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Determination of $^{15}N/^{14}N$ and $^{13}C/^{12}C$ in Solid and Aqueous Cyanides

Craig A. Johnson

U.S. Geological Survey, Box 25046, MS 963, Denver, Colorado 80225

The stable isotopic compositions of nitrogen and carbon in cyanide compounds can be determined by combusting aliquots in sealed tubes to form N_2 gas and CO_2 gas and analyzing the gases by mass spectrometry. Free cyanide ($CN^-_{aq} + HCN_{aq}$) in simple solutions can also be analyzed by first precipitating the cyanide as copper(II) ferrocyanide and then combusting the precipitate. Reproducibility is ±0.5‰ or better for both $\delta^{15}N$ and $\delta^{13}C$. If empirical corrections are made on the basis of carbon yields, the reproducibility of $\delta^{13}C$ can be improved to ±0.2‰. The analytical methods described herein are sufficiently accurate and precise to apply stable isotope techniques to problems of cyanide degradation in natural waters and industrial process solutions.

Cyanide (CN^-_{aq}) is used in the mining industry, particularly at mines where gold and silver are extracted from ores by heap leach cyanidation,[1] and also in the photoprocessing and electroplating industries. Cyanide is also released naturally by certain bacteria and fungi and by the degradation of cyanogenic glycoside- or lipid-producing plants.[2] The chemistry of cyanide is quite complex due to the fact that it can form a wide variety of compounds and complexes.[3] Because cyanide is highly toxic, its degradation both in natural waters and in industrial process solutions has been and continues to be the subject of intensive study.[4,5]

The purpose of this report is to present an analytical method that allows stable isotope techniques to be applied to the study of cyanide degradation. The method permits analysis of $^{15}N/^{14}N$ and $^{13}C/^{12}C$ in solid cyanide salts and in free cyanide ($CN^-_{aq} + HCN_{aq}$) contained in simple aqueous solutions. The same method holds promise for isotopic analysis of complexed cyanide by first carrying out conventional reflux-distillation for acid dissociable complexes[6] and then analyzing the CN^-_{aq} collected in the alkaline trap. To date there has been only one cyanide-related study employing stable isotope techniques. In that study,[7] ^{15}N-labeled HCN was used in a soil utilization experiment, and nitrogen isotope analyses were performed on ammonia (NH_3), one of the cyanide degradation products. There have been no direct analyses of the stable nitrogen or carbon isotopic compositions of cyanides.

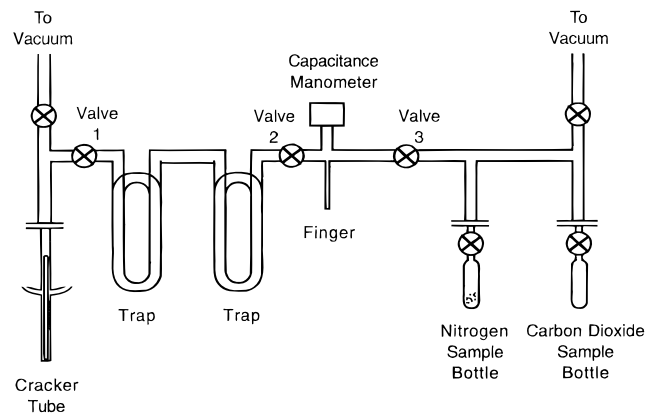

Figure 1. Diagram of the vacuum line used for gas extraction. The line is constructed from Pyrex tubing and Kontes O-ring valves. Vacuum is supplied by a mercury diffusion pump backed by a mechanical pump.

EXPERIMENTAL SECTION

Solid cyanide salts are prepared for analysis by combusting them to form CO_2 and N_2 gases. The combustion is carried out in 9-mm-o.d. Vycor tubes. Prior to use, the tubing is cut into 22-cm lengths, sealed at one end, and baked at 500 °C in a muffle furnace overnight. Sample numbers are then inscribed on the tubes with a diamond pencil. Two grams of cupric oxide wire (Baker, 1820-01), previously baked for 4 h at 600 °C and sieved, is loaded into the tube, followed by a quantity of sample corresponding to ~75 μmol of CN, followed by 1 g of copper shot (20−30 mesh, Baker 1720-01). Samples should be finely powdered to maintain near-quantitative yields. The tubes are attached to a vacuum line and pumped for a minimum of 4 h to a final pressure of ~10^{-6} Torr. They are then sealed at 15-cm length and placed in a muffle furnace that has been preheated to 500 °C. The temperature is raised to 850°C, held for 15−30 min, and slowly lowered to room temperature.

To extract and purify the CO_2 and N_2, a sealed tube is placed in a Pyrex tube cracker and attached to a vacuum line like that shown in Figure 1. After the line is evacuated, the traps are cooled to liquid nitrogen temperature, and valve 3 is closed. The tube is cracked, and CO_2 is allowed to condense in the traps. The manometer reading is then recorded and converted to the N_2 yield using a prior pressure−gas quantity calibration. Valve 3 is then opened, and the N_2 gas is condensed onto ~100 mg of type 5-Å molecular sieves ($^1/_8$-in. pellets, Linde) in either a stopcock-sealed Pyrex bottle or a 6-mm-o.d. Pyrex tube. When the transfer is complete, the stopcock is closed or the tube is sealed using a torch.

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Next, valves 1 and 3 are closed, and the liquid nitrogen on the traps is replaced with dry ice and 2-butoxyethanol. The CO_2 is condensed in the finger with liquid nitrogen, and the finger is warmed to room temperature after closing valve 2. The manometer reading is recorded, allowing the CO_2 yield to be calculated using a prior pressure−gas quantity calibration. The CO_2 is then frozen into a stopcock-sealed bottle or a Pyrex tube. At this point the extraction is complete, and the procedure can be repeated for additional samples.

Cyanide solutions are prepared by dissolving a known amount of NaCN in deionized water. One gram of NaOH is added per 100 mL of solution to favor CN^-_{aq} over HCN_{aq}. HCN_{aq} is undesirable because it has a high enough vapor pressure that it can evaporate from standing solutions and fractionate the isotopes in the remaining CN^-_{aq}. The solutions, even those containing NaOH, can undergo shifts in $\delta^{13}C$ and $\delta^{15}N$ of a few tenths of a ‰ after 1 week. It is thus important that solutions to be used as isotopic standards be freshly prepared and that they be stored in containers with a minimum of head space. Cyanide is extracted from the solutions by precipitating it as copper(II) ferrocyanide ($Cu_2Fe(CN)_6 \cdot xH_2O$). To accomplish this, solutions of ferrous chloride (254 mg of $FeCl_2 \cdot 4H_2O$ in 100 mL of deionized water) and cupric chloride (436 mg of $CuCl_2 \cdot 2H_2O$ in 100 mL of deionized water) are prepared. Ferrous sulfate and cupric sulfate solutions have also been used, but there is evidence that they lead to slightly poorer results. Five milliliters of the ferrous chloride solution is added to the sample, followed by 5 mL of the cupric chloride solution. For a typical sample with 5 mg of CN^-_{aq}, this represents twice the stoichiometric requirement. It is important that the ferrous chloride solution be freshly prepared to ensure that the iron is in reduced form. The solution is then acidified with HCl to a pH of ~1 in order to dissolve the ferrous hydroxide that usually forms. The precipitate is filtered using a Millipore device with a 1-μm acetate filter and allowed to dry. Precipitates are combusted by the method described above. The acidification step is critical because the presence of ferrous hydroxide greatly lengthens the filtration time and will also interfere with the combustion. The amount of cyanide contained in a typical sample is well below the lethal dose for humans (1−3 mg/kg body weight by ingestion).[3] Nevertheless, *it is recommended as a safety precaution that solutions be prepared, precipitated, acidified, and filtered in a fume hood.*

The isotopic compositions of the N_2 and CO_2 gases are measured using a Finnigan MAT 252 mass spectrometer equipped with a dual viscous inlet system. The isotope ratios are compared with those of N_2 and CO_2 reference gases previously calibrated against NIST-distributed standards. Results are reported in δ notation, where δ (in ‰) $= (R_{SA}/R_{ST} - 1) \times 1000$. For nitrogen, R_{SA} and R_{ST} refer to the ratio $^{15}N/^{14}N$ in the sample and air N_2, respectively; for carbon, R_{SA} and R_{ST} refer to the ratio $^{13}C/^{12}C$ in the sample and Vienna Pee Dee Belemnite (VPDB), respectively. The precision of the mass spectrometer measurement is typically ±0.02‰ or better for $\delta^{13}C$ and ±0.05‰ or better for $\delta^{15}N$.

There are a number of isobaric interferences that can cause problems in the mass spectrometer measurement if oxidized nitrogen gases or reduced carbon gases are produced, if N_2 and CO_2 are incompletely separated during the extraction, or if leaks occur. For example, any N_2O contaminating the CO_2 samples will affect the measured ion currents at $m/z = 44$, 45, and 46 and may lead to erroneous $\delta^{13}C$ values. Similarly, CO_2, CO, H_2, H_2O, or air N_2 contamination of the N_2 samples may affect the measured ion currents at $m/z = 28$ or 29 leading to erroneous $\delta^{15}N$ values. To monitor gas purity, ion currents are measured at $m/z = 44$ (CO_2), 40 (Ar), 32 (O_2), 30 (N_2O, NO_x), and 18 (H_2O) for representative N_2 gases and are compared with those of the pure N_2 reference gas. Similarly, ion currents are measured at $m/z = 30$ (N_2O, NO_x) and 18 (H_2O) for representative CO_2 gases and are compared with those of the pure CO_2 reference gas. The data are used only to search for impurities. No calibration of ion current versus contaminant concentration has been attempted.

Table 1. Analyses of Unknowns[a]

sample	$\delta^{15}N$ (meas)	$\delta^{13}C$ (meas)	$\delta^{13}C$ (yield-corr)	n[b]
NaCN no. 1	−1.5 ± 0.4	−25.6 ± 0.5	−26.4 ± 0.2	7
NaCN no. 2	0.4 ± 0.1	−32.4 ± 0.3	−33.5 ± 0.1	2
$K_3Fe(CN)_6$ no. 1	−1.2 ± 0.3	−24.1 ± 0.3	−24.8 ± 0.1	5
$K_3Fe(CN)_6$ no. 2	−0.8	−24.2	−24.9	1
$K_4Fe(CN)_6 \cdot 3H_2O$	−0.4	−34.7	−35.1	1
solution of NaCN no. 1	−1.3 ± 0.1	−26.3 ± 0.1		4

[a] Isotopic compositions are given as δ values in permil (‰) relative to AIR for nitrogen and relative to VPDB for carbon. [b] Number of replicate analyses.

RESULTS AND DISCUSSION

The analytical results for NaCN, $K_3Fe(CN)_6$, $K_4Fe(CN)_6 \cdot 3H_2O$, and precipitates from NaCN solutions are given in Table 1. For individual samples, the reproducibility is ±0.4‰ or better (1σ) for $\delta^{15}N$ and ±0.5‰ or better for $\delta^{13}C$. Analyses of precipitates gave $\delta^{15}N$ and $\delta^{13}C$ values analytically indistinguishable from the values that were obtained for the starting NaCN salt.

The results of interfering mass scans (Table 2) indicate that the CO_2 gases contain insignificant H_2O and N_2O/NO_x. In the N_2 gases, Ar is at or below background levels, indicating that atmospheric leaks are minimal. Oxygen in the same gases is highly variable, probably due to variable reactivity of the copper shot, but it has little effect on the $\delta^{15}N$ measurement. Nitrous oxide and CO_2 are indistinguishable from background.

Yields for carbon ranged from 50% to 100%; the lower yields reflect, at least in part, samples that were inadequately ground or reaction times that were too short for complete combustion. For individual samples there is a systematic positive shift in $\delta^{13}C$ with decreasing yield (Figure 2). The mean regression slope for the samples is −0.041‰/% yield. If corrections are made using this value, the reproducibility of the $\delta^{13}C$ measurements is improved from ±0.5‰ to ±0.2‰ (Table 1). The agreement between the measured and gravimetrically predicted values for standards (see below) is also improved, which suggests that the yield correction also improves accuracy. Yields for nitrogen could not always be determined due to the significant O_2 in some gas samples. The results for low-O_2 samples suggest that there is a small negative shift in $\delta^{15}N$ with decreasing yield (Figure 2). However, the magnitude of the shift is about 0.01‰/% yield, substantially smaller than that for $\delta^{13}C$. The resulting error in $\delta^{15}N$ for the analyses reported in Table 1 is probably a few tenths of a ‰ at most. No yield corrections have been made to the measured $\delta^{15}N$ values.

To evaluate the accuracy of the method, three standards were prepared by mixing NaCN no. 2 and $K_3Fe(CN)_6$ no. 1 in known weight proportions. The mixtures were then analyzed and the results compared to the δ values predicted from the weight ratios

Table 2. Results of Interfering Mass Scans[a]

	m/z					
	18(H_2O)	30(N_2O/NO_x)	32(O_2)	40(Ar)	44(CO_2)	n[b]
			CO_2			
NaCN	0.069	0.028				4
$K_3Fe(CN)_6$	0.026	0.020				2
pure CO_2 reference gas	0.035-0.083	0.020-0.027				4
			N_2			
NaCN		0.175	2.418	0.000	0.055	6
$K_3Fe(CN)_6$		0.186	3.115	0.023	0.060	5
$K_4Fe(CN)_6 \cdot 3H_2O$		0.253	21.021	0.002	0.063	1
solution of NaCN		0.171	3.839	0.000	0.043	4
pure N_2 reference gas		0.069-0.219	0.000-0.016	0.000-0.032	0.038-0.081	9

[a] Results are expressed as percentage of the $m/z = 44$ peak for CO_2 and as percentage of the $m/z = 28$ peak for N_2. Averages are given for gases produced by combustion; the complete ranges are given for the pure reference gases. [b] Number of replicate analyses.

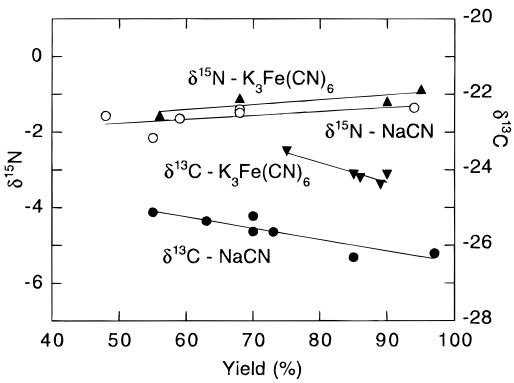

Figure 2. Variation in δ values with yield for replicate analyses of NaCN no. 1 and $K_3Fe(CN)_6$ no. 1.

Table 3. Analyses of Gravimetrically Calibrated Standards

	$\delta^{15}N$			$\delta^{13}C$		
standard[a]	gravimetry	meas	diff	gravimetry	meas	diff
68.5% A, 31.5% B	−0.1	−0.2	0.1	−30.7	−30.6	−0.1
47.0% A, 53.0% B	−0.4	−0.4	0.0	−28.9	−29.1	0.2
30.6% A, 69.4% B	−0.7	−0.3	−0.4	−27.5	−27.3	−0.2

[a] Standards are physical mixtures of NaCN no. 2 (A) and $K_3Fe(CN)_6$ no. 1 (B). Compositions of A and B are given in Table 1.

and the isotopic data given in Table 1. The yield-corrected $\delta^{13}C$ values differ from the predicted values by 0.2‰ or less, and the measured $\delta^{15}N$ values differ from the predicted values by 0.4‰ or less (Table 3). The close agreement is consistent with accuracy being within the precision of the technique, although the agreement cannot be taken as absolute proof of accuracy.

Vycor tubes containing reagents but no sample have also been run through the combustion and extraction procedures to determine whether there are significant blank contributions. About 3 μmol of CO_2 and 0.1 μmol of N_2 are typically produced. The $\delta^{13}C$ value of the CO_2 is −22‰. For the samples analyzed in this study, the CO_2 blank correction was ignored because it was smaller than the analytical uncertainty. The blank N_2 gases were too small for mass spectrometric measurement. However, a blank correction for $\delta^{15}N$ is unlikely to be necessary given the high probability that the $\delta^{15}N$ value differs from that of the sample by no more than a few tens of ‰. For example, a blank $\delta^{15}N$ value as high as 50‰ would lead to an error of only 0.1‰ in the analysis of a typical sample.

The analytical techniques described herein are sufficiently robust to begin using stable isotope techniques in cyanide degradation studies. An important first step is the determination of the N and C isotopic fractionations characteristic of the different degradation mechanisms (e.g., volatilization, oxidation, complexation, biodegradation).[3] This information will allow isotopic analysis to be used to identify the specific mechanism(s) responsible for cyanide loss in industrial settings or in laboratory experiments. In a separate report, we have given preliminary estimates for the isotopic fractionations characteristic of volatilization.[8] Isotopic analysis will also provide quantitative information on mass balance in cyanide degradation.

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