United States
Environmental Protection
Agency

Environmental Monitoring
Systems Laboratory
Las Vegas NV 89114

Research and Development

EPA/600/S4-86/021 July 1986

EPA

Project Summary

Performance of RCRA Method 8280 for the Analysis of Dibenzo-*p*-Dioxins and Dibenzofurans in Hazardous Waste Samples

J. M. Ballard, T. L. Vonnahme, N. J. Nunn,
D. R. Youngman, and Stephen Billets

Further evaluation of RCRA Method 8280 for the analysis of chlorinated dibenzo-*p*-dioxins and dibenzofurans, has been performed. The Method has been modified to enable the quantitation of total tetra- through octa-chlorinated dibenzo-*p*-dioxins and dibenzofurans, and has been applied to six different sample matrices derived from industrial polychlorophenol sources and also from fly-ash, still-bottom, and Missouri soil samples. An interlaboratory validation of the Method has been conducted in two phases: Phase I required the analysis of spiked and unspiked clay and sludge samples for certain specified analytes, and Phase II required the analysis of 10 samples of soil, sludge, fly-ash and still-bottom 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 been determined. In addition, a comparison was made of the Contract Laboratory Program carbon column cleanup (without backflush) with the corresponding backflush procedure used in the proposed RCRA Method.

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

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 co-carcinogenic properties in addition to acute toxicity. Because of its chemical stability, lipophilic 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 (PCDD's), many of the others (and also of the 135 chlorinated dibenzofurans [PCDF's] which have similar genesis, structures, and properties) are known to possess relatively high toxicity to humans and animals. For this reason, the entire class of PCDD's and PCDF's is of environmental concern.

The first synthesis of 2,3,7,8-TCDD was reported in 1872, and only sporadic reports of the preparation of PCDD's, containing two, four, or eight chlorine atoms, appeared in the literature during the years 1941-1965. Particular interest in 2,3,7,8-TCDD, and in the PCDD's and PCDF's in general, increased markedly with the discovery in the early 1970's of the same teratogenic and toxic effects with certain commonly used herbicides, e.g., 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), as were observed with 2,3,7,8-TCDD. Analysis of 116 samples of 11 different pesticides

produced during the period 1950-1970 revealed the presence of PCDD contamination (tetra- through octa-chlorinated) in 42 percent of the samples. Consideration of the chemistry of pesticide manufacture indicated that PCDD's could be formed in competing side-reactions of the polychlorophenol precursors. The domestic use of 2,4,5-T was subsequently banned, and the military use of Agent Orange (1:1 mixture of 2,4,5-T and 2,4-dichlorophenoxyacetic acid) as a defoliant in Vietnam was discontinued, both in the early 1970's. Because of the widespread usage of pesticides potentially contaminated with PCDD's, a Dioxin Monitoring Program was set up by the EPA in 1973 to develop an analytical method capable of detecting 2,3,7,8-TCDD in environmental samples at the part per trillion (ppt) level. This effort formed the basis of the National Dioxin Strategy of the Agency.

Although the most ubiquitous routes of non-occupational exposure of the general population to dioxins have probably been *via* the use of contaminated pesticides and from the emissions of municipal waste incinerators, the most concentrated waste sources of 2,3,7,8-TCDD are the tars and sludges resulting from the commercial preparation of 2,4,5-trichlorophenol (2,4,5-TCP). This latter fact was highlighted during an investigation in 1975-1977 of unexplained animal deaths at various horse arenas in Missouri. It was discovered that the sites had been sprayed with a mixture of waste oil and distillation residues from the manufacture of 2,4,5-TCP which were contaminated with 2,3,7,8-TCDD. Subsequent investigation of chemical waste dump-sites in New York State (Hyde Park; Love Canal), where wastes from the manufacture of 2,4,5-TCP had been buried, also revealed the presence of substantial amounts of 2,3,7,8-TCDD.

As a result of this experience, it was concluded by the EPA that samples containing tetra-, penta-, and hexa-CDD's and CDF's are likely to exhibit increased toxicity (40 CFR 261:1978, January 14, 1985), and a method to analyze hazardous wastes for the relevant PCDD's and PCDF's was included in the Resource Conservation and Recovery Act (RCRA) requirements for hazardous waste monitoring as published in the Federal Register (40 CFR 65:14514, April 4, 1983). A single-laboratory evaluation of the RCRA Method 8280 for the analysis of PCDD's and PCDF's in hazardous waste has been the subject of a previous report prepared for the Office of Solid Waste (EPA-600/4-85/082). 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. Major revisions to the Method as first published in 1983 were necessary to accommodate the analysis of complex samples such as sludge and still-bottom.

The revised Method 8280 has subsequently undergone a period of continual development, and this summary presents results obtained during the further evolution of the Method.

Study Design

Changes made to the proposed Method since publication of the previous report are summarized as follows: in order to improve the accuracy of quantitation of the hepta- and octa-CDD's and CDF's, 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 co-eluting polychlorinated diphenyl ethers (PCDE's) are not contributing to the signal response due to PCDF's, 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 perfluorotri-*n*-butylamine (FC-43) were substituted for those based on the use of decafluorotriphenylphosphine (DFTPP). The section on the calculation of concentrations of analytes was expanded to include a procedure for measuring unknown PCDD and PCDF isomers.

The performance of the Method was initially examined by its application 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 in two parts. A two-part study was used because the Method had been extensively improved since its publication in the Federal Register, and it was felt that participating laboratories would be unfamiliar with some of the revised 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-CDD's and CDF's in complex samples containing the analytes at both low and extremely high levels; no spiking was used for these samples. A method detection limit study using a available $^{13}C_{12}$-labeled PCDD and PCD isomers spiked into seven different sam ple matrices was also performed. A com parison of the EPA Contract Laborator Program (CLP) carbon column cleanu without and with a backflush elution pro cedure was conducted to test the ade quacy of the CLP method for the deter mination of total PCDD's and PCDF's.

Results

The single-laboratory application of th Method to the determination of PCDD' and PCDF's in complex environmenta samples (e.g., fly-ash, still-bottom, an wastes from the industrial use of penta and tri-chlorophenol) has routinely yield ed excellent recoveries (60 to 85 percent of the spiked internal standard $^{13}C_{12}$-2,3 7,8-TCDD (see Tables 1 and 2). This indi cates that the extraction and cleanup pro cedures are able to accommodate sample ranging from those with a high aqueou content to viscous oils and chemical slud ges. It can be assumed that endogenou PCDD's and PCDF's are extracted wit equal success if matrix effects are not i effect.

In the absence of a full range of stan dard reference materials, the accuracy o the Method is rather difficult to assess However, data obtained from Phase I o the interlaboratory study indicate that th Method is biased high and that the bia appears to decrease as the concentration of the analytes increase (see Table 3). Data from the method detection limit (MDL study can be used as an indicator of intra laboratory precision. For seven replicate determinations of a TCDF and a PeCDD i fly-ash, with each at a measured concen tration of 2.6 times their final calculated MDL's, the relative standard deviation (RSD's) were 12.3 percent and 12.2 per cent, respectively. Similar determination for a PeCDF and a TCDD which were mea sured at a level 6.0 and 4.4 times thei MDL's gave RSD's of 5.2 percent and 7.2 percent, 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 mean value for 114 determinations of 11 analytes spiked into clay at the 5 ppb level was 6.02 ± 2.78 ppb.

The mean value for 16 determinations of two analytes spiked into clay at the 2.5 ppb level was 3.56 ± 2.35 ppb.

The mean value for 57 determinations of six analytes spiked into sludge at the 125 ppb level was 126.4 ± 57.9 ppb.

The good overall recovery (greater than

Table 1. *Analysis[a] of PCP Process Samples Using Method 8280*

PCCD/ 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	51520[c]	67176[c]	2166[c]	978[c]	38195[c]	17956[c]	59600[c]	12945[c]	24700[c]	12300[c]
OCDD	72300[c]	154000[c]	2670[c]	2550[c]	59100[c]	24500[c]	106000[c]	16500[c]	26300[c]	15000[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 detection limit for the sample matrix. Detection limits are estimated as 5 ppb for the tetra- through hexa-isomers and as 10 ppb for the hepta- and octa-isomers.
[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 which was added after dilution; the values are corrected for $^{13}C_{12}$-2,3,7,8-TCDD recovery.

Table 2. *Analysis[a] of PCP Process Sample (B-5) and 10 TCP Process Samples Using Method 8280*

PCCD/ PCDF	Water B-5 (ppb)	Sawdust H-3 (ppb)	Soil H-7a (ppb)	Soil H-7b (ppb)	Soil H-7c (ppb)	Water I-1 (ppb)	Sludge I-2 (ppb)	Sludge I-11 (ppb)	Soil I-12c (ppb)	Soil I-14a (ppb)	Soil I-14b (ppb)
TCDD	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PeCDD	ND	385	ND	ND	ND	ND	30	ND	ND	ND	ND
HxCDD	0.072	2680[d]	ND	ND	ND	110[d]	2410[d]	399	ND	ND	ND
HpCDD	2.5[c]	2314[c]	ND	ND	ND	1677[c]	42134[c]	4404[c]	ND	37	ND
OCDD	1.25[c]	1250[c]	5.5	ND	ND	345[c]	14658[c]	4080[c]	ND	20	ND
TCDF	0.024	3598[d]	ND	ND	ND	3.9[d]	201	68	ND	ND	ND
PeCDF	ND	1908[d]	ND	ND	ND	ND	429	23	ND	ND	ND
HxCDF	0.017	11903[d]	ND	ND	ND	233[d]	5496[d]	626	ND	ND	ND
HpCDF	0.136	1374[d]	ND	ND	ND	108[c]	2768[c]	622[c]	ND	ND	ND
OCDF	0.029	94[c]	ND	ND	ND	16[c]	239[c]	151[c]	ND	ND	ND
$^{13}C_{12}$-2,3,7,8-TCDD percent recovery	67.3	95.2[e]	71.2	76.4	72.3	—[f]	77.1	75.6	84.9	78.7	84.1

[a] Mean of duplicates except for samples B-5 and I-1 which are the result of single determinations. Concentrations shown are for the total of all isomers within a given homologous series.
[b] ND is below detection limit for the sample matrix. Detection limits are 5 ppb for soil, sawdust, sludge, and are 0.01 ppb for water.
[c,d] Due to the very high levels of some hexa-, hepta-, or octa-CDD/CDF isomers, some samples were diluted, and the PCDD's and PCDF's noted were quantified versus $^{13}C_{12}$-OCDD[c] or $^{13}C_{12}$-1,2,3,4-TCDD[d]; the values are corrected for $^{13}C_{12}$-2,3,7,8-TCDD recovery.
[e] Some interference at the quantitation ion was noted.
[f] Gross interference at the quantitation ion was noted.

Table 3. *Interlaboratory Test of Method 8280, Phase I: Accuracy and Bias of Results*

Sample Type	Spike Level (ppb)	Number of Determinations	Accuracy (Percent)	Bias (Percent)	± SD of Bias Estimate
Clay	2.5	16	142.4	+42.4	±11.8
Clay	5.0	114	120.4	+20.4	± 5.21
Sludge	125	57	101.1	+ 1.12	± 6.14

50 percent) 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 program. Phase II of the interlaboratory study which required the quantitation of total tetra- through octa-CDD's and CDF's in 10 aliquots of 4 sample types, also provided 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 percent. 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 which sometimes contained endogenous amounts of the target analytes at low and at extremely high levels; this led to a large dilution requirement which eliminated the value of the isotopic dilution method of quantitation.
2. The need for an analysis which required the identification, confirmation, and quantitation of an unknown number of peaks for each congener often without an authentic reference standard which could be used to confirm the identification of each congener.

In general, the Method performed well *when the laboratories followed the protocol.* A visual examination of the data showed that approximately 85 percent of the values reported by the 5 laboratories and used in the statistical analysis were consistent among the laboratories.

Statistical analysis of the Phase II data revealed that:

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

Method detection limits of eight $^{13}C_{12}$-labeled PCDD's and PCDF's spiked into reagent water were found to be in the low ppt range (less than 10 ppt); 42 of 48 values determined for 6 environmental samples were less than 5 ppb (see Table 4).

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) and determined using Method 61 (capillary column GC/MS with selected io monitoring).

An experimental comparison of th Contract Laboratory Program (CLP) carbo column cleanup (the backflush procedur is not used) with the backflush procedur used in Method 8280 was undertaken be cause the CLP method should be faste and should consume much less solven while it does not require HPLC equipment Twin open carbon columns were spike with a standard solution containing a mix ture of 11 PCDD's and PCDF's. The firs column was eluted with a 2-mL and a 5-mL aliquot of toluene; the second co lumn was eluted similarly in the reverse flow direction. The four fractions were analyzed separately, and the recoveries (see Table 5) indicated that although the CLP cleanup as written is very satisfactory for the determination of 2,3,7,8-TCDD (and possibly other tetra- and penta-CDD's and CDF's) it is not adequate for the deter mination of hexa-, hepta-, and octa-CDD's and CDF's. However, the combination of an open carbon column with a backflush procedure gave an acceptable perform ance for the tetra- through octa-substi tuted congeners.

Recommendations

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

1. The Method should allow for the use of disposable, open carbon columns as an option to the currently specified HPLC carbon column cleanup. This would allow for an increase in the rate of sample throughput and would also reduce solvent consumption.

Table 4. *Method Detection Limits of $^{13}C_{12}$-Labeled PCDD's and PCDF's 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	0.13	0.07	0.40	1.81	0.75	0.13
1,2,3,7,8-PeCDD	2.35	0.70	0.25	1.47	2.46	2.09	0.18
1,2,3,6,7,8-HxCDD	6.63	1.24	0.55	2.26	16.2	5.02	0.25
1,2,3,4,6,7,8-HpCDD	5.45	1.60	1.41	3.39	4.59	8.14	0.49
OCDD	7.37	1.35	2.27	7.68	10.1	23.2	1.34
2,3,7,8-TCDF	0.58	0.11	0.06	0.36	2.26	0.48	0.04
1,2,3,7,8-PeCDF	1.50	0.33	0.06	0.58	1.61	0.80	0.09
1,2,3,4,7,8-HxCDF	2.53	0.83	0.30	1.15	2.27	2.09	0.17

[a] *Sample size 1,000 mL.*
[b] *Sample size 10 g.*
[c] *Sample size 2 g.*
[d] *Sample size 1 g.*
Note: The final sample-extract volume was 100 µL for all samples.

Table 5. *Percent Recovery[a] of PCDD's and PCDF's from CLP Carbon Column*

	Method as Written (without Backflush)			Method Modified (with Backflush)		
Analyte	*2 mL Toluene Fraction*	*Additional 5 mL Toluene Fraction*	*Total*	*2 mL Toluene Fraction*	*Additional 5 mL Toluene Fraction*	*Total*
2,3,7,8-TCDF	*81.5*	*ND*	*81.5*	*83.0*	*ND*	*83.0*
1,2,3,4-TCDD	*80.0*	*ND*	*80.0*	*80.3*	*ND*	*80.3*
2,3,7,8-TCDD	*87.6*	*ND*	*87.6*	*87.6*	*ND*	*87.6*
1,2,3,7,8-PeCDF	*71.0*	*14.0*	*85.0*	*85.4*	*ND*	*85.4*
1,2,3,4,7-PeCDD	*80.9*	*ND*	*80.9*	*87.5*	*ND*	*87.5*
1,2,3,4,7,8-HxCDF	*35.9*	*43.0*	*78.9*	*74.5*	*9.8*	*84.3*
1,2,3,4,7,8-HxCDD	*39.6*	*46.0*	*85.6*	*80.3*	*9.8*	*90.1*
1,2,3,4,6,7,8-HpCDF	*7.8*	*52.6*	*60.4*	*54.4*	*25.5*	*79.9*
1,2,3,4,6,7,8-HpCDD	*13.4*	*62.0*	*75.4*	*57.8*	*22.6*	*80.4*
1,2,3,4,6,7,8,9-OCDD	*ND*	*50.8*	*50.8*	*48.2*	*25.8*	*74.0*
1,2,3,4,6,7,8,9-OCDF	*ND*	*36.0*	*36.0*	*45.7*	*26.9*	*72.6*

[a]*Results of a single determination.*
ND = Not detected.

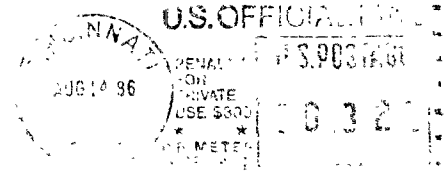
2. The use of stacked acidic/basic silica gel columns instead of multiple liquid-liquid partitioning in the extraction/cleanup procedures should be investigated. This would eliminate the problems of emulsion formation currently encountered and would also greatly reduce the quantities of corrosive wastes generated.
3. 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.
4. 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.
5. Because of the known elution overlap of some tetra-substituted isomers with penta-substituted isomers (and other potential overlaps between homologous groups), the multiple ion detection (MID) descriptors should be modified to include at least one ion for each overlapping homologue.
6. 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.
7. Kovats Indices should be determined for available PCDD's and PCDF's. This would aid laboratories in the identification of isomers not known or available to them and would be useful in a GC screening program.
8. The need to monitor for polychlorinated diphenyl ethers (PCDE's) in the final sample extract should be investigated.
9. A source of a well-defined GC performance standard should be identified. Column performance guidelines should be established for a variety of columns.
10. Sample reanalysis requirements given the presence of low and of very high levels of target analytes should be defined.

☆U.S.Government Printing Office: 1986 — 646-116/40618

J. M. Ballard, T. L. Vonnahme, N. J. Nunn, and D. R. Youngman are with Lockheed Engineering and Management Services Company, Inc., Las Vegas, NV 89114.
***Stephen Billets** is the EPA Project Officer (see below).*
The complete report, entitled "Performance of RCRA Method 8280 for the Analysis of Dibenzo-p-Dioxins and Dibenzofurans in Hazardous Waste Samples," (Order No. PB 86-193 679/AS; Cost: $11.95, 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 Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
P.O. Box 15027
Las Vegas, NV 89114

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268



Official Business
Penalty for Private Use $300
EPA/600/S4-86/021

0000329 PS

U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604