



Project Summary

Analytical Methods Evaluation for Applicability in Leachate Analysis

Foppe B. DeWalle, Theodore Zeisig, John F. C. Sung, Donald M. Norman, Jack B. Hatlen, Edward S. K. Chian, Michael G. Bissel, Kim Hayes, and Donald E. Sanning

Thirty-two laboratories in the United States and Canada conducted round-robin analyses of leachate samples. Samples were analyzed for up to 28 parameters to evaluate accuracy and precision of the methods employed. The 28 parameters included physical parameters (pH, oxidation reduction potential, conductivity, turbidity, and solids), organics (chemical oxygen demand, total organic carbon, organic nitrogen, and free volatile fatty acids), anions (sulfate, phosphate, chloride, nitrate, and bicarbonate), and cations (alkali metals, alkaline earth metals, transition metals, and heavy metals).

Individual parameter coefficients of variation ranged from 32 percent to 210 percent. Significant differences were noted between results from colorimetric methods and from titrimetric and physical methods. The average recovery for spiked parameters varied widely for individual parameters.

The most applicable method for analysis of each parameter is recommended. Use of the standard addition technique is required in each laboratory to determine the matrix depression or enhancement for each type of leachate sample.

The accuracy (i.e., agreement between measured and actual amounts) and the precision (i.e., reproducibility) of different analytical methods were evaluated in depth. Thirty-two laboratories submitted final analytical results.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, 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).

Technical Discussion

Leachate samples were collected from nine locations chosen to represent different climatic conditions, varying site age, and a wide range of chemical oxygen demand (COD). A double quantity of leachate was collected from one of the sites so that a spiked sample could also be analyzed. Therefore, the nine sites provided ten leachate samples.

The leachate samples were collected, chilled, anaerobically sorted, and immediately shipped by air to Stanford University. At Stanford, each sample was emptied anaerobically into a 150-liter vessel, thoroughly mixed, placed in 55 one-liter glass containers and 110 five-hundred-ml polyethylene containers, and chilled for distribution by air freight to the participating laboratories. After complete mixing of the double-quantity sample, half of the sample was spiked with each of the chemical parameters to a concentration of about 25 percent of the original concentration in the unspiked sample.

The participating laboratories recorded analytical information on a Stanford Reporting Form that was manually

edited before key punching. All major computations and data file management were performed on the Control Data Cyber 173 and CDC 6400 dual main-frame system of the Academic Computer Center at the University of Washington. The leachate data base was maintained on disc and magnetic tape files. Most of the data preprocessing programs used for data sorting and the computation of sample statistics were written in FORTRAN, compiled with the University of Minnesota Fortran compiler (Version 5.1), and executed under the CDC NOS/BE (Version 1.2) operating system. The statistical package Minitab II was used extensively in the statistical analysis and plotting of the leachate data. The report concentration levels were processed with a G12.5 format specification for all 28 parameters. A G13.6 format specification was used for the average and standard deviation computed for the concentration levels.

The data from each parameter were analyzed using the following approach. The within- and between-laboratory standard deviations were plotted against the concentration level to determine if a transformation of the data was required to make the variability at different levels of the parameter approximately equal. Quantile-quantile plots were then constructed for the original and transformed data and used to determine if the distributions of the original or the transformed data were reasonably close to a normal distribution. To determine if systematic differences exist between the analytical methods used and between laboratories, a ranking procedure was used. Finally, the analysis of variance was used to estimate the between-laboratory, laboratory-sample-interaction, and within-laboratory variance components.

A statistical evaluation of the data revealed that the overall coefficient of variation (i.e., the standard deviation as

a percentage of the average) ranged from 32 percent for the COD determination to 210 percent for the cadmium determination. The between-laboratory component of variation was larger than the within-laboratory component. The largest portion of the variation, however, was due to a sample laboratory interaction (i.e., the laboratories' relative results change for different leachate samples).

Further, the results of the leachate analysis more closely resembled a lognormal distribution than a normal distribution. The standard deviation of the data in the lognormal scale is equivalent to the coefficient of variation of the data in the original scale of measurement as calculated through a first order Taylor expansion. The standard deviations for the different parameters/variables are shown in Table 1. The overall standard deviation σ_R is approximately 1.5 times larger than the be-

Table 1. Standard Deviations for All Reporting Laboratories and for Those Reporting Three Replicates

Parameter/ Variable	All Reporting Laboratories		Labs Reporting Three Replicates	
	σ_R	σ_L	σ_{LS}	σ_W
pH	0.349	0.152	0.108	0.052
ORP	123	93	68	30
Turbidity	2.01	1.47	1.09	0.114
Conductivity	0.464	0.225	0.174	0.026
Volatile Acids	1.01	0.627	0.855	0.151
COD	0.324	0.20	0.212	0.066
TOC	0.602	0.294	0.493	0.069
Total Residue	0.574	0.517	0.185	0.062
Volatile Residue	0.764	0.638	0.45	0.172
Organic Nitrogen	1.50	1.02	0.671	0.265
Ammonia Nitrogen	0.89	0.923	0.69	0.110
Sulfate	1.80	0.603	1.47	0.774
Total Phosphorus	1.45	1.20	0.610	0.563
Chloride	0.923	0.494	0.80	0.055
Alkalinity	0.380	0.222	0.358	0.033
Nitrate Nitrogen	1.98	1.50	1.32	0.193
Sodium	0.545	0.125	0.578	0.037
Potassium	0.661	0.388	0.438	0.056
Calcium	0.74	0.642	0.336	0.046
Magnesium	0.594	0.109	0.676	0.036
Barium	1.41	1.05	1.19	0.043
Iron	0.532	0.281	0.354	0.053
Zinc	1.35	1.03	0.797	0.103
Lead	0.962	0.648	0.644	0.308
Chromium	1.71	1.32	0.727	0.665
Cadmium	2.16	1.78	0.440	1.04
Copper	1.42	1.14	0.832	0.251
Nickel	1.08	0.732	0.842	0.365

σ_R = Overall standard deviation.

σ_L = Between laboratory standard deviation.

σ_{LS} = Laboratory sample interaction standard deviation.

σ_W = Standard deviation within laboratories.

tween-laboratory standard deviation component σ_L . The overall standard deviation was especially large for the analysis of cadmium, nitrate nitrogen, turbidity, sulfate, chromium, organic nitrogen, copper, zinc, and barium.

Since leachate differs from water and wastewater in both content and concentration, interferences can lead to erroneous results when water and

wastewater methods are used for leachate analyses. Table 2 shows the percent variance associated with the following water/wastewater methods: (1) EPA Methods for Chemical Analysis of Water and Wastes (1974); (2) ASTM Part 31: Water (1975); and (3) Standard Methods (1971).

Substantial differences existed between different analytical methods,

especially between manual and automated methods. Colorimetric methods tended to give values that were sometimes different from those of physical methods. Differences likewise existed among instrumental methods. Pretesting of storage time indicated that no time effect existed to produce a variation in the analytical results, nor did the particular dilutions have a major effect on the

Table 2. Percent of Variance Ranges for Three Methods Used to Analyze Water and Wastewater

Parameter/ Variance	Method	EPA (1974)	ASTM (1975)	Standard Methods
		σ (%)	σ (%)	σ (%)
pH	Electrometric	1.6-3.1	— ^a	—
ORP	Electrometric	—	5-10 mV	—
Turbidity	Photometric	1.6-26	—	—
Conductivity	Electrometric	7-8.2	≤1	8.6-7.8
Volatile Acids	Chromatographic	—	—	—
COD	Manual reflux	6.58	±13 mg/L	6.5
TOC	IR detection	80-7.8	4.2-3.2	5-10
Total Residue	Gravimetric	—	—	5-9.7
Volatile Residue	Gravimetric	—	—	6.5
Organic Nitrogen	Kjeldahl N	99-26	—	—
	Automated Phenate	24.6-31.8	—	—
	Distillation	58-14.5	—	69.8-21.6
Ammonia Nitrogen	Selected Ion Electrodes	3.8-2.2	—	—
	Automated Phenate	0.35-1.1	—	—
	Direct Nesslerization	—	—	38.1-11.6
	Direct Phenate	—	—	39.2-26.0
Sulfate	Turbidimetric	26.7-5.9	5	9.1
	Automated Chloranilate	0.3-1.5	—	—
	Gravimetric	—	10	4.7
Total Phosphorus	Automated Ascorbic Acid	47.2-22	—	—
	Manual Ascorbic Acid	30-14.5	—	—
Chloride	Mercuric Nitrate	9.06-2.96	45.3-2.7	3.3
	Ferricyanide	—	0-5.6	—
	Argentometric	—	—	4.2
Alkalinity	Potenti	15.8-4.0	—	—
Nitrate Nitrogen	Automated Cadmium Reduction	4.1-26.3	—	0.0-20
	Manual Cadmium Reduction	—	—	96.5-9.2
	Brucine	57.5-17.3	—	66.7-15.4
Sodium	Flame Photometric	—	65.1-1.7	17.3
	Direct A.A.	1.5	—	—
Potassium	Flame Photometric	—	45.9-1.35	15.5
	Direct A.A.	10.3-10.2	—	—
Calcium	EDTA Titrimetric	—	—	9.2
	Direct A.A.	0.3-0.6	20.3-7.3	—
Magnesium	Direct A.A.	4.76-2.5	67.8-8.7	10.5
Barium	Direct A.A.	10.8-6.5	—	10
Iron	Direct A.A.	609-21	56-6.25	16.5
	Phenanthroline	—	—	25.5
Zinc	—	314-34.5	55-5.3	8.2
Lead	—	114-33	57-7.4	23.5
Chromium	—	105-28.4	29.4-9.6	26.4
Cadmium	—	350-23	0-8.7	21.6-43.8
Copper	—	81-17	33.8-3.95	11.2
Nickel	—	5.5-0.8	52.4-2.6	—

^a—Not reported.

Table 3. Recommended Methods for Leachate Analysis

Leachate Parameter	Recommended Method
pH	Electrometric method on fresh sample, using glass electrode and temperature correction.
Oxidation reduction potential	Electrometric method on fresh sample, using platinum electrode with the calomel reference electrode.
Turbidity	Nephelometric method on a fresh sample.
Conductivity	Electrometric method using platinum electrode and temperature correction.
Free volatile fatty acids	Chromatographic method. COD determination should also be conducted.
Chemical oxygen demand	Manual dichromatic reflux method using the ferrous ammonium sulfate titration.
Total residue	Drying method at 104°C.
Volatile residue	Drying at 550°C without prior filtration of sample.
Organic nitrogen	Kjeldahl manual titration.
Ammonia nitrogen	Distillation tritration method.
Sulfate	Gravimetric method.
Total phosphorus	Ascorbic acid method using the persulfate digestion step.
Chloride	Potentiometric titration.
Alkalinity	Potentiometric method with titration to inflection point of about pH 4.5.
Nitrate	Cadmium reduction method after separate determination of the nitrite ion.
Sodium and Potassium	Atomic absorption or manual flame or automated flame emission method.
Calcium, Magnesium, Barium	Atomic absorption spectrophotometric.
Heavy metals (Fe, Zn, Pb, Cr, Cd, Cu, Ni)	Direct aspiration atomic absorption spectrophotometric method.

outcome of the analysis. However, concentration ranges of a leachate constituent can produce a major effect on the analysis. This concentration effect was found to be particularly evident in spiked samples (i.e., the recovery rates varied widely for individual parameters).

From this study, the authors recommend preferred methods for leachate analyses (Table 3), and general reasons are given for selecting a particular analytical method as being the most applicable.

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Foppe B. DeWalle, Theodore Zeisig, John F. C. Sung, Donald M. Norman, and Jack B. Hatlen are with the University of Washington, Seattle, WA 98195; Michael G. Bissel and Kim Hayes are with Stanford University, Stanford, CA 96205.

Donald E. Sanning is the EPA Project Officer (see below).

The complete report, entitled "Analytical Methods Evaluation for Applicability in Leachate Analysis," (Order No. PB 81-172 306; Cost: \$24.50, subject to change) will be available only from:

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Cincinnati, OH 45268

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