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**Methods for analysis of $^{15}\text{N}/^{14}\text{N}$ and $^{13}\text{C}/^{12}\text{C}$ in solid and aqueous
cyanides - An interim report**

by

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Analysis of $^{15}\text{N}/^{14}\text{N}$ and $^{13}\text{C}/^{12}\text{C}$ in solid and aqueous cyanides - An interim report

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ABSTRACT

The stable isotopic compositions of nitrogen and carbon in cyanide compounds can be determined by combusting the compounds to form N_2 gas and CO_2 gas, and analyzing the gases by mass spectrometry. Free cyanide ($\text{CN}^-_{aq} + \text{HCN}_{aq}$) 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 permil or better for $\delta^{13}\text{C}$ and ± 0.3 permil or better for $\delta^{15}\text{N}$. Hydrated compounds do not combust as well or as reproducibly as anhydrous compounds. Deliquescent compounds such as NaCN should be dried by heating before analysis. The analytical methods described herein are sufficiently reliable to apply stable isotope techniques to problems of cyanide degradation at active and abandoned heap leach mines.

INTRODUCTION

Cyanide (CN^-_{aq}) is used at mines throughout the world to extract Au and Ag from their ores. The fact that cyanide is toxic has led to a public perception that the processing of ores can lead to environmental contamination. There are, however, a number of processes by which CN^-_{aq} can degrade naturally, among them volatilization as HCN , precipitation, complex formation, and biodegradation (see Smith and Mudder, 1991 for a review). Unfortunately, the rates and relative importance of these different degradation mechanisms are in many cases uncertain.

This report is the first step in the development of a new field of study, the stable isotope geochemistry of cyanide compounds and their degradation products. The overall objective of this work is to develop a tool for (1) identifying specific degradation mechanisms at mine sites, and (2) investigating degradation rates and controls. To date there has been only one cyanide-related study in which stable isotopes were employed. In that study (Strobel, 1967), ^{15}N -labelled HCN was used in a soil utilization experiment. The only species that was analyzed isotopically was ammonia (NH_3), one of the cyanide degradation products. To my knowledge, there have been no direct analyses of the stable nitrogen or carbon isotopic composition of cyanides.

Herein I report a method for measuring $^{15}\text{N}/^{14}\text{N}$ and $^{13}\text{C}/^{12}\text{C}$ in cyanide salts and in free cyanide ($\text{CN}^-_{aq} + \text{HCN}_{aq}$) contained in simple solutions. The same method holds promise for the analysis of cyanide complexes, such as $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Fe}(\text{CN})_6^{3-}$, by first carrying out a conventional reflux-distillation for either weak acid dissociable or strong acid dissociable cyanide (e.g., USEPA, 1986), and then analyzing the CN^-_{aq} collected in the alkaline trap. The extension of these methods to cyanide complexes is currently in progress.

EXPERIMENTAL METHOD

Solid cyanide compounds are prepared for analysis by combusting them to form CO_2 and N_2 gas. The combustion is carried out in 9 mm OD, 7 mm ID Vycor tubes. Prior to use the tubing is broken 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, previously baked for 4 hours at 600°C and sieved, then are loaded into the tube, followed by the sample, followed by 3 grams of copper shot. The purpose of the cupric oxide and copper is to control the oxygen fugacity during combustion so that the products are CO_2 and N_2 . It is likely that smaller quantities of both reagents would suffice. The tubes then are attached to a vacuum line and pumped for a minimum of 4 hours to a final pressure of about 10^{-6} torr. They are sealed at 15 cm length, and placed in a muffle furnace that has been preheated to 500°C . The temperature is then raised to 850°C and held for 1 hour, and then slowly lowered to room temperature. In practice, power to the furnace is simply turned off.

To extract and purify the CO_2 and N_2 , the sealed tubes are placed in Pyrex tube crackers and attached to a vacuum line like that shown in Figure 1. The crackers are equipped with sintered glass frits. A wad of silica wool is added between the Vycor tube and the frit to prevent fine cupric oxide powder from migrating into the vacuum line. We avoid sticky vacuum grease by using tube crackers with an O-ring rather than ground glass seal at the knuckle. For ease of cracking, the Vycor tubes are scored and positioned at the base of the knuckle.

After the tube cracker is attached to the vacuum line and 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. Complete condensation requires about 4 minutes. The manometer reading is then recorded and converted to the nitrogen yield using a prior pressure-gas quantity calibration. Valve 3 is then opened and the N_2 gas is condensed onto type 5a molecular sieve in either a stopcock-sealed Pyrex bottle or a 6mm OD Pyrex tube. When the transfer is complete, the stopcock is closed or the tube is sealed using a torch.

Next, valves 1 and 3 are closed and the liquid nitrogen on the traps is replaced with dry ice+2-butoxyethanol. The carbon dioxide sublimates and is condensed in the finger with liquid nitrogen. The finger is warmed to room temperature after closing valve 2 and the manometer reading is recorded allowing the carbon yield to be calculated using a prior pressure-gas quantity calibration. The carbon dioxide is then frozen into a stopcock-sealed bottle or a 6mm OD 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 and 10 g NaOH in 1 liter of deionized water. The purpose of the NaOH is to favor CN^-_{aq} over HCN_{aq} ; the latter has a high vapor pressure and readily evaporates from standing solutions. Cyanide is extracted from the solutions by precipitating it as copper(II)ferrocyanide ($\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot x\text{H}_2\text{O}$). To accomplish this, solutions of ferrous sulfate (178 mg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 ml deionized water) and cupric sulfate (204 mg CuSO_4 in 100 ml deionized water) are prepared. Five ml of the ferrous sulfate solution and 5 ml of the cupric sulfate solution are added to quantitatively precipitate the free cyanide. For a typical sample containing 2.5 mg CN^-_{aq} , this represents twice the stoichiometric requirement. It is important that the ferrous sulfate solution be freshly prepared to insure that the iron is in reduced form. The solution is then acidified with hydrochloric acid to a pH of about 1 in order to dissolve the ferrous hydroxide that usually forms. The distillate is filtered using a Millipore device with 1 micron acetate filter, and allowed to dry. Filtrates are

combusted by the method described above. The acidification step is critical; the presence of ferrous hydroxide greatly lengthens the filtration time and will also interfere with the sealed tube combustion.

The isotopic compositions of the N_2 and CO_2 gases are measured using a Finnigan MAT 252 triple collecting mass spectrometer. The isotope ratios are compared with those of N_2 and CO_2 reference gases previously calibrated against NIST-distributed standards. The precision of the mass spectrometer measurement is typically $\pm 0.02\text{‰}$ or better for $\delta^{13}C$ and $\pm 0.05\text{‰}$ or better for $\delta^{15}N$.

There are a number of isobaric interferences which 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 carbon dioxide samples will affect the measured ion currents at $m/e=44$, 45, and 46 leading to erroneous $\delta^{13}C$ values. Similarly, CO_2 , CO , H_2 , H_2O , or atmospheric N_2 contamination of the nitrogen samples may affect the measured ion currents at $m/e=28$ and/or 29 leading to erroneous $\delta^{15}N$ values. It is also desirable to know whether the addition of ferrous and cupric sulfate to the solutions leads to sulfate coprecipitation and subsequent SO_2 production on combustion. To monitor gas purity, ion currents are measured at $m/e=44$ (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 $m/e=64$ (SO_2), 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 detectable impurities. No calibration of ion current versus contaminant concentration was attempted.

RESULTS AND DISCUSSION

The analytical results for reagent grade NaCN, solutions prepared from the same reagent NaCN, reagent grade $K_3Fe(CN)_6$, and industrial grade NaCN obtained in briquet form from an active heap leach operation are given in Table 1. For the reagent grade compounds the reproducibility of the measured isotopic compositions are $\pm 0.2\text{‰}$ for $\delta^{15}N$ and $\pm 0.4\text{‰}$ for $\delta^{13}C$, respectively. The accuracy of the analyses is somewhat difficult to evaluate inasmuch as these are the first reported analyses of cyanide species. The analyses with near 100% yields are the most reliable because, barring canceling errors, they represent near-complete breakdown of the cyanide compound and near-complete conversion to N_2 gas and CO_2 gas. The other analyses with lower yields gave nitrogen (as N_2) and carbon (as CO_2) in the 1:1 atomic ratio predicted from the stoichiometry (Table 1), and gave δ -values indistinguishable from the analyses with near 100% yields. The low yields are thus not due to production of CO , N_2O or NO_x ; they would seem to result from incomplete breakdown of the sample. In addition, there appears to be no significant isotope fractionation during the oxidation reaction. Grinding may be required to achieve complete yields.

For the industrial grade NaCN, both the yields and the isotopic compositions are more erratic. Powder X-ray diffraction revealed that the material contains substantial $NaCN \cdot 2H_2O$. Anhydrous NaCN is known to be deliquescent, and the briquet was apparently hydrated during its storage, probably several years in duration, at the mine site. This problem may be a common one in the combustion of NaCN samples that have been stored without attention to keeping them dry. The H_2O interferes with the oxidation reaction in such a way that the carbon and nitrogen yields depart dramatically from the 1:1 ratio characteristic of cyanides. Placing the samples in a drying oven overnight at 90 or 150°C improved

the consistency of the replicates and resulted in compositions more like the reagent grade materials.

The NaCN solutions that were analyzed display nitrogen isotope values and reproducibility similar to the reagent NaCN from which the solutions were prepared (Table 2). The carbon isotope values, however, are on average 0.7‰ smaller than the solid NaCN results. It is difficult to know whether the difference is significant given the variability of the NaCN δ -values and the variability of the solution δ -values. However, the uniformly high C:N of the solution yields supports the suggestion that the combustion is somewhat more complicated than for anhydrous cyanide salts. This complication is currently under investigation.

Vycor tubes containing reagents but no sample have been run through the combustion and extraction procedure to determine whether there are significant blank contributions. About 3 micromoles of CO₂ and 0.1 micromole of N₂ are typically produced. The $\delta^{13}\text{C}$ value of the CO₂ is -22.8 ‰; blank corrected $\delta^{13}\text{C}$ values for the samples are given in Table 1. For most samples the corrected values are not significantly different from the measured values because the blank is a fairly small proportion of the sample-derived CO₂, and the isotopic composition of the blank is not dramatically different from the isotopic composition of the sample. The blank N₂ gases were too small for mass spectrometric measurement. A correction for $\delta^{15}\text{N}$ is unlikely to be necessary, however, given the high probability that the $\delta^{15}\text{N}$ value differs from that of the sample by no more than a few tens of permil. For example, a blank $\delta^{15}\text{N}$ value as high as 50‰ would lead to an error of only 0.1‰ in the analysis of a typical sample.

With respect to gas purity, the results in Tables 3 and 4 indicate that the CO₂ gases contain insignificant amounts of H₂O and SO₂. Carbon dioxide extracted from the industrial grade NaCN may contain a small amount of N₂O or NO_x. The quantity appears to be quite small, however, and it is unlikely to have a significant effect on the $\delta^{13}\text{C}$ measurement. The N₂ gases overall appear to be quite pure with H₂O, N₂O/NO_x, O₂, Ar, and CO₂ at background or only slightly higher levels. Slight leaks can apparently occur during the extraction, as in sample 2, but they do not lead to significant shifts in the measured $\delta^{15}\text{N}$ values (Table 1). Nitrogen derived from the unheated industrial grade NaCN differs from the other nitrogen gases in that they contain substantial O₂ and Ar, and lesser but significant CO₂. It is extremely unlikely that all four of the samples leaked during their extractions. The contaminant gases were almost certainly associated with the samples, and may have been acquired during hydration of the briquets through adsorption or some other mechanism. Heating overnight was effective in removing the contaminants. They may have contributed to the poor combustion results for the unheated samples.

A final observation on accuracy is that the compositions determined herein resemble the compositions of the ingredients from which commercial cyanide compounds are generally synthesized, coke and atmospheric N₂. Coals, the materials from which coke is derived, have an average $\delta^{13}\text{C}$ value of -25‰, and atmospheric nitrogen has a $\delta^{15}\text{N}$ value of 0‰ (see Faure, 1986 for a review).

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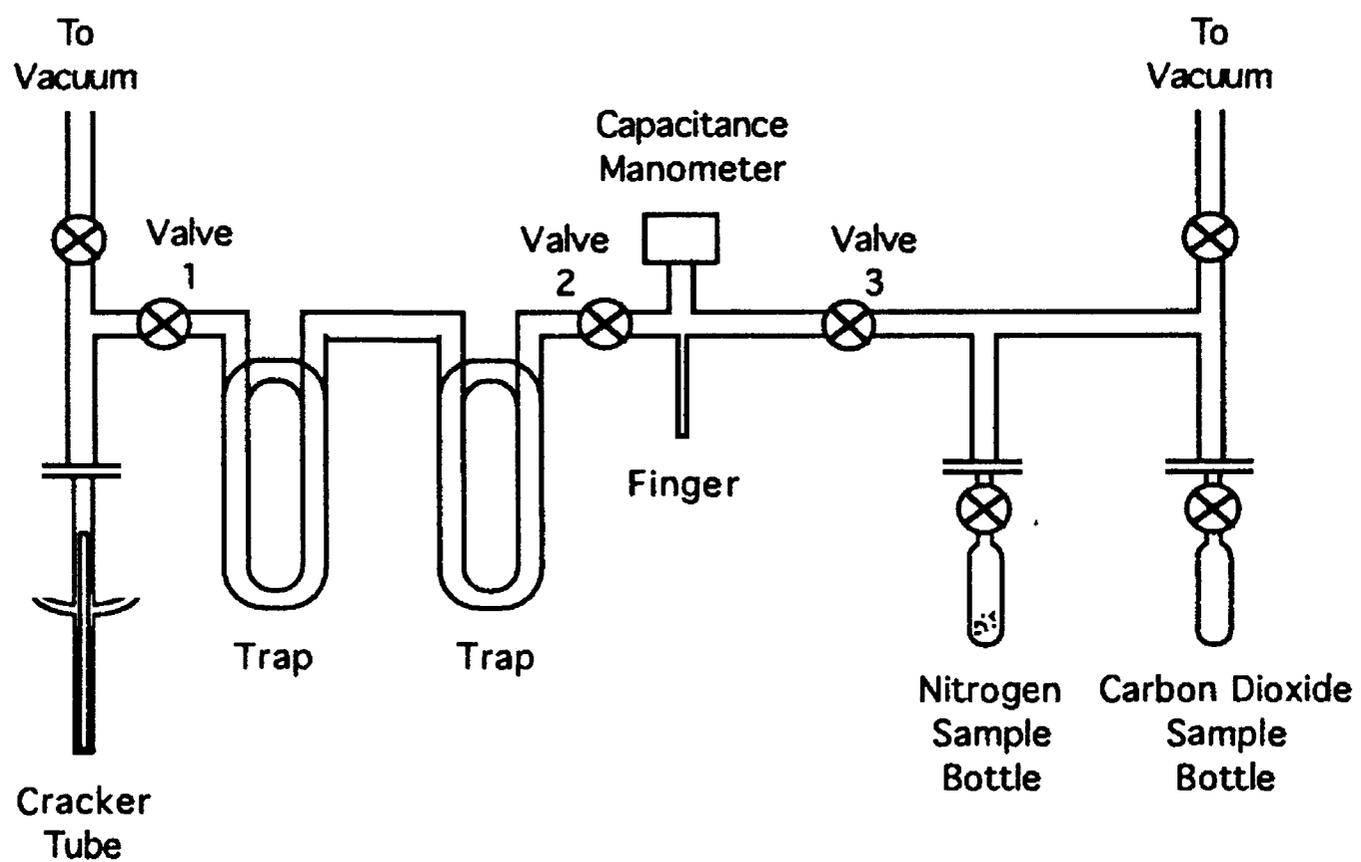


Figure 1. Diagram of the vacuum line used for gas extraction. The line is constructed from Pyrex tubing and Kontes O-ring valves. Vacuum is supplied by a mercury diffusion pump backed by a mechanical pump.

Table 1.-Analytical results (isotopic compositions are given as δ -values in permil (‰) relative to air for nitrogen and relative to PDB for carbon).

Sample no	Wt	N ₂ yield	$\delta^{15}\text{N}_{\text{AIR}}$	CO ₂ yield	$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{13}\text{C}_{\text{PDB}}$ (blank corr)	C/N (atoms)
Reagent grade NaCN:							
9	4.8 mg	94%	-1.4‰	97%	-26.2‰	-26.3‰	1.0
14	5.0	68	-1.4	85	-26.3	-26.4	1.2
44	6.2	55	-2.1	55	-25.1	-25.2	1.0
60	7.6	59		63	-25.4	-25.4	1.1
Reagent grade K₃Fe(CN)₆:							
1	3.8	90	-1.2	90	-24.1	-24.2	1.0
2	4.4	95	-0.9	89	-24.4	-24.5	0.9
Industrial grade NaCN:							
3	3.5	24	-0.0	48	-17.4	-16.9	2.0
4	4.3	6	1.3	46	-16.8	-16.4	7.5
15	6.9	141	-4.5	28	-20.1	-19.9	0.4
16	10.3	113	-2.2	4	-12.7	-8.0	0.04
20 (90°C)	7.2	38	1.5	64	-24.1	-24.2	1.7
21 (90°C)	4.7	11	1.7	51	-21.4	-21.3	4.4
26 (150°C)	9.2	9	2.4	31	-22.3	-22.3	3.5
Reagent grade NaCN in solution:							
36	11.6		-1.3		-26.2	-26.4	1.4
37	12.7		-1.4		-26.3	-26.4	1.4
38	11.8		-1.5				1.7
46	12.7		-1.9		-27.0	-27.1	1.6

Table 2. Averages of nitrogen and carbon isotopic analyses.

	$\delta^{13}\text{C}_{\text{PDB}}$	St Dev	$\delta^{15}\text{N}_{\text{AIR}}$	St Dev	Number
Reagent grade NaCN	-25.8‰	0.5	-1.6‰	0.3	4
Reagent grade $\text{K}_3\text{Fe}(\text{CN})_6$	-24.2	0.2	-1.0	0.2	2
Industrial grade NaCN (preheated only)	-22.6	1.2	1.8	0.4	3
Reagent grade NaCN in soln	-26.5	0.4	-1.5	0.2	4

Table 3. Results of interfering mass scans on cyanide-derived CO₂ and pure reference CO₂, expressed in volts as percentage of the m/e=44 peak

Sample	m/e		
	18 (H ₂ O)	30 (N ₂ O,NO _x)	64 (SO ₂)
Reagent grade NaCN:			
9	0.054%	0.028%	
44	0.071		
60	0.084		
Reagent grade K₃Fe(CN)₆:			
1	0.024	0.020	
2	0.027	0.024	
Industrial grade NaCN:			
3	0.045	0.034	
4	0.047	0.032	
16	0.589	0.048	
26 (150°C)	0.050	0.043	
Other cyanide extractions:			
5			0.000
6			0.000
7			0.000
8			0.000
Pure CO₂ reference gas:			
	0.083	0.020	
	0.076	0.023	
	0.063	0.027	
	0.035		

Table 4. Results of interfering mass scans on cyanide-derived N₂ and pure reference N₂, expressed in volts as percentage of the m/e=28 peak

Sample	m/e				
	18 (H ₂ O)	30 (N ₂ O,NO _x)	32 (O ₂)	40 (Ar)	44 (CO ₂)
Reagent grade NaCN:					
9	0.012%	0.076%	0.016%	0.000%	0.053%
14	0.021	0.071	0.024	0.000	0.050
Reagent grade K₃Fe(CN)₆:					
1	0.006	0.098	0.580	0.112	0.068
2	0.006	0.160	0.042	0.007	0.050
Industrial grade NaCN:					
3	0.060	0.121	4.918	2.141	0.212
4	0.157	0.172	14.835	2.018	0.294
15	0.039	0.146	2.772	1.762	0.092
16	0.034	0.175	2.267	2.050	0.098
20 (90°C)	0.030	0.267	0.085	0.000	0.050
21 (90°C)	0.028	0.155	0.415	-0.003	0.058
26 (150°C)	0.039	0.117	0.098	0.000	0.032
Reagent grade NaCN in soln:					
36	0.017	0.159	-0.008	-0.001	0.038
37	0.017	0.149	-0.001	0.000	0.038
Pure N₂ reference gas:					
	0.029	0.171	-0.013	0.001	0.062
	0.036	0.090	-0.014	-0.002	0.038
	0.004	0.069	0.003	0.031	0.054
	0.051	0.219	-0.001	0.000	0.072
	0.009	0.080	0.016	0.032	0.081
	0.003	0.070	0.003	0.031	0.053
	0.005	0.072	0.007	0.031	0.072
	0.004	0.074	0.003	0.031	0.065