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A Gas Chromatographic Method for Determining Residues of Sodium Cyanide in Vegetation and Soil

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Sodium cyanide is used as a predacide in the M-44 cartridge (U.S. Environmental Protection Agency Registration Number 6704-75), a spring-loaded ejection device to control predation on sheep by coyotes. Although sodium cyanide is extremely toxic, its use in the cartridge has not been considered to be a potential source of hazard in the environment because of the instability of the chemical, the operation of the cartridge (which contains less than 1 g of sodium cyanide and ejects most of it into the coyote's mouth), and the restricted use of these devices. However, to satisfy requirements by regulatory agencies, it was necessary to determine the persistence of sodium cyanide in the environment and assess residue levels in plants and soil resulting from the use of the M-44 cartridge.

Although there are several analytical methods for sodium cyanide, a method was not available that could be applied to this study. The standard Liebig method (AOAC OFFICIAL METHODS OF ANALYSIS 1975, ACS REAGENT CHEMICALS 1975) which involves titration of cyanide ions with silver nitrate is used primarily for assaying samples containing large amounts of sodium cyanide. Commonly used color spot tests (GUATELLI 1964), although very sensitive, are subject to various types of interferences and are only qualitative or semi-quantitative at best. Several colorimetric methods (ASTM STANDARDS 1970, GUATELLI 1964, GOULDEN et al. 1972) and gas chromatographic methods (MYERSON and CHLRIDZINSKI 1975, NOTA and PALOMBARI 1973, NOTA et al. 1976) that have been reported could not be used because they were not applicable to plant samples. We have developed an analytical procedure for the determination of sodium cyanide in vegetation and soil with a sensitivity of about 0.1 ppm. It involves the acid hydrolysis of sodium cyanide to produce hydrogen cyanide in an enclosed system, and measurement of the hydrogen cyanide in the headspace by gas chromatography with either an electroconductivity or a thermionic detector.

EXPERIMENTAL

Field Test

Sodium cyanide (nominal purity, 95-99.7%) was sprinkled by hand directly from a single cartridge onto randomly selected 1-ft^2 plots of vegetation or soil. Each plot received 0.88 g

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of sodium cyanide, the amount contained in a cartridge. Thirty plots each of vegetation (consisting of primarily crested wheat grass, Agropyron cristatum) and soil (predominantly loam) were prepared. Vegetation and soil samples were scheduled for collection from five plots at each of six sampling periods, from less than 1 day to 6 weeks after application. Soil samples were taken as scheduled, but vegetation sampling was discontinued after 2 days because the 2-day samples showed no detectable residues. All the vegetation was cut near the base, just above the surface of the soil. Soil samples consisted of scrapings, 1/4-1/2 inch deep, from the entire surface area of the plot. Five subsamples from each plot sample were analyzed on the same day of collection.

Analytical Procedure

Sample Preparation and Analysis: Vegetation samples were cut into about 1-inch lengths with hand scissors. To minimize losses of sodium cyanide from the surface, samples were not homogenized with a mechanical blender but were mixed as uniformly as possible by hand. A 5-g subsample was placed in a 125-ml Erlenmeyer flask, 25 ml of methanol and 0.5 ml of 2% aqueous sodium hydroxide were added, and the mixture was shaken by hand for 5 minutes. The supernatant layer was filtered into a 50-ml Erlenmeyer flask. The flask was placed in a water bath at 50^{o} C and the sample taken just to dryness with a stream of nitrogen gas. The flask was capped with a gas-tight skirted rubber stopper, and 20 ml of air was withdrawn from the flask with a gas-tight syringe. With another syringe, 0.5 ml of 14N H_2SO_4 was added to convert sodium cyanide to hydrogen cyanide gas. An appropriate volume of gas, depending on the estimated concentration, was withdrawn from the headspace with a gas-tight syringe and injected into the gas chromatograph.

Soil samples did not require the sodium hydroxide extraction step used for vegetation. A 2-g subsample from a plot was directly hydrolyzed with acid in a sealed flask to generate hydrogen cyanide for gas chromatographic analysis.

The concentration of hydrogen cyanide in the headspace was determined by comparing the gas chromatographic response obtained for the sample against a standard curve prepared from injections of varying amounts of a hydrogen cyanide gas reference. The reference was prepared by hydrolyzing a known amount of sodium cyanide (from the same source as test samples) under the same conditions as the samples.

Gas Chromatography: Gas chromatographic measurements were made on a Varian 1200* gas chromatograph equipped with a Tracor Coulson conductivity detector (first samples, through 2 days), or a Micro-Tek MT-220 gas chromatograph equipped with a Tracor N-P alkali thermionic detector (2-, 3-, 6-week samples). A 4-ft

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* Reference to trade names does not imply Government endorsement of commercial products.

x 1/4-inch O.D. glass column packed with Chromosorb 101, 80/100 mesh, was used. The column temperature was 100° C and helium was used as the carrier gas.

RESULTS AND DISCUSSION

The analytical method was evaluated with vegetation and soil samples fortified with varying amounts of sodium cyanide. Recoveries ranged from 39% at the lower levels to 88% at the higher levels for vegetation, and from 70% to 93% for soil (Table 1).

TABLE 1

Recoveries of Sodium Cyanide from Fortified Vegetation and Soil Samples

Sodium cyanide, added ppm, wet weight[a]	Recovered, % (S.D.) Plant	Recovered, % (S.D.) Soil
1	46 (2.1)	70 (7.7)
5	39 (4.7)[b]	86 (3.0)
10	59 (2.3)	93 (2.1)
20	88 (1.1)	88 (6.6)

[a] Added to 5-g samples, N=5 for each level.

[b] Low recoveries are attributed to samples standing too long after addition of acid.

The lower recoveries for vegetation samples may have been due to losses that occurred in the alkaline extraction step and during evaporation of the extract solution to dryness. Recoveries were generally poorer at the lower levels for both vegetation and soil, possibly because of the loss of small amounts of hydrogen cyanide either through solubility in the water or through decomposition. The relatively lower recovery obtained for the plant samples fortified at the 5-ppm level is attributed to a slight deviation from the procedure used for the other samples. Instead of analyzing the headspace by gas chromatography immediately after addition of the acid, the gas chromatographic analysis in this instance was performed after addition of acid to all five samples. Consequently, some loss of hydrogen cyanide probably occurred during the time that elapsed between addition of the acid and analysis of the headspace. Later studies confirmed that the concentration of hydrogen cyanide in the headspace gradually decreases upon standing. To minimize losses, the headspace should be analyzed as soon as possible after addition of the acid.

Residue data obtained for the field test are shown in Table 2. Because of the large variations in residue levels found among subsamples, the values shown are ranges for the five subsamples analyzed from each plot. The much larger variations for vegetation than for soil samples collected on the day of application probably results from uneven surface distribution of sodium cyanide on vegetation which differed in types and density of growth among the plots. Residue levels in vegetation decreased rapidly within 24 hours and were below the detectable level of 0.5 ppm after only 2 days. The lower limit of 0.5 ppm was based on the sensitivity of the conductivity detector that was being used at the time. Better sensitivity was obtained later with the use of a thermionic detector for the gas chromatographic analysis.

Residues in soil also dropped rapidly within 2 days after application, but appeared to level off. Despite periods of some rain and snow, 0.5-6 ppm were found after 2 weeks, and 0.1-0.6 ppm after 6 weeks. This persistence of sodium cyanide could be

TABLE 2

Sodium Cyanide Residues in Vegetation and Soil Samples from Field Test

Sampling time, after application	Range of sodium cyanide in subsamples[a] ppm (wet weight)				
	Plot 1	Plot 2	Plot 3	Plot 4	Plot 5
Vegetation	Plots[a]				
Same day	33-360	1259-1799	7-369	9-14	3-4
1 day	ND[b]-1.5	ND-4.9	ND-1	ND-0.9	ND-0.9
2 days	ND	ND	ND	ND	ND
Soil					
Same day	662-1528	274-898	87-898	137-867	159-350
1 day	7-10	6-11	7-22	4-17	5-11
2 days	1-4	3-8	2-3	2-7	2[c]
2 weeks	0.5-1	1-2	1-2	1-6	2-3
3 weeks	0.4-0.6	0.3-0.7	0.6-1	0.7-1	0.5-1
6 weeks	0.4-0.6	0.2-0.4	0.1[d]	0.1-0.2	---

[a] Five 5-g subsamples of vegetation and five 2-g subsamples of soil were analyzed from each plot. No sodium cyanide was found in vegetation or soil samples taken from the area before application.

[b] ND = not detected with conductivity detector (sensitivity, 0.5 ppm).

[c] All five subsamples had 2 ppm.

[d] All five subsamples had 0.1 ppm (thermionic detector, sensitivity 0.1 ppm).

attributed to the alkalinity of the soil in the plots which showed pH measurements ranging from 7.3 to 9.2. In acidic soils, sodium cyanide would be expected to degrade much more rapidly.

The very small amounts of sodium cyanide found in the vegetation and soil samples after only 2 days indicate that contamination of the environment from use of M-44 cartridges is highly unlikely. Sodium cyanide accidentally discharged from a cartridge would probably be dispersed so that its concentration in vegetation or soil would be considerably less than the trace amounts found in the 1-ft^2 test plots. Since an average of one cartridge (containing less than 1 g of sodium cyanide) per 10 acres is the normal application rate, hazardous accumulations of sodium cyanide would not be expected to occur.

This analytical method is applicable only to cyano compounds that readily produce hydrogen cyanide in the presence of acid. Therefore, compounds such as cyanates, thiocyanates, and cyanides of heavy metals that require more extensive digestion with acid to liberate hydrogen cyanide would not be measured. The formation of these compounds from sodium cyanide seems unlikely, however. Previous studies (STROBEL 1967) with doubly labeled cyanide, $^{14}C^{15}N$, indicate that cyanide is metabolized to carbon dioxide and ammonia by microorganisms in soil.

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