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DETERMINATION OF CYANIDE IN SOILS AND WASTES BY ION CHROMATOGRAPHY

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ABSTRACT: Ion chromatography was evaluated for its ability to measure free cyanide (CN) in environmental samples. Liquid and soil samples as well as composted sewage sludge were treated with known amounts of CN as KCN. Samples were digested and analyzed for CN using EPA Method 9010 and ion chromatography. Ion chromatography proved to be advantageous over Method 9010 due to more rapid sample analysis with greater or equal accuracy. Furthermore, the detection ranges were greatly expanded when the Method 9010 colorimetric procedure of quantification was replaced with ion chromatography. When the Method 9010 distillation procedure was combined with ion chromatographic quantification, CN results were favorable for both aqueous and solid samples. The detection range increased by 92%, and 1.5 hours were saved with the new procedure. Ion chromatography holds promise for improving CN analysis as well as for increasing the spectrum of samples which can be analyzed.

KEYWORDS: Cyanide, ion chromatography, soil, and solid waste.

INTRODUCTION

Cyanide (CN) may occur in soils and water as a result of improper disposal of CN-containing industrial wastes (Brooks, 1992; DeBell, *et al.,* 1982; Galceran, *et al.,* 1990; Martin, 1992). In addition, naturally occurring CN is produced as a result of microbial activity (Kunz, *et al.,* 1992). The detection and quantitative determination of CN in soils is integral to the proper assessment and ultimate remediation of contaminated media due its potential impacts on public health and the environment.

Currently existing techniques for CN determination are inadequate in terms of the range of concentrations that can be detected as well as in terms of the types of samples that can be analyzed. The currently accepted EPA method for CN detection, Standard Method 9010 (U.S. Environmental Protection Agency, 1986), is used to determine CN concentration in aqueous wastes and leachate. The method involves rigorous sample distillation in an acidic environment, liberation of HCN gas, HCN collection in an alkaline absorbing solution, and measurement of CN concentration via colorimetric analysis of a cyanide-chloramine-pyridine complex. The detection range is limited to 0.01-0.4 μg/mL CN, a range which is impractical when considering the concentrations of CN that may occur in soils as a result of the introduction of industrial wastes (Martin, 1992). The U.S. Environmental Protection Agency (1992) considers a soil "heavily contaminated" with CN in the 100-500 mg/kg range.

A number of methods for CN analysis currently exist (Blanco and Maspoch, 1984; Dionex, 1986; Ingersoll, *et al.,* 1981; Meeussen, 1992; Okuno, *et al.,* 1979;

Table 1. Selected properties of soils and waste samples.

Material	Classification	TOC[1] (%)	Cd	Cu	Fe	Zn	pH	EC[2] (dS/m)
			μg/g					
Glynwood topsoil	Fine, illitic, mesic, Aquic Hapludalf	1.00	0.005	0.02	9.05	1.55	6.7	0.315
Glynwood subsoil		0.99	0.005	0.02	13.80	0.005	6.6	0.313
Pemberton	Loamy, mixed, mesic Arenic Hapludults	1.05	0.005	0.01	3.86	7.50	6.7	0.422
Composted sewage sludge		30.5	0.015	0.02	53.25	3.90	4.8	11.56

[1] TOC = Total organic carbon.
[2] EC = Electrical conductivity.

Owerbach, 1985). Ingersoll, *et al.* (1981) outlined a three-step process for analyzing samples containing metal-CN complexes: 1) dissociation of the complexes using competing ligands; 2) distillation; and 3) quantification of CN using an ion selective electrode. Meeussen (1992) described an automated method for CN determination using UV irradiation to decompose metal-CN complexes followed by distillation of the sample and then by spectrophotometric analysis. Okuno, *et al.* (1979) outlined procedures for CN analysis using gas chromatography. Although the above methods are successful in the measurement of CN, these methods are specific for aqueous samples only. Few methods exist for CN determination in soils, and less information is available on CN measurement in solid wastes. A method using distillation and differential pulsed polarography has been developed for soil analysis (Adeloju and Gawne, 1986). A major drawback of their method, however, is the distillation time needed to achieve acceptable recovery rates — up to four hours is required for soil samples. A microdiffusion procedure developed by Dartnall and Burns (1987) realized CN recovery rates of only 60% from soils.

The colorimetric analysis for CN detection outlined in Method 9010, in addition to having a restrictive detection range, is a time-consuming procedure. Furthermore, the cyanide-chloramine-pyridine complex is susceptible to rapid color loss and must be handled as a hazardous waste. Ion chromatography (IC) may serve as a possible replacement for colorimetric analysis. In 1983, the Dionex Corporation developed a method for CN detection via IC. The method provides for accurate, reproducible determinations of CN in aqueous samples without relying on time-dependent color formation reactions. In addition, the generation of hazardous by-products is minimized.

The purpose of the reported research was to develop a technique for CN quantification in soils and wastes employing detection by ion chromatography. Specifically, the objectives were: to 1) develop a more efficient method for determination of CN in aqueous samples; to 2) expand the range of CN

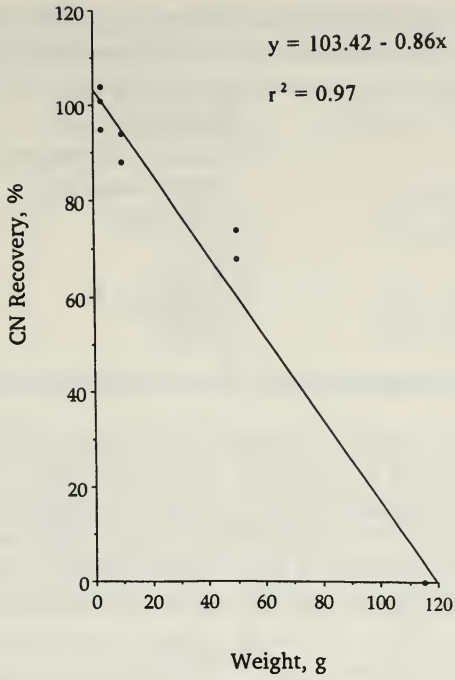

Figure 1. Percent CN recovery from Glynwood soil as a function of initial soil weight.

concentrations which could be detected using IC; and to 3) expand the range of samples that could be analyzed with the Method 9010 distillation process combined with IC to include soils and solid wastes.

MATERIALS AND METHODS

Samples of Glynwood and Pemberton soils were collected from agricultural fields in a corn-soybean rotation (Table 1). Subsoil material was collected from 50 to 75 cm below the surface. Composted sewage sludge was collected at the Southwesterly Compost Facility, Columbus, Ohio. The soil and waste samples were collected with a sampling tube, composited, and brought to the laboratory, where they were air-dried, crushed, and sieved to pass a 2-mm sieve.

The concentrations of Cd, Cu, and Zn were obtained from dilute HCl extracts (Nelson, *et al.*, 1959). A 2.0 g sample of soil was added to 20 mL of 0.1 N HCl and centrifuged for 5 minutes. The clear supernatant was then analyzed by atomic absorption spectroscopy (AAS). Fe determination was performed as described by Olson and Ellis (1982). A 10 g sample of soil was extracted using a solution of 0.005 M DTPA, 0.1 M TEA, and 0.01 M $CaCl_2$ (pH 7.3). The resulting mixture was shaken at 180 opm for 2 hours. After shaking, the samples were filtered through Whatman No. 42 filter paper and analyzed via AAS. Total organic carbon concentration was analyzed using a Dohrmann Carbon analyzer; pH was measured on a 1:1 solids:water sample using a Fisher pH meter. Electrical conductivity was measured on a 1:1 extract using a YSI conductivity meter.

Table 2. Operating conditions for ion chromatographic determination of CN.

Separator column	Dionex HPIC-AS7
Guard column	Dionex HPIC-AG7
Eluant	0.5 M CH_3CO_2Na, 0.1 M NaOH, 0.5 % ethylenediamine
Eluant flow rate	0.9 mL/min
Injection loop	200 µL
Output voltage	0-1 Volts
Output range	300-300 nA
Pressure	1400 psi
Electrode	Ag

CN Treatments. Aqueous samples were spiked with CN solutions ranging in concentration from 0.1 to 1.0 µg/mL. CN was added as KCN in H_2O adjusted to pH 9.0. Soil and composted sludge samples were treated with the pH 9.0 KCN solution as well. Final CN concentrations in the solids was 10 µg CN/g solids.

Colorimetric Procedure. Liquid samples analyzed for CN were distilled according to the procedure outlined as Method 9010 (U.S. Environmental Protection Agency, 1986). A 500-mL sample was placed in a 1 L boiling flask and 5 mL of 1.25 N NaOH was added. Through the air inlet tube, a slow stream of air was introduced so that approximately 3 bubbles per second appeared in the solution in the boiling flask. Lead acetate paper was used to check the samples for sulfides. A 50 mL sulfamic acid solution was added, if samples were suspected to contain NO_2 or NO_3. After allowing the solution to mix for three minutes, 50 mL of 1:1 H_2SO_4 followed by 20 mL of $MgCl_2$ were added through the air inlet tube. The solution was heated to boiling and refluxed for 1 hour. Fifty mL of the alkaline-absorbing solution was withdrawn and mixed with 15 mL of 1 M NaH_2PO_4 and 2 mL of chloramine-T. A 5 mL pyridine barbituric acid solution was added next. Absorbance was read at 578 nm in a 1-cm cell within 15 minutes.

Ion Chromatography Procedure. The ion chromatograph (IC) used was a Dionex Model 2000-i instrument with a pulsed amperometric detector (Dionex

Table 3. A comparison of Method 9010 and ion chromatography for CN determination in aqueous samples with and without distillation.

	Actual	Method 9010	IC
	µg/ml		
Not distilled	0.1	0.09 ± 0.04	0.10 ± 0.008
	0.5	0.54 ± 0.06	0.55 ± 0.009
	1.0	1.02 ± 0.07	1.13 ± 0.01
Distilled	0.1	0.07 ± 0.01	0.1 ± 0.005
	0.5	0.49 ± 0.03	0.5 ± 0.01
	1.0	1.00 ± 0.03	1.0 ± 0.01

Table 4. A comparison of the percent recovery of CN from 2.5 g of composted sewage sludge with and without EDTA.

Method	Ligand	CN Recovery (%)
9010	—	36 ± 0.02
IC	—	75 ± 0.07*
9010	EDTA	61 ± 0.08
IC	EDTA	100 ± 0.05*

* Significant at the $\alpha = 0.05$ level.

Corp., Sunnyvale, California; Table 2). An eluant containing 0.5 M sodium acetate, 0.1 M NaOH, and 0.5% ethylenediamine (Pohlandt-Watson, 1986) was used for CN detection. The concentration of CN present in the samples was recorded by measurement of peak heights obtained with a Dionex 4270 Integrator.

RESULTS

Aqueous samples were analyzed for CN content both before and after distillation to determine if boiling and subsequent CN recovery in the alkali trap solution would affect overall recovery. The CN recovery rates both in distilled and undistilled aqueous samples were similar for IC and colorimetric determinations (Table 3). CN determinations using ion chromatographic analysis, however, showed a higher degree of accuracy and lower standard deviations than those of colorimetric analysis.

Soil and Sludge Analysis. The Method 9010 distillation procedure was applied to the soils and sludge listed in Table 1, following which all materials were analyzed colorimetrically as well as via IC. Method 9010 is designed for aqueous sample analysis only. Therefore, the method was modified for the digestion of solids. Originally, 115 g of CN-treated soil or sludge was added to the distillation flask. Due to bumping, plugging of the air inlet tube, and foaming of the soil-CN mixture, 115 g soil was too much to allow for complete distillation. The amount of soil distilled also had a negative relationship with the amount of CN recovered (Figure 1). Large amounts of soil may have allowed excessive metal-CN complexation. A soil weight of 2.5 g was found to be satisfactory for proper digestion and subsequent CN measurement.

The soils and sludge were evaluated for content of metals and total organic carbon (TOC) to determine the relationship between metal and TOC content and % CN recovery. The % CN recovery obtained from distilling 2.5 g of sample ranged from 98% to 100% for the soils (data not tabulated) but was only 75% for the sludge (Table 4). Recovery using IC was significantly higher (as indicated by the *t*-test) than recovery via Method 9010. The sludge had the highest concentrations of Cd and Fe (0.015 and 53.25 μg/g, respectively) compared to the other samples. Furthermore, the sludge had an EC which was 27 times that of the nearest soil sample, the Pemberton. Such solute concentrations increase the

Table 5. Regression equations and coefficients of determination (R^2) for soil TOC and metals and CN recovery by ion chromatography.

	Equation	R^2
TOC	$Y = 73.36 \times 10^{(-6.04e-3X)}$	0.62 n.s.*
Cd	$Y = 88.78 \times 10^{(-17.18X)}$	0.61 n.s.
Cu	$Y = 533.33X + 57.67$	0.02 n.s.
Fe	$Y = 77.78 \times 10^{(-3.81e-3X)}$	0.57 n.s.
Zn	$Y = -2.57X + 74.72$	0.17 n.s.

* Not significant.

probability of CN complexation. Several CN complexes are very difficult to dissociate prior to detection (Ingersoll, *et al.,* 1981). To obtain higher CN recovery rates with the sludge, 0.1 g of ethylenediamine tetraacetic acid (EDTA) was added to the distillation vessel. EDTA complexes with metals, thus inhibiting the metals from reacting with CN. Distillation with the addition of EDTA provided for 100% CN recovery from the sludge (Table 4). Regression analysis revealed that TOC, Cd, Cu, Fe, and Zn concentrations were correlated, though not significantly, with CN recovery from the soil and sludge samples (Table 5).

The colorimetric results for CN in soil and sludge were considerably lower than those measured with IC (Table 4). Since the colorimetric test was designed for aqueous samples only, the soils and sludges may introduce impurities (e.g., organic compounds) that interfere with the CN-pyridine-chloramine color complex. The IC results were consistent and reproducible for both soil and sludge samples. The chromatograms obtained for soil analysis had sharp peaks, indicating a lack of interfering compounds.

The detection range of the IC for CN was from 0.01 to 14 μg/mL, which is a 92% increase in range over that available with the colorimetric procedure. In addition, IC was faster; sample preparation and analysis using the colorimetric procedure took 1.75 h, whereas the IC procedure required only 0.25 h. Furthermore, hazardous waste production is minimized in the IC method, as the pyridine barbituric acid solution (Method 9010) is not used.

CONCLUSIONS

Ion chromatography was found to be a more accurate method of determining CN concentration in aqueous samples as well as a more accurate and consistent method for soil and sludge analysis due to the lack of interference that occurs using colorimetric analysis. The distillation outlined in Method 9010 for aqueous samples containing CN can be used to distill soil and sludge, with 2.5 g of sample yielding optimum results. The addition of EDTA to soils and sludges with high metal content is necessary to eliminate the CN-metal complexes present. Due to expanded detection ranges, rapid sample analysis, greater accuracy, and a lack of

hazardous by-products, ion chromatography appears to be superior to Method 9010 for determining the presence of CN.

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LITERATURE CITED

Adeloju, S.B. and T. Gawne. 1986. Determination of soluble cyanide in soil samples by differential pulse polarography. Anal. Chim. 188: 275-280.

Blanco, M. and S. Maspoch. 1984. Determination of cyanide by a highly sensitive indirect spectrophotometric method. Talanta 31: 85-87.

Brooks, S.J. 1992. Reclamation of the Timberline Heap Leach: Tooele County, Utah. U.S. Dep. Interior, Bur. Land Manage., Washington, D.C., BLM/SC/PT-92/002+3042, 12 pp.

Dartnall, A.M. and R.G. Burns. 1987. A sensitive method for measuring cyanide and cyanogenic glucosides in sand culture and soil. Biol. Fertil. Soils 5: 141-147.

DeBell, R.M., M.L. Shea, E. Heyder, and D.R. Knight. 1982. Improved methods for cyanide and thiocyanate measurements. Naval Submarine Res. Lab. Rep. 976, 10 pp.

Dionex. 1986. Direct determination of cyanide in strongly alkaline solutions. Dionex, Sunnyvale, California, 1 p.

Galceran, M.T., R. Rubio, and G. Rauret. 1990. Assessment of groundwater contamination subsequent to an environmental release. Waste Manage. 10: 261-268.

Ingersoll, D., W.R. Harris, and D.C. Bomberger. 1981. Ligand displacement methods for the determination of total cyanide. Anal. Chem. 53: 2254-2258.

Kunz, D., O. Nagappan, J. Silva-Avalos, and G.T. Delong. 1992. Utilization of cyanide as a nitrogenous substrate by *Pseudomonas fluorescens* NCIMB 11764: Evidence for multiple pathways of metabolic conversion. Appl. Environ. Microbiol. 58: 2022-2029.

Martin, T.H. 1992. Chasing those elusive cyanide ions. Plating and Surface Finishing 79: 23-26.

Meeussen, J.C.L. 1992. Chemical speciation and behavior of cyanide contaminated soils. Ph.D. Thesis, Wageningen Agr. Univ., Wageningen, The Netherlands, 133 pp.

Nelson, J.L., L.C. Boawn, and F.G. Viets, Jr. 1959. A method for assessing zinc status of soils using acid-extractable zinc and "titratable alkalinity" values. Soil Sci. 88: 275-283.

Olson, R.V. and R.E. Ellis, Jr. 1982. Iron. *In:* A.L. Page, R.H. Miller, and D.R. Keeney (Eds.), *Methods of Soil Analysis, Part 2,* pp. 301-312, Amer. Soc. Agron., Madison, Wisconsin, 1159 pp.

Okuno, I., J.A. Whitehead, W.H. Higgins, and P.J. Savarie. 1979. A gas chromatographic method for determining residues of sodium cyanide in vegetation and soil. Bull. Environ. Contam. Toxicol. 22: 386-390.

Owerbach, D. 1985. A discussion of the method for the determination of free cyanide in water and wastewater by microdiffusion. J. Testing Evaluation 13: 123-126.

Pohlandt-Watson, C. 1986. A revised ion chromatographic method for determination of free cyanide. Mintek Rep. M283, 3 pp.

U.S. Environmental Protection Agency. 1986. Standard Method 9010: Total and amenable cyanide (colorimetric, manual). *In: Test Methods for Evaluating Solid Waste, Volume 1C: Laboratory Manual Physical/Chemical Methods,* pp. 1-9, U.S. Environmental Protection Agency, SW-846, 468 pp.

_____. 1992. Reclamation and redevelopment of contaminated land: II. European case studies. EPA/600/R-92/031, 285 pp.