Waste Testing and Quality Assurance

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Foreword

This publication, *Waste Testing and Quality Assurance,* contains papers presented at the Symposium on Solid Waste Testing and Quality Assurance, which was held in Washington, DC, 15–18 July 1986. The symposium was sponsored by ASTM Committee D-34 on Waste Disposal, the United States Environmental Protection Agency, and The American Public Works Association. David Friedman, EPA, served as symposium chairman and was the editor of this publication.

Overview

This volume, which highlights the latest developments in the areas of waste and environmental media sampling, property and hazard testing, and chemical and biological analysis, will focus on developments in the fields of leachability estimation, analytical method development and evaluation, and quality assurance. The papers included in this volume emphasize testing methodology and quality assurance practices that are being developed or applied to implementing the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) hazardous waste management programs.

Leachability Estimation

Land disposal is a widely employed method of managing both hazardous and nonhazardous wastes. For many wastes it may be the only practical option. A major concern with land disposal is the potential for the waste to release its toxic constituents and the consequent contamination of groundwater. The STP includes several papers dealing with leachate quality prediction.

During and prior to disposal, various measures can be taken to minimize the potential leachability of wastes destined for land disposal. In addition to site design to minimize contact between the waste and leaching media present at the site, a commonly employed waste treatment technique to minimize leachability is solidification, or fixation as it is also known. Such processes work by converting the waste into an impermeable monolithic mass. However, the acceptance of such processes depends on an ability to ensure that the waste will retain its monolithic nature during long-term disposal. In their paper "Methods for Evaluating Solidified Waste," Hannak et al. present an overview of studies that are being conducted in the United States and Canada to evaluate short-term laboratory testing methods appropriate to determining the long-term stability and leaching potential of solidified wastes. In addition to leachability, the authors examine tests for measuring a waste's resistance to the environmental stress imposed by the climactic vagaries of freezing and thawing and wet and dry conditions.

In 1980, the Environmental Protection Agency (EPA) promulgated the Extraction Procedure (EPA Method 1310) to be used for determining whether a waste should be classified as a hazardous waste due to its potential to leach certain toxic species under specified codisposal mismanagement conditions. In 1986, EPA proposed to replace the Extraction Procedure with the Toxicity Characteristic Leaching Procedure (EPA Method 1311). The procedure involves an 18-h extraction of a sample with either an acetic acid or a sodium acetate solution and subsequent analysis of the extract for a variety of elemental and organic constituents. This new procedure offers a number of advantages over Method 1310. These include an applicability to evaluating the leachability of both elemental and organic species, including volatile organic compounds, a reduction in the potential for operator error, and a reduction in the extraction time.

To validate the procedure, three waste samples were sent to 24 different laboratories for extraction and analysis. Eighteen of the laboratories participated in the organic analysis and all 24 participated in the metals analysis. The results and statistical analysis of the collaborative test, which forms the basis for EPA's decision to propose the new waste testing procedure, are presented by Blackburn et al. in their paper titled "Collaborative Study of the Toxicity Characteristic Leaching Procedure (TCLP).

As they did in 1979 for Method 1310, the Electric Power Research Institute sponsored a multiple laboratory collaborative study to evaluate the variability and reproducibility of Method 1311. In his paper "Round Robin Study of Leaching Methods as Applied to Solid Wastes from Coal-Fired Power Plants," Murarka presents the results of both the 1979 study and this latest effort which demonstrates that the reproducibility of Method 1311 is equal to or better than that of Method 1310. The study also examines the causes of the variance when conducting evaluations of waste leachability and discusses the relative importance of the various factors.

Analytical and Testing Methods

On a molecular basis, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is one of the most toxic environmental contaminants known to result from our industrial society. Although 2,3,7,8-TCDD is the most toxic of the 75 chlorinated dibenzo-p-dioxins, many of the others are known to possess high toxicity to humans and animals. The "dioxins," and the chlorinated dibenozofurans which have a similar genesis, are thus of very great environmental concern. They are formed during the commercial synthesis of a number of industrial chemicals as well as in a variety of processes involving halogen-containing precursors, heat, and an organic source (for example, municipal waste combustion).

Method 8280 was published by EPA in 1983 for use in determining the presence and concentration of chlorinated "dioxins" and "furans" in environmental matrices. The method has undergone a period of continual development, inprovement, and evaluation in order to accommodate the variety of complex matrices encountered in waste testing and environmental monitoring. In their paper "Development and Validation of RCRA Method 8280 for Dioxins and Furans," Billets, et al. compare the performance of the 1983 version of Method 8280 and the improved method resulting from the work performed by EPA's Environmental Monitoring and Systems Laboratory at Las Vegas, NV.

Inductively coupled plasma emission spectroscopy offers a sensitive method for simultaneously determining the presence and concentration of a large number of elements in environmental samples. As part of its efforts to lower testing costs, EPA developed a standard ICP protocol (Method 6010) and initiated interlaboratory collaborative testing of the protocol. Hinners et al., in "Interlaboratory Evaluation of ICP-AES Method 6010," describe the results of the evaluation and the quality control procedures that need to be followed to obtain accurate results.

The increasing demands faced by laboratories serving the waste management community require innovative approaches to saving time and expense in testing. Illustrative of such novel approaches is the work described by Callio to adapt the hydride generation approach used when analyzing for arsenic and selenium by atomic absorption spectroscopy to the multielement inductively coupled plasma (ICP) spectroscopy method. The paper "Hydride Generation Methods for Determination of Arsenic, Antimony, and Selenium" outlines a sample preparation procedure and instrumental parameters for the simultaneous determination of arsenic, antimony, and selenium using ICP spectroscopy.

Heavy elements, such as lead and mercury, create notorious environmental problems because of their propensity to undergo environmental transformations. These transformed species often present significantly different transport, toxicity, and persistence properties than the form of initial deposition. Accurately assessing the risks associated with heavy element contamination therefore requires knowledge, not only of the concentration of the element present, but also the form that it is present in. Olson et al., in "Methods for the Analysis of Organometallic Compounds in Wastes," describe how combinations of chromatographic molecular separation coupled with element-selective detectors can yield reliable determinations of the organometallic species present in waste matrices.

Used petroleum oils serve as a valuable energy source due to their high BTU content. Im-

proper burning of such oils, however, can present significant environmental hazards. One such hazard is the release of halogenated toxic organic compounds to the air when contaminated oil is used as a fuel. To prevent health risks resulting from the burning of used oils containing spent halogenated solvents and other halogenated organics, in 1985 EPA promulgated regulations establishing standards for waste oil burned as fuel in nonindustrial boilers. The rule presumes that oils with a total halogen content exceeding 1000 mg/L have been mixed with hazardous spent halogenated solvents and are not suitable for use in nonindustrial boilers. This ruling presents problems for those involved in the collection, recycling, and reuse of waste oils. Transporters, reprocessors, and burners of waste oil must test each batch of waste oil to insure that it meets EPA specification. These tests should ideally be done at the point of collection or reuse to avoid the time and expense of laboratory analysis. In their paper "Development of a Portable Testing Procedure for Monitoring Halogenated Solvents in Waste Fuels," Tarrer et al. describe one such test that is being developed to meet this need. Their work is illustrative of the novel, low-cost approaches to testing that have to be developed to meet the needs of the waste management program.

When faced with the problem of analyzing wastes and other environmentally important samples, the analyst is often faced with the task of selecting which of a number of competing methods to use. While the methods vary in terms of their strengths and weaknesses (for example, time for an analysis, sensitivity, precision), detailed comparative information is often not available for use in making the selection. In an effort to select appropriate methods for determining selenium in various sample matrices, Iskander et al. evaluated different approaches to sample preparation and analysis. Their paper, "Comparative Study of Preparative and Analytical Techniques for the Determination of Selenium in Water, Sediment, and Vegetation Matrices," will serve to assist other analysts faced with determining this potentially toxic and difficult-to-analyze environmental contaminant.

Quality Assurance

The primary goal of a quality assurance program is to ensure that the data gathered to answer a question is of known quality. Unless the quality of the data is known, then the decision maker will not be in a position to determine if the accuracy and precision of the data is sufficient to answer the question. The RCRA regulations require that owners of hazardous waste land disposal facilities monitor the groundwater beneath the site. Groundwater monitoring serves a number of purposes. These include: early detection of leakage, determination of the zone of contamination at leaking sites, and assessment of the risk posed by groundwater contamination.

In 1985, the EPA established the Hazardous Waste Ground Water Task Force to evaluate how well facilities were complying with the groundwater monitoring regulations. The paper by Kangas et al., "Quality Assurance on the Groundwater Monitoring Task Force Facility Assessment Program," provides an overview of the quality assurance activities performed by the Task Force during evaluation of six facilities. It provides examples of quality assurance procedures found appropriate for facility monitoring. Evaluation of analytical data and laboratory performance through integration of information from performance evaluation samples, laboratory audits, and laboratory analytical control charts is emphasized.

One critical component of any waste characterization or facility monitoring program is the competence of the laboratory that will be analyzing the field samples. One approach to ensure that laboratories possess at least a minimum level of competency is through the operation of a laboratory certification program. The Office of Quality Assurance within the New Jersey Department of Environmental Protection develops laboratory standards for the Department's environmental regulations and administers a laboratory certification program. Their RCRA laboratory certification program is designed to evaluate laboratory competence in the areas of

hazard classification using waste characteristics, inorganic analysis, organic analysis, and miscellaneous SW-846 testing procedures. The paper, "RCRA Laboratory Certification" by Hirst et al. describes the New Jersey system and issues associated with the establishment of certification programs.

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Contents

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Development and Validation of RCRA Method 8280 for Dioxins and Furans

REFERENCE: Billets, S., Ballard, J. M., Vonnahme, T. L., Nunn, N. J., and Youngman, D. R., **"Development and Validation of RCRA Method 8280 for Dioxins and Furans,"** *Waste Testing and Quality Assurance, ASTM STP 999,* D. Friedman, Ed., American Society for Testing and Materials, Philadelphia, 1988, pp. 1-13.

ABSTRACT: RCRA Method 8280 for the analysis of chlorinated dibenzo-*p*-dioxins and dibenzofurans, as published in the *Federal Register* in April 1983, revealed the need for several modifications to allow for the determination of the target analytes in complex matrices, such as industrial sludge and still-bottom samples. Details of these modifications and of the subsequent application of the revised method to a limited number of samples which were analyzed in the course of a multilaboratory evaluation are reported.

Further evaluation of RCRA Method 8280 for the analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans has been performed. The Method has been modified to provide for the quantitation of total tetra- through octa-chlorinated dioxins and dibenzofurans and has been applied to sample matrices derived from industrial polychlorophenol sources as well as to fly-ash, still-bottom, and Missouri soil samples. As an additional test of Method performance, an interlaboratory validation study was conducted in two parts. A two-part study was used because the Method had been extensively revised since its publication in the *Federal Register,* and it was felt that participating laboratories would be unfamiliar with some of the proposed procedures. The first phase was intended to allow the participants to acquire familiarization with the Method by analyzing relatively simple matrices for a few specified analytes which had been spiked into the samples. The second phase required the total quantitation of tetra- through octa-CDDs and CDFs in complex samples containing the analytes at both low (ppt) and extremely high (ppm) levels; no spiking was used for these samples. A method detection limit study using all available $^{13}C^{12}$-labeled PCDD and PCDF isomers spiked into seven different sample matrices was also performed, and the results indicated both matrix and homolog specific differences.

The revised Method 8280 has undergone a period of continual development; new documentation which will be reported includes Method performance data on complex samples from polychlorophenol use processes, results from an interlaboratory study of the revised method, and method detection limits of selected PCDDs and PCDFs in a variety of environmental and hazardous waste matrices.

KEY WORDS: PCDD, PCDF, waste analysis

On a molecular basis, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) is one of the most poisonous synthetic chemicals known. The compound has been shown in animals to possess teratogenic, embryotoxic, carcinogenic, and cocarcinogenic properties in addition to acute toxicity. Because of its chemical stability, lyophilic character, and extreme toxicity, it presents potentially severe health hazards to the human population. Although 2,3,7,8-TCDD is the most toxic of the 75 chlorinated dibenzo-*p*-dioxins (PCDDs), many of the others [as well as the 135 chlorinated dibenzofurans (PCDFs) which have similar genesis, structures, and properties] are

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known to possess relatively high toxicity to humans and animals. For this reason, the entire spectrum of PCDDs and PCDFs is of environmental concern.

Based on this information, it was concluded that samples containing tetra-, penta-, hexa-, hepta-, and octa-CDDs and -CDFs are likely to exhibit increased toxicity. A method to analyze hazardous wastes for the relevant PCDDs and PCDFs was included in the Resource Conservation and Recovery Act (RCRA) requirements for hazardous waste monitoring. A single-laboratory evaluation of RCRA Method 8280 for the analysis of PCDDs and PCDFs in hazardous waste has been the subject of a previous report prepared for the Office of Solid Waste. That report presented results obtained with sample matrices including pottery clay, a Missouri soil, a fly ash, a still bottom from a chlorophenol-based herbicide production process and an industrial process sludge.

The revised Method 8280 has undergone a period of continual development, and this report presents results obtained during the further evolution of the Method. The Method has now been modified to enable the quantitation of total tetra- through octa-chlorinated dioxins and dibenzofurans and has been applied to six different sample matrices derived from industrial polychlorophenol sources and also to fly-ash, still-bottom, and Missouri soil samples. An interlaboratory validation of the Method was conducted in two phases: Phase I required the analysis of spiked and unspiked clay and sludge samples for certain specified PCDD/PCDF analytes, and Phase II required the analysis of soil, sludge, fly-ash, and still-bottom samples for total tetra- through octa-chlorinated dioxins and dibenzofurans. Method detection limits of $^{13}C_{12}$-labeled polychlorinated dioxins and dibenzofurans in seven matrices have also been determined. A flow chart for the proposed method is shown in Fig. 1.

RCRA Method 8280 for the analysis of chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans, as published in the *Federal Register* in April 1983, revealed the need for several modifications to allow for the determination of the target analytes in complex hazardous waste matrices, such as industrial sludge and still-bottom samples. Subsequently, the Method has been further refined in several important ways as needed for the characterization and assessment aspects of RCRA. A summary of these changes is as follows: In order to improve the accuracy of quantitation of the hepta- and octa-CDDs and -CDFs, a second internal standard ($^{13}C_{12}$-OCDD) is added together with $^{13}C_{12}$-2,3,7,8-TCDD prior to sample workup. Some of the ions specified in the multiple ion detection (MID) descriptors have been changed so as to increase sensitivity by monitoring the most intense ion in the isotopic cluster. To ensure that coeluting polychlorinated diphenyl ethers (PCDEs) are not contributing to the signal response due to PCDFs, the molecular ion of the appropriate PCDE was included in each MID descriptor. In addition, the criteria for the positive identification of PCDD and PCDF isomers were made more explicit. Instrument tune criteria employing PCDD standard reference materials were substituted for those based on the use of decafluorotriphenylphosphine (DFTPP). The section on the calculation of concentrations of the target analytes was expanded to include a procedure for measuring unknown PCDD and PCDF isomers.

This report presents data on the performance of the Method as it was applied to the analysis of a variety of wastes derived from the use of polychlorophenols in the wood-preserving industry. As an additional test of Method performance, an interlaboratory validation study was conducted. This study was divided into two phases because the Method had been extensively revised since its first publication in the *Federal Register*, and it was felt that participating laboratories would be unfamiliar with some of the proposed procedures. The first phase was intended to allow the participants to acquire familiarization with the Method by analyzing relatively simple matrices for a few specified analytes which had been spiked into the samples. The second phase required the total quantitation of tetra- through octa-CDDs and -CDFs in complex samples containing the analytes at both low and extremely high concentration levels; no spiking was used for these samples. A method detection limit study using all available $^{13}C_{12}$-labeled PCDD and PCDF isomers spiked into seven different sample matrices was also performed and will be reported.

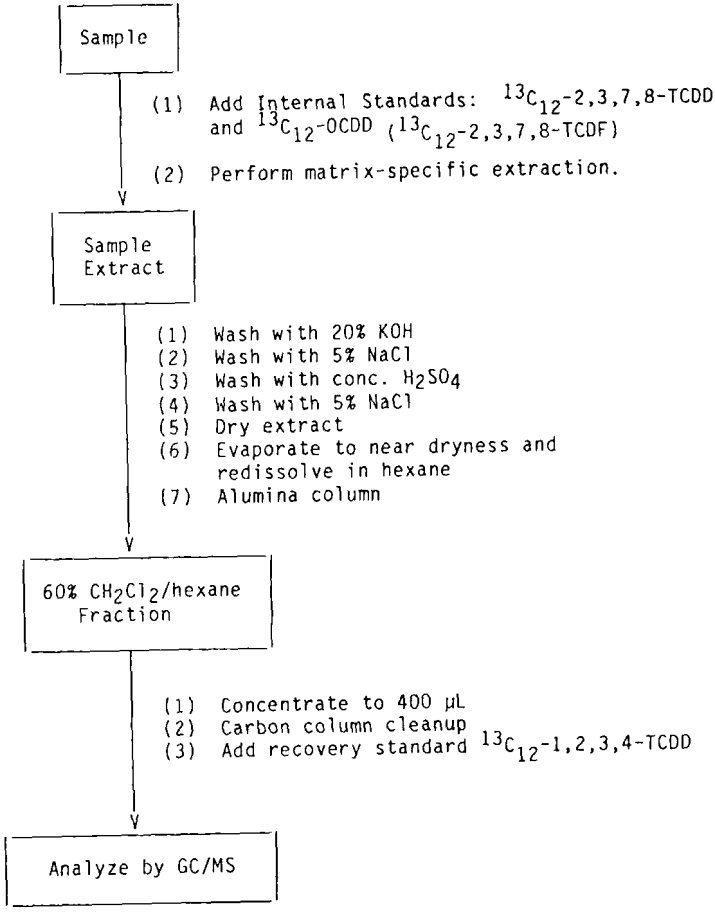

FIG. 1—*Method 8280 flow chart for the analysis of PCDDs and PCDFs.*

Data obtained from Phase I of the interlaboratory study indicate that the Method is biased high and that the bias appears to decrease as the concentrations of the analytes increase. Data from the method detection limit (MDL) study can also be used as an indicator of intralaboratory precision. For seven replicate determinations of a TCDF and a PeCDD in fly-ash with each at a measured concentration of 2.6 times their final calculated MDLs, the relative standard deviations (RSDs) were 12.3 and 12.2%, respectively. Similar determinations for a PeCDF and a TCDD, which were measured at a level 6.0 and 4.4 times their MDLs, gave RSDs of 5.2 and 7.2%, respectively.

Encouraging results were obtained from Phase I of the interlaboratory study in which specific analytes spiked into clay and sludge samples were quantitated. The good overall recovery (greater than 50%) of the internal standard and the small differences between the spiked concentrations and the mean measured values both indicate that the Method can provide acceptable data in a multilaboratory evaluation. Phase II of the interlaboratory study which required the quantitation of total tetra- through octa-CDDs and -CDFs in 10 aliquots of four sample types also provided generally satisfactory results. The internal standards ($^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-OCDD) were recovered in overall acceptable yields ranging from 51 to 82%. However,

quantitation of the analytes was less precise than in Phase I. Two major, probable reasons for this are as follows:

1. The complex samples themselves, some of which contained endogenous amounts of the target analytes at low and at extremely high levels. This required a large dilution effect which minimized the value of the internal standard.
2. The analysis required the identification, confirmation, and quantitation of unknown peaks for each congener without an authentic reference material which could be used to confirm the identification.

Statistical analysis of the Phase II data revealed that:

1. The recovery of the $^{13}C_{12}$-2,3,7,8-TCDD internal standard was a function of sample type, whereas that of the $^{13}C_{12}$-OCDD internal standard was not.
2. The laboratories were equivalent in accuracy for all analytes except OCDD.
3. The laboratories were equivalent in precision for 31 of the 40 possible matrix/analyte combinations.

As a result of the experience gained during the single- and multilaboratory testing of the Method with a variety of environmental samples, several modifications and areas of further study are recommended as follows:

1. The Method should allow for the use of disposable, open carbon columns as an option to the HPLC carbon column cleanup. This would allow for an increase in the rate of sample throughput and would also reduce solvent consumption.
2. Gas chromatography (GC) conditions should be modified to improve the resolution between the internal standard ($^{13}C_{12}$-2,3,7,8-TCDD) and the recovery standard ($^{13}C_{12}$-1,2,3,4-TCDD). If this cannot be readily achieved, then use of an alternative recovery standard should be considered.
3. The elution windows (defined by first and last eluting isomers) of the tetra- through octa-CDD and -CDF congeners should be established for the GC conditions used in the Method.
4. Method 8280 should be written to require as many GC/MS analyses as necessary by using the appropriate MID descriptors whenever an elution overlap is noted in a sample. The descriptors should include at least one ion for each overlapping homologue.
5. Kovats Indices should be determined for available PCDDs and PCDFs. This would aid laboratories in the identification of isomers not known or available and would be useful in a GC screening program.
6. The need to monitor for polychlorinated diphenyl ethers (PCDEs) in the final sample extract should be investigated.
7. A source of a well-defined GC performance standard should be identified. Column performance guidelines should be established for a variety of columns.

These changes have been incorporated into the final version of the Method.

In order to assess method performance, ten waste samples derived from the industrial use of pentachlorophenol (PCP) were provided to the EPA. These samples together represent four different matrix types: sludge, fuel oil, alcohol-diluted fuel oil, and soil. The range of matrix types encompassed is expected to be representative of those to be analyzed under RCRA regulations and is expected to provide varying degrees of sample complexity.

Each sample was analyzed in duplicate for the quantitation of total tetra- through octa-CDDs and -CDFs. Two criteria were applied to confirm that peaks in the extracted ion current profiles (EICPs) of the quantitation ions were due to the targeted analytes and were not due to either interferences or spurious noise signals. These were the following:

1. Signal-to-noise ratio greater than 3 to 1.

2. The presence of the confirmation ion such that the relative intensity of the quantitation ion and the confirmation ion was within the limits specified in the Method.

Signal responses that did not meet these criteria are reported as "ND" (not detected). Quantitation was usually performed against $^{13}C_{12}$-2,3,7,8-TCDD as the internal standard, and values were corrected for the recovery using this compound as an isotopic diluent. However, due to the extremely high levels of hexa-, hepta-, or octa-CDDs/CDFs present in some samples, these analytes were quantitated against $^{13}C_{12}$-1,2,3,4-TCDD or $^{13}C_{12}$-OCDD added to the extracts after dilution. It is a disadvantage of the quantitation method that multiple GC/MS analyses are therefore required for samples containing both low and high analyte concentration level. To spike the sample with the appropriate $^{13}C_{12}$-standard at the levels found would have caused an unnecessarily large expense. Whenever possible, sample rerun requirements were imposed to lessen the need for quantitation by anything other than the isotopic diluent. Several characteristics are evident in the data presented in Table 1. First is the total absence of detectable levels of TCDD in all of the ten samples and the occurrence of PeCDD in only three samples; second is the very high levels of hepta- and octa-CDD present in the PCP process samples.

For purposes of this study, the method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a given matrix containing the target analyte. The data for this study were obtained using all available $^{13}C_{12}$-labeled analytes spiked into seven different sample types at a concentration of twice the estimated MDL of each analyte. This experimental design was used in order to obtain MDL values in each matrix without spiking with unlabeled PCDDs and PCDFs and without changing the integrity of the sample. In order to establish an appropriate spiking level, the MDL was estimated as that concentration at which the response of the appropriate quantitation ion gave a signal/noise ratio of 3 to 1. Statistical considerations required that a minimum of seven replicates of each sample type should be processed through the entire analytical method. Two initial replicates were tested to verify the reasonableness of the MDL estimate for each sample type. When a reasonable spiking level had been achieved, five more determinations were made at the same spike concentration. The standard deviation (S) of the mean concentration determined for each analyte was then calculated from the seven replicate measurements for each of the seven matrix types. The MDL was then calculated from the equation

$$\text{MDL} = t_{(n-1,1-\alpha\,=0.99)} \times (S)$$

where $t_{(n-1,1-\alpha\,=0.99)}$ is the Student's t value appropriate for a 99% confidence level and a standard deviation estimate with $n - 1$ degrees of freedom. Therefore

$$\text{MDL} = 3.143(S)$$

The concentration (C_s) of each analyte in each sample was determined with reference to the $^{13}C_{12}$-1,2,3,4-TCDD internal standard, which was spiked after sample workup to give a final concentration of 40 pg/μL.

The eight $^{13}C_{12}$-labeled PCDDs and PCDFs used in this study and their MDLs in the seven sample matrices are listed in Table 2. Several characteristics and trends are apparent in the data: $^{13}C_{12}$-2,3,7,8-TCDD/TCDF usually had the lowest MDL values for each sample type while $^{13}C_{12}$-HpCDD/OCDD usually had the highest. As might be expected, the MDL values for all analytes generally increased in passing from the "clean" sample types (reagent water, fly ash) to the more complex, organics-containing matrices (still bottom, industrial sludge). The MDL for $^{13}C_{12}$-2,3,7,8-TCDD in reagent water (0.44 ppt) determined in this study using Method 8280 compares well with the value reported for 2,3,7,8-TCDD in reagent water (2 ppt)

TABLE 1—*Analysis[a] of PCP process samples using Method 8280.*

PCDD/ PCDF	Sludge B-6d, ppb	Fuel oil B-7b, ppb	Sludge B-8b, ppb	Sludge B-12h, ppb	Fuel oil A-2g, ppb	Alcohol fuel oil A-3g, ppb	Sludge A-4g, ppb	Soil A-5g, ppb	Soil A-6.1g, ppb	Soil A-6.2g, ppb
TCDD	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND
PeCDD	ND	ND	ND	ND	ND	ND	ND	ND	27	ND
HxCDD	2150	2186	ND	ND	2079	762	726	283	730	396
HpCDD	51 520[c]	67 176[c]	2166[c]	978[c]	38 195[c]	17 956[c]	59 600[c]	12 945[c]	24 700[c]	12 300[c]
OCDD	72 300[c]	154 000[c]	2670[c]	2550[c]	59 100[c]	24 500[c]	106 000[c]	16 500[c]	26 300[c]	15 000[c]
TCDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PeCDF	ND	154	ND	ND	246	ND	ND	ND	61	ND
HxCDF	68	2933	ND	ND	2852	76	1568	65	252	56
HpCDF	343	1342	ND	ND	1913	1118	1948	533	1695	434
OCDF	4100[c]	7500[c]	ND	76	447	741	3200[c]	900[c]	3080[c]	1690[c]
$^{13}C_{12}$-2,3,7,8-TCDD percent recovery	66.8	69.0	64.3	67.8	69.2	60.0	62.9	77.0	75.4	74.8

[a]Mean of duplicates; concentrations shown are for the total of all isomers within a given homologous series.

[b]ND is below the detection limit for the sample matrix. Detection limits are estimated as 5 ppb for the tetra- through hexaisomers, and 10 ppb for the hepta- and octaisomers.

[c]Due to the extremely high levels of HpCDD, OCDD, and OCDF detected in the GC/MS analysis, the extracts were diluted after normal quantitation of the tetra-, penta-, hexa-CDD/CDF and hepta-CDF. HpCDD, OCDD, and OCDF were then quantitated versus $^{13}C_{12}$-1,2,3,4-TCDD added after dilution; the values are corrected for $^{13}C_{12}$-2,3,7,8-TCDD recovery.

TABLE 2—*Method detection limits of $^{13}C_{12}$-labeled PCDDs and PCDFs in reagent water (ppt) and environmental samples (ppb).*

$^{13}C_{12}$-Labeled Analyte	Reagent Water[a]	Missouri Soil[b]	Fly Ash[b]	Industrial Sludge[c]	Still Bottom[d]	Fuel Oil[d]	Fuel Oil/ Sawdust[b]
2,3,7,8-TCDD	0.44	0.17	0.07	0.82	1.81	0.75	0.13
1,2,3,7,8-PeCDD	1.27	0.70	0.25	1.34	2.46	2.09	0.18
1,2,3,6,7,8-HxCDD	2.21	1.25	0.55	2.30	6.21	5.02	0.36
1,2,3,4,6,7,8-HpCDD	2.77	1.87	1.41	4.65	4.59	8.14	0.51
OCDD	3.93	2.35	2.27	6.44	10.1	23.2	1.48
2,3,7,8-TCDF	0.63	0.11	0.06	0.46	0.26	0.48	0.40
1,2,3,7,8-PeCDF	1.64	0.33	0.16	0.92	1.61	0.80	0.43
1,2,3,4,7,8-HxCDF	2.53	0.83	0.30	2.17	2.27	2.09	2.22

NOTE: The final sample-extract volume was 100 μL for all samples.
[a]Sample size 1000 mL.
[b]Sample size 10 g.
[c]Sample size 2 g.
[d]Sample size 1 g.

which was determined using Method 613 (capillary column GC/MS with selected ion monitoring). The MDL procedure, involving seven replicate determinations of each of the eight analytes in each of seven sample matrices, generated other data (percent recovery, precision) which is of interest in assessing the performance of Method 8280. These data are presented in Tables 3 and 4. It can be seen that good recoveries were obtained and that the precision at low spike levels was acceptable.

Phase I of the interlaboratory study was intended to allow participating laboratories an opportunity to become familiar with the requirements of the revised Method 8280. This phase of the study was considered necessary since extensive revisions had been made to the original version of the Method. These included: (1) changes in the procedure for the extraction of analytes from the sample; (2) modification of the open column alumina chromatography cleanup; (3) deletion of the HPLC cleanup; (4) addition of a carbon column cleanup; and (5) incorporation of internal and recovery standards into the Method.

Five laboratories were selected by the Contract Laboratory Program to participate in the study. Each was provided with samples, analytical standards, isotopically labeled internal and recovery standard solutions, and the revised Method. Also provided were: detailed supplemental instructions which included guidance on the sample size, the volume of the final extract, typical MID descriptors, typical reconstructed ion chromatograms (RIC), and the reporting

TABLE 3—*Percent recovery of $^{13}C_{12}$-labeled PCDDs and PCDFs from fuel oil.*

$^{13}C_{12}$-Labeled Analyte	Concentration (pg/μL) in Final Extract		RSD, %	Mean Recovery, %
	Spiked	Measured		
2,3,7,8-TCDD	40	29.7	8.0	74.3
1,2,3,7,8-PeCDD	80	56.8	11.7	71.0
1,2,3,6,7,8-HxCDD	120	110.7	14.4	92.3
1,2,3,4,6,7,8-HpCDD	150	118.3	21.9	78.9
OCDD	250	232.8	31.7	93.1
2,3,7,8-TCDF	20	12.9	11.9	64.5
1,2,3,7,8-PeCDF	40	27.7	9.2	69.3
1,2,3,4,7,8-HxCDF	80	57.2	11.7	71.5

TABLE 4—*Percent recovery of $^{13}C_{12}$-labeled PCDDs and PCDFs from industrial sludge.*

$^{13}C_{12}$-Labeled Analyte	Concentration (pg/μL) in Final Extract		RSD, %	Mean Recovery, %
	Spiked	Measured		
2,3,7,8-TCDD	40	25.3	10.2	63.3
1,2,3,7,8-PeCDD	80	56.7	16.5	70.9
1,2,3,6,7,8-HxCDD	80	90.6	15.8	113.3
1,2,3,4,6,7,8-HpCDD	120	128.6	16.7	107.2
OCDD[a]	175	...	16.2	...
1,2,3,7,8-TCDF	20	15.6	14.6	78.0
1,2,3,7,8-PeCDF	40	26.4	14.1	66.0
1,2,3,4,7,8-HxCDF	80	49.5	14.8	61.9

[a]Peak shape was distorted by very high level of interferent.

requirements for data and deliverables. Each laboratory was provided with the six samples which had been prepared by personnel of the referee Laboratory who also analyzed these samples.

The results obtained by the referee laboratories' personnel who were familiar with the Method, although not obtained as part of the blind study, were valuable for comparison and are included in the relevant tables.

A very simple, qualitative measure of how well the combined extraction, chromatographic cleanup, and GC/MS analysis prescribed in the Method deals with the various analytes may be obtained by noting the number of target analytes for which values were reported by each laboratory. As shown in Table 5, at least one laboratory in addition to referee detected all of the analytes, and two laboratories reported 12 of 13. Relatively lower reporting by Laboratories II and IV is presumed to be due to lack of familiarity with the extraction and cleanup procedures and may be expected to improve with experience.

A more quantitative measure of the extraction and cleanup efficiency is provided by monitoring the percent recovery of the internal standard ($^{13}C_{12}$-2,3,7,8-TCDD) which was added to the sample immediately prior to extraction. Table 6 shows that three of the participating laboratories, apart from the referee, obtained acceptable results (mean recovery greater than 40%). The two other laboratories reported mean recoveries of less than 30%.

A summary of results obtained from the sludge samples is described in Table 7 and the results of the study are summarized as follows:

TABLE 5—*Interlaboratory test of Method 8280, Phase I: Summary of analytes reported by participating laboratories.*

Sample	Number of Analytes Spiked	Referee Lab	Number of Analytes Reported by Each Laboratory				
			I	II	III	IV	V
Clay Spike No. 1	13	13	13	8	12	11	12
Clay Spike No. 2	13	13	13	8	12	4	12
Sludge Spike No. 1	6	6	6	3	4	6	4
Sludge Spike No. 2	6	6	6	3	4	6	4