure 1. Setup and equipment used for the synthesis

The $K_4[Fe(C^{15}N)_6]$ formed was precipitated from solution under the addition of 98% ethanol (VWR, Germany) in 1:4 *v/v* ratio. The precipitate was vacuum-filtered through 292-grade filter paper (VWR, Germany). Thus, it was separated from the second product (KCl) and not reacted $KC^{15}N$, both still likely to be present in the solution. The $K_4[Fe(C^{15}N)_6]$ filter residue was redissolved with deionized water to separate it from the filter paper and the resulting solution was dried at 45°C (to obtain the trihydrate form) for 48 h. The yield is ~70% based on the $KC^{15}N$ used. To ensure the high ^{15}N enrichment in the final product, the KCN used for the synthesis was ^{15}N-enriched to >99 atom% (at%).

2.3 Quality Assurance

Commercial, not labeled potassium ferrocyanide trihydrate ($K_4[Fe(CN)_6]*3H_2O$, Merck, Germany) was used as reference substance to which the synthesized product was compared. The following parameters have been taken

into account for the qualitative and quantitative analyses:

(i)   **Fundamental vibrational modes:** to identify the presence of the fundamental vibrational modes characteristic for ferrocyanide ions, the synthesized $K_4[Fe(C^{15}N)_6]*3H_2O$ was scanned on a Fourier transform infrared spectrometer (FTIR) and the resulting spectrum was compared to that of the commercial $K_4[Fe(CN)_6]*3H_2O$. In addition, commercial potassium ferricyanide ($K_3[Fe(CN)_6]$) and the $KC^{15}N$ used for the synthesis were scanned to identify the presence of ferric iron or simply bound cyanide in the synthesized product.

(ii)   **CN:** the total water soluble ($CN_{T\,H_2O}$) and weak acid dissociable CN (CN_{WAD}) concentration and content of the synthesized $K_4[Fe(C^{15}N)_6]*3H_2O$ and the commercial $K_4[Fe(CN)_6]*3H_2O$ were measured in standard solutions, prepared with the two substances and the results were compared.

(iii)   **Elemental components:** iron (Fe^{2+}), potassium (K^+) and chlorine (Cl^-) concentrations and contents of the synthesized $K_4[Fe(C^{15}N)_6]*3H_2O$ and the commercial $K_4[Fe(CN)_6]*3H_2O$ were measured in standard solutions, prepared with the two substances and the results were compared.

(iv)   **^{15}N enrichment:** the dry product was measured on an isotope ratio mass spectrometer (IRMS) together with $KC^{15}N$ and commercial $K_4[Fe(CN)_6]*3H_2O$ and the results were compared.

2.4 Analytical Procedures

FTIR Analysis. Small amount (~100 μg) of the prepared dry $K_4[Fe(C^{15}N)_6]*3H_2O$ and the commercial $K_4[Fe(CN)_6]*3H_2O$ was scanned on a Tensor 27 FTIR spectrometer (Bruker Optik GmbH, Germany) in attenuated total reflection (ATR) mode and the resulting spectra were compared.

CN Analysis. Weak acid dissociable and total CN concentrations in the prepared standard solutions of the synthesized $K_4[Fe(C^{15}N)_6]*3H_2O$ and the commercial $K_4[Fe(CN)_6]*3H_2O$ were determined spectrophotometrically on a flow injection analysis system (MLE FIA Compact, Gesellschaft für Analysentechnik HLS, Salzwedel, Germany) according to DIN EN ISO 14403:2002. The limits of detection (LOD) of the system are 0.01–1.10 mg L^{-1} with limits of quantification (LOQ) of 0.02–1 mg L^{-1}.

Total CN was measured following acid digestion and distillation of 5 ml of the standard solutions on a micro distillation system (MICRO DIST®, Lachat Instruments, A Hatch Company Brand, US) according to the Lachat Equivalent Method QuickChem 10-204-00-1-X.

Elemental Analysis. Iron (Fe^{2+}) and potassium (K^+) concentrations in the prepared standard solutions of the synthesized $K_4[Fe(C^{15}N)_6]*3H_2O$ and the commercial $K_4[Fe(CN)_6]*3H_2O$ were determined on a Unicam iCAP 6000 Duo ICP-AES with a CID68 detector (Thermo Fisher Scientific, Germany). The concentration of chlorine (Cl^-) ions in the standard solutions was determined on a Dionex DX 500 and DX 120 IC system (Thermo Fisher Scientific, Germany).

Isotope (^{15}N) Analysis. The ^{15}N enrichment was analysed on a Thermo Delta V Advantage IRMS (Thermo Fisher Scientific, Germany) with a ConFlo III open split interface (Finningan, Thermo Electron Bremen, Germany) and coupled to a Vario EL III elemental analyzer (Elementar Analysensysteme GmbH Hanau, Germany).

3. Results and Discussion

3.1 Fundamental Vibrational Modes

The comparison of the synthesized and the commercial ferrocyanide complexes showed slight but not fundamental differences in the vibrational modes of the two substances.

Figure 2 shows comparatively the absorbance spectra of $K_4[Fe(C^{15}N)_6]$ (a), $K_4[Fe(CN)_6]$ (b), $K_3[Fe(CN)_6]$ (c) and $KC^{15}N$ (d).
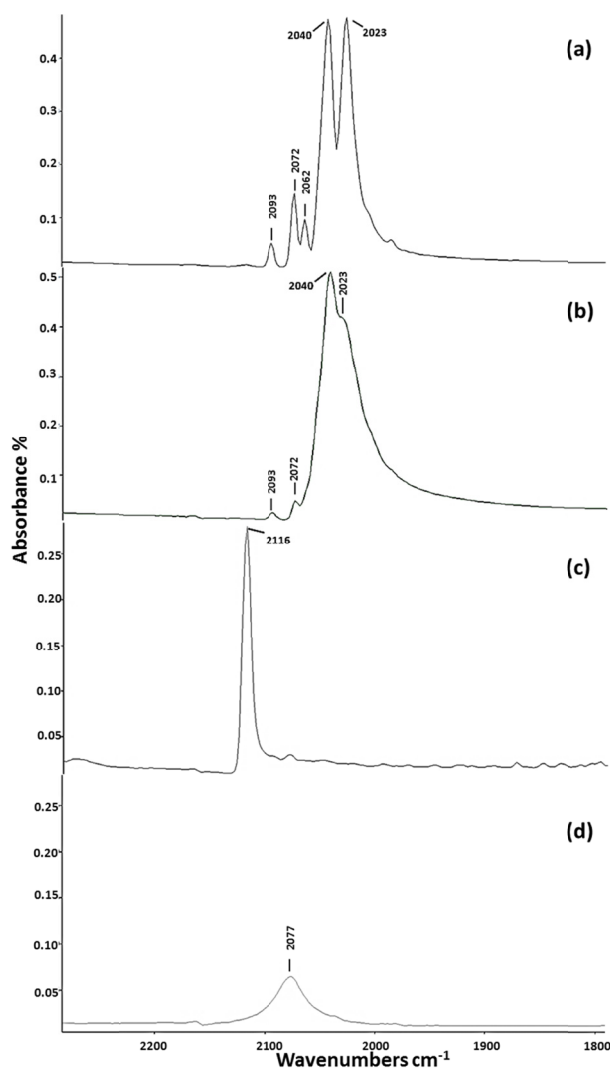
Figure 2. FTIR spectra of synthesized ^{15}N-labeled potassium ferrocyanide (a), commercial potassium ferrocyanide (b), commercial potassium ferricyanide (c) and commercial ^{15}N-labeled potassium cyanide (d). The characteristic vibrational bands of ferrocyanide ions in (a) and (b) indicate the qualitative similarity of the synthesized and the commercial product. The absence of ferric and simply bound cyanide ions in the synthesized product is confirmed by the lack of their characteristic peaks (c, d) in (a)

The strongest vibrational band in the two ferrocyanide substances was detected in the region between 2000 and 2098 cm^{-1} (Figure 2 a, b). The broad band in this region has been previously reported (Gaffar & Abd-Elrahman, 2001; Klyuev, 1965) and is characteristic for ferrocyanide (Fe^{II}–C≡N) containing compounds (Miller & Wilkins, 1952) as it is the region for the stretching vibration of the ferrocyanide ($[Fe^{II}(CN)_6]^{4-}$) ion (Gaffar & Abd-Elrahman, 2001; Miller & Wilkins, 1952). Five (Figure 2 a) and four (Figure 2 b) distinctive peaks have been identified on the broad band between 2000 and 2098 cm^{-1} of the synthesized and the commercial product, respectively. Although very similar, the two spectra are not identical. They differ mainly in the strong 2023 cm^{-1} band in the $K_4[Fe(C^{15}N)_6]$ spectrum (Figure 2 a), present as a shoulder in the $K_4[Fe(CN)_6]$ spectrum (Figure 2 b). Additional difference is the presence of a weak 2062 cm^{-1} band in the spectrum of the synthesized product, which could not be observed in the $K_4[Fe(CN)_6]$ spectrum but might also belong to the cyanide (–C≡N) stretching mode (Gaffar & Abd-Elrahman, 2001). All remaining bands, which could be identified, were identical in the two products. The 2023, 2040, 2062 and 2093 cm^{-1} bands in the synthesized product (Figure 2 a) are to a high extent identical to those reported in the literature (Gaffar & Abd-Elrahman, 2001; Klyuev, 1965; Miller & Wilkins, 1952). The small deviations in the exact position of the bands usually result from the different IR devices used and their resolution power. The splitting of the broadest band in the $K_4[Fe(C^{15}N)_6]$ spectrum to two components with equal intensity (bands at 2023 and 2040 cm^{-1}, Figure 2 a) has been observed in the same region

of a $K_4[Fe(CN)_6]$ spectrum by Klyuev (1965).

He explained the splitting with disrupted symmetry of the perfect octahedron of the $[Fe^{II}(CN)_6]^{4-}$ anion, caused by alteration of the valence state of the central atom, due to the small differences in the outer shell of the Fe^{2+} and Fe^{3+} ions ($3d^6$ in Fe^{2+} and $3d^5$ in Fe^{3+}). No explanation could be suggested for the absence of the 2062 cm^{-1} band in the spectrum of the $K_4[Fe(CN)_6]$ (Figure 2 b). In spite of the differences in the main vibrational band of the two potassium ferrocyanide substances, they both possessed the fundamental vibrational modes of the ferrocyanide ion. Hence, it could be concluded that the two products are qualitatively identical.

The single, very strong vibrational band at 2116 cm^{-1} in the spectrum of the commercial potassium ferricyanide Figure 2 c is characteristic for the ferricyanide ($[Fe^{III}(CN)_6]^{3-}$) ion (Klyuev, 1965; Miller & Wilkins, 1952) and was not observed in the two potassium ferrocyanide spectra. Hence, oxidation of the ferrous to ferric iron during the synthesis was not likely to have taken place and the presence of ferricyanide (Fe^{III}–C≡N) as an impurity could be excluded in both products due to the lack of the characteristic band at 2100–2120 cm^{-1} (Figure 2 a, b).

The spectrum in Figure 2 d was used as a reference to identify the presence of unreacted $KC^{15}N$ in the synthesized product. The absence of the 2077 cm^{-1} band in the spectrum in Figure 2 a and the very low levels of weak acid dissociable CN measured in the synthesized product (Table 1) were evident for the absence of $KC^{15}N$ in the synthesized product. These results indicate that the commercial and the synthesized labeled potassium ferrocyanide are qualitatively identical.

3.2 CN and Elemental Components

Table 1 shows the median concentrations and masses of the elemental components of $K_4[Fe(CN)_6]$ and $K_4[Fe(C^{15}N)_6]$, calculated according to the mass of the substance used to produce the standard solutions. The concentration and mass of the weak acid dissociable CN fraction of the $K_4[Fe(C^{15}N)_6]$ complex was considered equal to the median levels measured in the $K_4[Fe(CN)_6]$ solutions. That is, provided that all unreacted $KC^{15}N$ has been separated in the last steps of the $K_4[Fe(C^{15}N)_6]$ synthesis, the measured weak acid dissociable CN (CN_{WAD}, Table 1) levels in the standard solutions of both complexes should be identical.

Table 1. Median set concentrations and masses of the elemental components of the commercial and the synthesized ^{15}N-labeled potassium ferrocyanide (n=5). The values were calculated using the mass of the two substances used for the preparation of the standard solutions. Measured values are given in parentheses

	$CN_{T\,H_2O}$		CN_{WAD}		Fe^{2+}		K^+		Cl^-	
	mg L^{-1}	mg	mg L^{-1}	mg	mg L^{-1}	mg	mg L^{-1}	mg	mg L^{-1}	mg
$K_4[Fe(C^{15}N)_6]$	101	10.1	0.03	0.003	36	3.6	101	10.1	17	1.7
	(117)	(11.7)	(0.07)	(0.007)	(38)	(3.8)	(105)	(10.5)	(1)	(0.1)
$K_4[Fe(CN)_6]$	101	10.1	0.03	0.003	36	3.6	101	10.1	-	-
	(111)	(11.1)	(0.03)	(0.003)	(35)	(3.5)	(97)	(9.7)	(0)	(0)

The chemical purity of the commercial $K_4[Fe(CN)_6]$ complex also excludes the presence of high levels of Cl^- in its standard solution. However, as a by-product of its synthesis (equation 3), Cl^- might be present in the $K_4[Fe(C^{15}N)_6]$ standard solution. The last two columns of Table 1 show the calculated maximum concentration and total mass of Cl^- ions, which could theoretically be present in the standard solution, provided the KCl separation from the final product in the last steps of the synthesis was incomplete.

The measured concentrations and masses of the elements compiling the synthesized and commercial potassium ferrocyanide substances are shown in parentheses in Table 1. Although the measured total CN concentrations deviate from the set concentrations, the concentrations measured in the commercial and the synthesized products are identical. The mass of weak acid dissociable cyanide in the synthesized product is only slightly higher than that of the commercial product and thus comparable to it. The iron and potassium concentrations and masses in the standard solutions do not deviate much from the set values and are in the correct stoichiometric relation to the measured CN levels.

The actual Cl^- content of the synthesized product was with ~1.6 mg less than the theoretical content (Table 1), which would have been measured, provided incomplete separation of the target product ($K_4[Fe(C^{15}N)_6]$) from the by-product (KCl) has taken place. Thus, the presence of high levels of Cl^- impurity in the synthesized product could be excluded. The above-described results showed that although not of high chemical purity and with small

deviations, the synthesized ^{15}N-labeled potassium ferrocyanide is quantitatively identical in its elemental components to commercial potassium ferrocyanide.

3.3 ^{15}N Enrichment

The ^{15}N enrichment of the synthesized $K_4[Fe(C^{15}N)_6]*3H_2O$ was determined to ensure it was identical in enrichment to the ^{15}N-labeled KCN, used for the synthesis. In the $K_4[Fe(CN)_6]*3H_2O$ sample both masses 28 ($^{14}N_2$) and 29 ($^{15}N^{14}N$) could be detected, with the 28 signal being stronger than the 29 signal. Although the ^{15}N-enrichment of the commercial $K_4[Fe(CN)_6]*3H_2O$ was with 0.3836 at% slightly elevated, it was close to that of the control (0.3662 at%). Hence, the enrichment of the substance was identical to the natural enrichment levels of 0.3663 at%. In the samples of the synthesized $K_4[Fe(C^{15}N)_6]*3H_2O$ and the commercial $KC^{15}N$, the 28 mass could not be detected, e.g. the sample signals contained solely the 29 signal. Thus, it could be demonatrated that all nitrogen atoms in the two substances were present as the ^{15}N isotope.

Overall, the results from the qualitative and quantitative analyses of the synthesized potassium ferrocyanide showed that with small deviations, the product was, regarding its functional and elemental components, identical to the commercial potassium ferrocyanide and regarding its ^{15}N enrichment, identical to the $KC^{15}N$ used for its synthesis.

4. Conclusions

The above described synthesis method is simple, straightforward, effective and does not require special laboratory conditions, equipment or consumables. Nevertheless, it delivers a product, qualitatively and quantitatively comparable to commercial ones. In addition, the high custom costs for the label can greatly be reduced. To trace their behavior and fate in different environmental compartments, further labeled metal and/or iron cyanide species can be synthesized in similar manner to better facilitate cyanide contamination-related research.

Acknowledgements

Conflict of Interest

The authors declare that they have no conflict of interests.

Ethical Standards Declaration

The authors declare that all the experiments conducted for this study were in compliance with the present German legislation.

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