



## Project Summary

# Interlaboratory Evaluation of Measurements for HCN and H<sub>2</sub>S Released from Wastes

Thomas A. Hinnners, Robert W. Handy, Doris J. Smith, and Edo D. Pellizzari

The objective of this project was to assess a proposed method for determining whether a waste is hazardous on the basis of its release of hydrogen cyanide or hydrogen sulfide upon contact with an acidic medium. This was accomplished by performing a single-laboratory evaluation of the method and by conducting an interlaboratory study to estimate method precision. The test method, proposed by the Environmental Protection Agency's Office of Solid Waste, involves acidifying a waste material to pH 2 and measuring the gaseous hydrogen cyanide (HCN) or hydrogen sulfide (H<sub>2</sub>S) evolved by means of stain tubes. This report contains a description of the interlaboratory study and an assessment of the proposed method for measuring HCN and H<sub>2</sub>S evolved from waste materials.

In the interlaboratory study, twelve laboratories analyzed eight cyanide-containing and eight sulfide-containing waste samples for the gaseous HCN or H<sub>2</sub>S evolved upon acidification. The twelve laboratories performed triplicate analyses of the test samples following a detailed set of instructions. Estimates of within-day and across-day repeatability with reproducibility were determined for the measurements.

Based on the interlaboratory results, the proposed method was shown to be potentially useful for measuring H<sub>2</sub>S evolved from waste materials. However, the measurements for HCN released from waste samples were not reliable because of an interfering stain on the detector tubes. Carbon dioxide can produce an interfering color change on HCN stain tubes. Mass spectrometric

measurements confirmed that the major gas evolved from the cyanide-containing waste samples was carbon dioxide.

*This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

The United States Environmental Protection Agency (EPA) has specified in the Federal Register (Vol. 45, No. 98, May 19, 1980, p. 33122) that a solid waste exhibits the characteristic of reactivity if "it is a cyanide- or sulfide-bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment." Presently, there are no suitable, validated methods for determining HCN or H<sub>2</sub>S evolved from waste materials.

The EAL Corporation, Richmond, California, has developed (under EPA Contract No. 68-03-2961 with the Environmental Monitoring Systems Laboratory-Las Vegas) a stain-tube method proposed by the EPA Office of Solid Waste. The method involved acidifying the waste material to pH 2 and measuring the gaseous hydrogen cyanide or hydrogen sulfide evolved by means of stain tubes. Gas detector tubes are available commercially that were designed to develop stains when exposed to specific gases. The length of the stain developed in a gas detector tube reflects

the amount of the specific gas sampled (when no other gas present causes a color change). Stain tubes with calibrated scales are available. Use of stain tubes to detect and measure toxic gases is rapid and requires no special instrumentation or extensive training. The present study was designed to further evaluate this method.

### Procedure

The interlaboratory study consisted of the analysis of eight sulfide-bearing and eight cyanide-bearing waste samples for the H<sub>2</sub>S or HCN evolved upon acidification. The cyanide-containing waste samples were obtained from metal processing operations, and the sulfide-containing waste samples were obtained from a paper mill, a tannery, a calcium sulfide plant, and a coal plant. Twelve laboratories participated in this study. They performed triplicate analyses of the test samples following a detailed set of instructions. In every case, two determinations were carried out on the same day and the third on a different day. In this way, estimates of within-day and across-day repeatability and reproducibility were obtained for the sample measurements. Before any test samples were analyzed, a quality control (QC) check solution was used to verify that the system was operating properly. The test samples included performance evaluation (PE) solutions containing concentrations of cyanide and sulfide unknown to the participating laboratories.

### Results

The results reported for the QC system checks and the quality assurance (QA) performance evaluation samples are summarized in Tables 1 and 2. Table 1 shows a 17-percent relative standard deviation for the HCN system check solution, which coincides with the 17-percent figure reported by the EAL Corporation for HCN. The QA performance evaluation results gave similar precision estimates. Table 2 shows interlaboratory precision estimates for the H<sub>2</sub>S quality assurance/quality control samples. The 68-percent average recovery in the gas phase for the generated H<sub>2</sub>S is in the range reported by the EAL Corporation and also found in preliminary work at the Research Triangle Institute, Research Triangle Park, North Carolina. It is noteworthy that the recovery in the gas phase for the generated HCN is between 5 and 6 percent, which is in the range reported by the EAL Corporation and confirmed by the Research Triangle Institute. When HCN and H<sub>2</sub>S are generated by acidifying salt solutions,

**Table 1.** Hydrogen Cyanide QA/QC Results

Lab No.*	QC System Check Mean Tube Reading, $\mu\text{L}$	QA Samples Mean Conc., $\mu\text{g/mL}$	
		PE-1	PE-2
01	31	8.4	2.5
02	25	6.6	3.2
04	28	8.0	2.8
05	23	7.1	2.3
07	24	6.8	2.6
08	22	6.8	2.4
09	32	7.5	2.7
10	22	6.5	2.4
11	33	10.5	3.4
12	**	**	**
14	**	**	**
Mean	26.7	7.6	2.7
Std. Dev.	4.4	1.3	0.38
% RSD†	17	17	14
HCN Added	454 $\mu\text{L}$	150 $\mu\text{g/mL}$	50 $\mu\text{g/mL}$
Mean Recovery	5.9%	5.1%	5.4%

\*Laboratories 03, 06 and 13 did not report data.

\*\*The PE and QC samples appear to have been interchanged.

†% RSD = percent relative standard deviation.

**Table 2.** Hydrogen Sulfide QA/QC Results

Lab No.*	QC System Check Mean Tube Reading, $\mu\text{L}$	QA Samples Mean Conc., $\mu\text{g/mL}$	
		PE-1	PE-2
01	21	0.0	3.8
02	22	0.2	2.2
04	16	0.0	4.1
05	37	0.0	3.0
06	31	0.1	4.5
07	18	0.3	2.2
08	24	0.0	4.3
09	22	0.0	3.9
10	24	0.0	2.8
11	26	0.0	4.4
12	21	1.5	2.4
14	24	1.2	4.4
Mean	23.8	0.06**	3.5
Std. Dev.	5.6	0.06**	0.92
% RSD†	24	100**	26
H <sub>2</sub> S Added	37 $\mu\text{L}$	0.0 $\mu\text{g/mL}$	5.0 $\mu\text{g/mL}$
Recovery	66%	—	70%

\*Laboratories 03 and 13 did not report data.

\*\*Outlier values from two laboratories have been excluded.

†% RSD = percent relative standard deviation.

recovery of these compounds in the gas phase is less than 100 percent because of the solubilities of these gases in aqueous media. The much lower recovery for HCN than for H<sub>2</sub>S is a reflection of the much larger partition coefficient between liquid and vapor phase for HCN than for H<sub>2</sub>S (238 versus 2.76 at 20°C).

The interlaboratory precision values for the HCN and H<sub>2</sub>S measurements are shown in Tables 3 and 4. The repeatability and reproducibility coefficients for the waste samples are listed and summarized in Tables 5 and 6. As defined in Standard E 173 of the American Society for Testing

and Materials (ASTM), the *repeatability coefficient* represents the 95-percent confidence limit for the difference between two determinations by a typical single laboratory expressed as a percentage of the average concentration for a sample and the *reproducibility coefficient* represents the 95-percent confidence limit for the difference between two determinations by two typical laboratories (one determination by each) expressed as a percentage of the average concentration for the sample. The repeatability and reproducibility values for the sulfide measurements are clearly superior to

**Table 3. Hydrogen Cyanide Precision**

Waste Sample†	Number of Measurements	Average Concentration (µg/mL)	RSD* (%)
HCN-A**	24	0.26	32
HCN-B	33	5.6	91
HCN-D	32	2.2	100
HCN-E	30	1.4	62
HCN-F	30	0.14	150
HCN-G	31	2.9	130
HCN-H	30	1.3	75

\*Relative standard deviation of individual measurements by all contributing laboratories.

\*\*Outlier values from one laboratory have been excluded.

†No measurable response was obtained for sample HCN-C.

**Table 4. Hydrogen Sulfide Precision**

Waste Sample†	Number of Measurements	Average Concentration (µg/mL)	RSD* (%)
H <sub>2</sub> S-A	36	0.48	140
H <sub>2</sub> S-B	36	2.4	140
H <sub>2</sub> S-D	36	415	27
H <sub>2</sub> S-E	36	3.8	27
H <sub>2</sub> S-F	33	862	64
H <sub>2</sub> S-G	35	367	56
H <sub>2</sub> S-H**	25	420	47

\*Relative standard deviation of individual measurements by all contributing laboratories.

\*\*Outlier values from one laboratory have been excluded.

†No measurable response was obtained for sample H<sub>2</sub>S-C.

**Table 5. Hydrogen Cyanide Repeatability and Reproducibility**

Waste Sample†	Parameter	Repeatability Coefficient (%)	Reproducibility Coefficient (%)
A*	within day	92	120
	across days	79; 64	140; 140
B	within day	130	250
	across days	180; 100	260; 280
D	within day	90	280
	across days	120; 170	320; 320
E	within day	73	220
	across days	81; 140	200; 200
F	within day	230	510
	across days	440; 370	450; 480
G	within day	350	410
	across days	260; 210	370; 330
H	within day	57	250
	across days	85; 110	190; 220
Average*	within day	150	290
	across days	170	280

\*Outlier values from one laboratory have been excluded.

†No data are shown for sample C because no measurable HCN was reported.

those for the cyanide measurements. Except for the repeatability of the H<sub>2</sub>S results, there are no appreciable differences for within-day and across-day measurements shown in Tables 5 and 6. In nearly every case, the precision between laboratories was poorer than within laboratories.

### Interference Study

Some cyanide waste samples caused difficulties during the interlaboratory study, as evidenced by the comments from the participating laboratories. The remarks indicated the presence of a common interferent in all of the samples.

Carbon dioxide (CO<sub>2</sub>) is known to react with HCN stain tubes to give a mottled orange-to-pink appearance. This coloring was reported by nearly all the participating laboratories. In the presence of a limited amount of carbon dioxide, the mottled pink color fades, and observation of a normal cyanide stain front is possible. With wastes containing more carbonate, an obscuring stain front, which develops on the detector tube, remains even after a prolonged gas sampling period. The outlier values cited in Tables 3 and 5 probably reflect the misreading of the interference stains for HCN stains.

Analysis of headspace gas after acidification of a cyanide waste confirmed that CO<sub>2</sub> was the major gas evolved. An attempt to trap the evolved carbon dioxide from this waste using a CO<sub>2</sub> stain tube placed in front of the hydrogen cyanide tube was not successful because of the large volume of CO<sub>2</sub> released. When CO<sub>2</sub> was purged from one problem waste (by adding water, adjusting the pH to 8 and stirring) before applying the test method, a readable HCN stain was obtained. Although there is a potential for loss of HCN at pH values below 12, ASTM Standard D2777 includes a pretreatment at pH 6 for some cyanide samples.

Since the coloring of HCN stain tubes by CO<sub>2</sub> appeared to be reversible to some extent, a gas sampling time in excess of the 30-minute period in the test method was investigated. The success of increasing the sampling time by an additional 30 minutes depended upon the amount of carbonate present in the sample. Samples with relatively low amounts of carbonate benefited most from this extra sampling time. In this situation, the diffuse coloration caused by carbon dioxide faded to give a readable hydrogen cyanide stain front. Samples with large quantities of carbonate benefited little if at all from this extra sampling time.

### Conclusions

The suitability of this stain-tube method for measuring the gaseous HCN and H<sub>2</sub>S released from some waste materials has been investigated and the following conclusions are presented:

1. Based mainly on the likelihood of CO<sub>2</sub> interference from cyanide-containing wastes, the use of this stain-tube method (in its present form) for measuring HCN evolved from waste materials is not recommended.
2. The partial-acidification purge technique to reduce the effect of carbon dioxide on HCN measurements

shows promise but caused as much as a 25-percent loss of HCN from standards.

- Based mainly on the absence of interferences and the reasonable analytical precision noted in this study, this stain-tube method represents a potentially useful technique for measuring H<sub>2</sub>S evolved from waste materials. Optimizing certain test parameters (stirring, acidification, sampling time) could improve the precision of the H<sub>2</sub>S measurements.

### Recommendations

- When CO<sub>2</sub> interference is encountered in HCN measurements, one could acidify another portion of the sample to a pH of 8 and stir the mixture (in a hood) until the evolution of gas has ceased before conducting the analysis according to the test method. However, some HCN, together with CO<sub>2</sub>, will be evolved by this procedure. For samples which still give an unreadable stain front, some improvement may be realized by extending the gas sampling time past 30 minutes.
- Future work should include an investigation of the advantages and disadvantages of performing the CO<sub>2</sub> purge for cyanide wastes at various pH levels with the pump on (but without the HCN detector tube in place). Loss of HCN during any CO<sub>2</sub>-purge procedure should be evaluated.
- Carbon dioxide interference with HCN measurements might prove avoidable by trapping water before it reaches the stain tube (to prevent carbonic acid formation) or by developing an HCN detector tube that involves a different stain reaction.

**Table 6. Hydrogen Sulfide Repeatability and Reproducibility**

Waste Sample†	Parameter	Repeatability Coefficient (%)	Reproducibility Coefficient (%)
A	within day	58	460
	across days	340; 280	450; 430
B	within day	20	460
	across days	270; 240	480; 470
D	within day	22	90
	across days	65; 82	71; 81
E	within day	21	57
	across days	86; 76	93; 76
F	within day	78	180
	across days	140; 150	230; 200
G	within day	55	160
	across days	72; 79	190; 220
H*	within day	84	120
	across days	120; 160	110; 150
Average*	within day	48	220
	across days	150	230

\*Outlier values from one laboratory have been excluded.

†No data are shown for sample C because no measurable H<sub>2</sub>S was reported.

The EPA author **Thomas A. Hinnert** is with the Environmental Monitoring Systems Laboratory, Las Vegas, NV 89114; **Robert W. Handy**, **Doris J. Smith**, and **Edo D. Pellizzari** are with Research Triangle Institute, Research Triangle Park, NC 27709.

**Werner F. Beckert** and **Thomas A. Hinnert** are the EPA Project Officers (see below).

The complete report, entitled "Interlaboratory Evaluation of Measurements for HCN and H<sub>2</sub>S Released from Wastes," (Order No. PB 85-138 659; Cost: \$11.50, subject to change) will be available only from:

National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: 703-487-4650

The EPA Project Officers can be contacted at:  
Environmental Monitoring Systems Laboratory  
U.S. Environmental Protection Agency  
P.O. Box 15027  
Las Vegas, NV 89114