Bull. Environ. Contam. Toxicol. (1984) 33:153–162

Environmental Contamination and Toxicology

Dioxin Analysis in Stack Emissions and in the Wash Water Circuit During High-Temperature Incineration of Chlorine-Containing Industrial Wastes

K. S. Brenner,[1]* H. Mäder,[1] H. Steverle,[1] G. Heinrich,[2] and H. Womann[2]

[1]BASF AG, ZHU, E 210, Untersuchungs laboratorium, D-6700 Ludwigshafen, and
[2]BASF AG, DUR/R, Rückstandsverbrennung, D-6700 Ludwigshafen,
Federal Republic of Germany

During the last 5 years publications have dealt with the analytical procedures for the determination of dioxins, especially the most toxic type, namely 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). In parallel, many measurements have been reported on the formation of polychlorinated dioxins (PCDD's) during different combustion processes, such as the burning of wood or the incineration of urban waste. A few articles giving emission data and detailed working parameters have been published. The same holds for the description of the disposed wastes, especially their content of chlorine compounds. The cited literature (Hutzinger et al. 1980, Little 1981, Cattabeni et al. 1978, Kimbrough 1980, Bontoyan 1979, Frei et al. 1983, Choudhry and Hutzinger 1982) can only give a short review of these subjects.

This article reports on the performance of a high-temperature incinerator for the disposal of chlorine-containing industrial wastes. The technology used is outlined, and a detailed description of the analytical methodology critically selected from the literature and adapted to our problems is given. In two test runs under different working parameters, the emissions in the stack gases and the wash water circuit were monitored with regard to PCDD's in particular.

MATERIALS AND METHODS

The installed incinerator, which has now been working very satisfactorily for almost 5 years, was described in detail by Womann (1979). The essential parts of the incinerator are: the feeding equipment, a rotating slag tap furnace, a secondary combustion chamber, a waste heat boiler and the scrubbing units (see Fig. 1). The feeding equipment allows the dosage of both liquid and solid wastes. The rotary kiln with a length of 10 m and an outside diameter of 4.5 m has a clay brick lining, which is covered by an "annular fur" or protective slag layer. This slag layer is maintained by the addition of sand. The temperature of the kiln wall can be estimated via melting temperature measurements of slag droplets and it is normally 1000°C or above (measured by pyrometry). There are two burners in the front wall of the kiln.

*To whom correspondence should be addressed

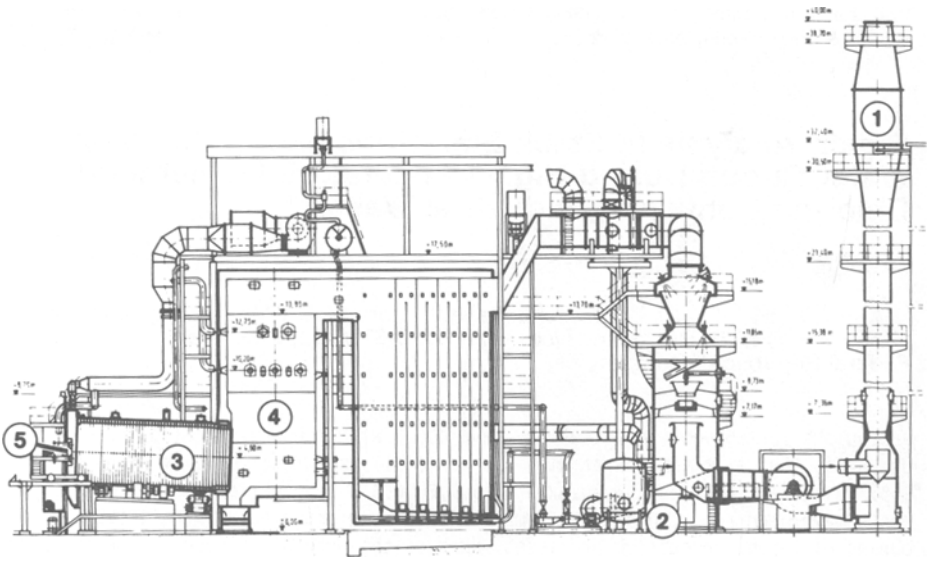


Fig. 1 Incinerator with rotating kiln (Womann 1979)

1 Stack, 23 m platform sampling site, 2 quench water sampling site, 3 kiln, 4 secondary combustion chamber, 5 burners in front wall of the kiln,

The kiln flue gases flow to a refractory-lined secondary combustion chamber, where they are completely burned. Four compressed-air atomizer burners combust liquid wastes in quantities to maintain preset temperatures of between 900 and 1400^{0}C.

The flue gases cool off to 250^{0}C in the waste heat boiler. It consists of a radiation chamber and nine flue passes, the design of which prevents ash baking. In two scrubber stages the flue gases are cooled from about 250^{0}C to 50-70^{0}C and HCl and SO_2 are scrubbed with NaOH/water. For details see Womann (1979).

The first experiment dealt with the sampling techniques and the analysis for the tetrachloro and octachloro-dioxins only, including the setup of the full analytical procedure. The second experiment was planned to confirm the preliminary results, to control the emissions for penta- to hepta-CDD's and to vary the conditions of incineration. We concentrated on the real "emmissions", namely the stack exhaust and wash water circuit. The stack exhaust was sampled at the 23 m platform of the chimney; the wash water was taken after sedimentation of the ashes (see sampling sites 1 and 2 in Fig. 1).

Three different techniques of gas sampling were used. The stack gases were taken from the center of the chimney via glass tubes connected directly to the samplers. Samples were taken during the entire test period of 1-2 hrs, so an average value was obtained and spike emissions would also have been monitored. Table 1 gives the sampling times and the gas volumes sampled.

a) Two large-volume impingers (volume 275 ml) were charged with 150 ml i-octane and connected in series. The resulting i-octane/water mixture was separated and prepared for the clean-up steps (Henschler, 1982). During the second experiment a large-volume ice-cooled water separator with an inlet jet (Fig. 2) was connected upstream of the impingers to separate most of the moisture from the flue gases.
b) The polyurethane foam plugs (TDI soft foam) were preextracted with water, acetone and n-hexane for 3 hrs under reflux (for general information see Moody and Thomas, 1982; Turner and Glotfelty 1977; Oehme and Stray 1982). Two of these extracted vacuum dried plugs (50 mm in length, 40 mm in diameter) were introduced in special sampling tubes (see Fig. 2c) tight enough to force the flue-gases homogeneously through the plugs. During the second test series a special ice-cooled water separator (see Fig. 2b) was also placed before the PU foam adsorber to maintain its good adsorptive characteristics by keeping off most of the moisture.
c) The charcoal absorbers were used only in the first experiment. This technique was abandoned because of interference from condensed moisture.

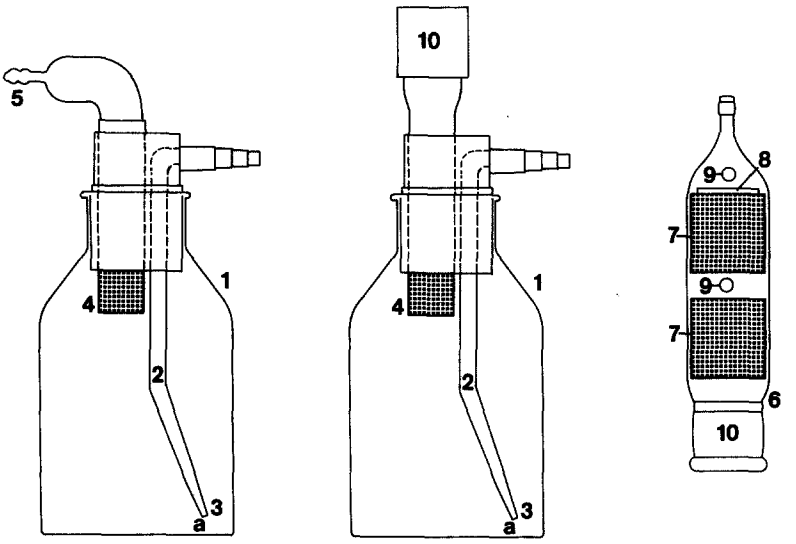
Table 1. Sampling times and gas volumes sampled

Experiment 1		
Sampler	sampling time [min.]	gas volume sampled [L] **
Impingers A_1, A_2*	352	4990
Impingers B_1, B_2*	348	4930
PU foam	345	4290
Charcoal absorber	346	4170

* Solvent losses due to evaporation were replaced at 30-min. intervals.
** Standard conditions

Experiments 2a and 2b		
Sampler	sampling time [min.]	gas volume sampled [L] *
2a) Impingers A_1, A_2	173	2140
Impingers B_1, B_2	173	1200
PU foam	173	1830
2b) Impingers A_1, A_2	175	1210
Impingers B_1, B_2	175	1210
PU foam	175	1950

* Standard conditions



2a 2b 2c

Fig. 2a-c
Water separator for combination with impinger (a) and PU foam absorber inlet (b); PU foam sampling tube (c)

Legend:
1 1 l wide-neck bottle (neck: 60 mm in diameter, height: 200 mm, width: 105 mm), 2 Inlet tube, glass, 10 mm outside diameter, 3 Jet bore about 1.5 mm in diameter; distance a to bottom edge about 10 mm, 4 G 0 glass frit, 20 mm in diameter, exit tube 25 mm in diameter, 5 Exit, to connect impinger, 6 Sampling tube, 7 PU foam plugs, 50 mm in length, 40 mm in diameter, 8 Glass frit disk, 9 Glass points, to hold PU plugs in position, 10 Male and female glass joints, to connect PU foam sampling tube (c) to separator (b)

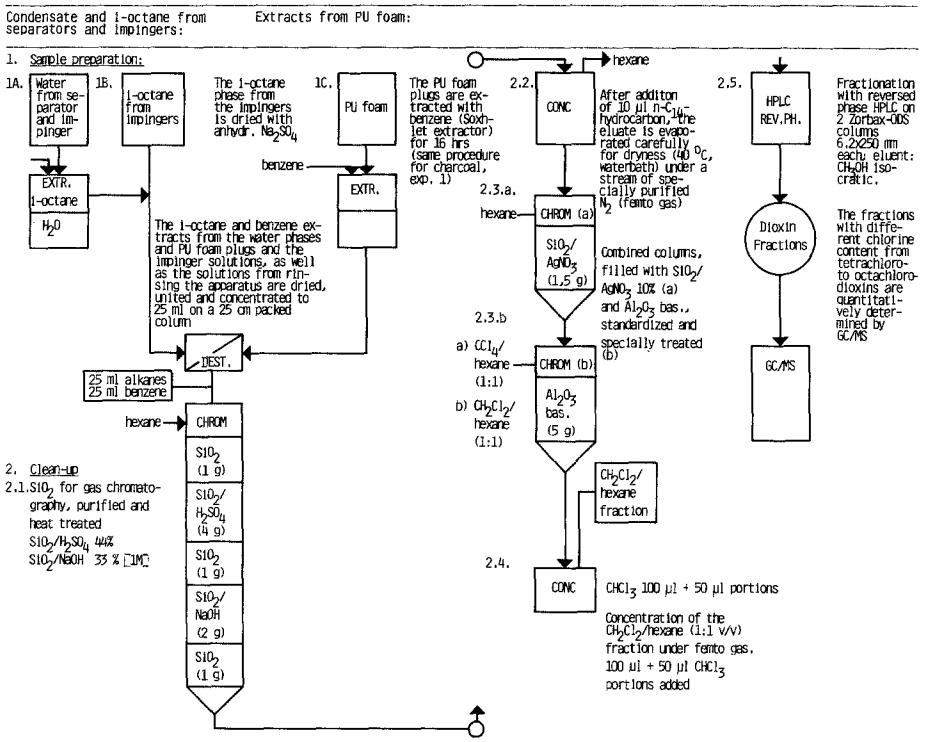
The wash water was sampled after sedimentation of the (small amounts) of sludge at sampling point 2. 1 l samples were taken every hour during the incineration time tested and were kept in glass-stoppered glass bottles.

The impinger solutions were separated into i-octane and water portions. The latter and the water from the water separators were extracted twice with i-octane. The unified i-octane solutions from each absorption chain (absorber solutions, water extracts and i-octane from rinsing the absorbers and separators) were dried with anhydrous sodium sulfate and carefully evaporated on a 25 cm packed column. The concentrate was introduced into the clean-up procedure.
The PU foam plugs were dried over KOH pellets under vacuum for 2 days to constant weight. The dry plugs were extracted in a Soxhlet extractor with benzene for about

16 hrs. During extraction the plugs were squeezed with a glass rod every 30 minutes. These extracts were united with the extracts from the separated water and, after solvent evaporation, the residue went through the clean-up procedure. The charcoal was dried under vacuum for about 2 days and extracted with benzene in a Soxhlet extractor. The procedure was similar to that for the PU foam plugs.

From the many clean-up procedures published we selected the work of Lamparski and Nestrick (1980; Lamparski et al. 1979, Fig. 3).

Fig. 3: Sample preparation and clean-up of water condensates, i-octane solutions from impingers and benzene extracts from PU foam and charcoal. For details see Lamparski and Nestrick (1980)



The adsorbents and pure gases (femto gas) were prepared and standardized according to Lamparski and Nestrick using 2,3,7,8-TCDD as elution standard. Sample preparation and clean-up procedures were controlled by the addition of isotopic pure $^{13}C_{12}$-2,3,7,8-TCDD and the other corresponding PCDD's (purchased from KOR Incorporated, Cambridge, MA, USA).

The sample preparation and clean-up procedures of Lamparski and Nestrick (1980) were modified to meet our requirements. In all 3 experiments sampling and analysis were carried out in duplicate. The detection limits in the 1 ppt range and the recovery rates were checked by internal and external standards using the acknowledged method (Lamparski and Nestrick 1980; Hutzinger et al. 1980).

The slag residues (2.6%) and the small amount of ash slurry were not analysed, because the slag melt undergoes temperatures of about 1100°C and it is therefore not expected to contain dioxins. The ashes (0.7%) pass through temperature zones of 1000°C to 1200°C before being washed out; thus adsorption of dioxins seems unlikely [Karasek and Viau (1983) did not find TCDD's in the fly ashes of an incinerator working at about 1040 ± 25°C].

A 30 m DB 5 fused silica column (0.26 mm i. diam., polarity similar to SE 54 silicon rubber) was mounted in the gas chromatograph of a Finnigan 4010 quadrupole spectrometer. The end piece of the column was connected directly to the ion source. The gas chromatograph was equipped with inlet splitter, septum flush and low volume injector. Operating conditions were: Injector: 270°C; column temperature: 100°C isoth., 3 min; temperature program: 100-180°C, 20°/min, 180-300°C, 4°/min; GC-MS interface temperature: 250°C; carrier gas: ~1 ml He/min; split ratio: 1:35 (30 ml/min split, 5 ml/min septum flush). Immediately before injection the temperature program was started while splitter and septum flush were closed. One minute later splitter and septum flush were opened again.
For mass specific detection and determination of the PCDD's, the spectrometer was run in MID mode, thus simultaneously monitoring the most characteristic and intense M^+-ions listed in table 2. After clean-up as described above, the quantitative determinations were carried out with internal and external calibration for 2,3,7,8-TCDD and with external calibration for the other PCDD compounds, using techniques published (Millard 1978).

The external calibration graph (peak areas vs. mass injected) for the GC/MS measurement was linear in the range of 5 to 500 pg/injection (peak areas from 200 to 2.5 x 10^4 units).

Table 2. Relative masses used for identification and quantitative determination

Compound	rel. masses monitored m/e
2,3,7,8-TCDD	320, 322
^{13}C-2,3,7,8-TCDD	332, 334
PCDD's	354, 356, 358
HCDD's	388, 390, 392
H_7CDD's	422, 424
OCDD	458, 460

Tables 3 and 4 give the technical parameters for the incinerator and the characteristic values for the incinerated wastes. During experiment 1a chlorine-containing waste (9% Cl) was incinerated, without any additional burning of chlorine-free residues. Experiment 2a was a blank run, feeding alcohols and aldehydes with a boiling point of >150°C only.
During experiment 2b the same type of distillation sump as in experiment 1, with 9% chlorine, was incinerated simultaneously with chlorine-free waste (ratio about 1:1.5), thus lowering the total chlorine feed to the kiln to an average of 3.5%. The chlorine-free waste was taken from the same batch as in experiment 2a and was fed into two burners in the kiln, thus giving a preheating effect. The chlorine-containing waste was fed into two burners in the secondary combustion chamber.

Table 3. Technical Parameters during Experiments 1 and 2

	kiln temp.	residence time[1] of gases	throughput kg/h	chlorine %	wash water circuit m^3/h, fresh throughput	Stack gases, mg/Nm^3 HCl	CO	O_2
Exp. 1	about 1000°C	3-7 sec	2800	9	200	8	5	14.5
Exp. 2a	" 1000°C	7	2860[2]	0	200	0	8	14.5
Exp. 2b	" 1000°C	7	1700[3]	0	200	5	5	14.5
		3	1100[3]	9				

1) 2 burners in kiln (7 sec), 2 burners in secondary combustion chamber (3 sec)

2) blank experiment, chlorine-free waste, 3) waste from experiment 2a was burned in the kiln during incineration of the chlorine-containing waste in the secondary combustion chamber

Table 4. Incinerated Wastes

	C %	Cl %	type of wastes
Exp. 1	60	9	Distillation sump from chlorinated phenols and cresols
Exp. 2a	53	0	Mixture of alcohols and aldehydes with a boiling point > 150°C
Exp. 2b	60	9	Distillation sump from chlorinated phenols and cresols

RESULTS AND DISCUSSION

The analytical results for the stack emissions and wash water samples are listed in Tables 5 and 6. A detection limit of < 1 ng/m^3 and < 1 ng/kg respectively could be verified. Only in a few cases the detection limit of the GC/MS measurement was somewhat higher at 2 to 6 ng/m^3, caused by interferences (contamination ?) from the multistep analytical process (see Fig. 3). The recovery rates could be improved in the second experiment to values of between 20% and 60%, depending on the analytical technique used. Nevertheless the low recovery rates of 5% to 10% have a minor influence on the confidence interval of the results, because the full analytical process was controlled by internal and external standards. We found no positive results for the homolog series from TCDD's to OCDD during experiments 1 and 2 at the ppt range (ng/m^3 and ng/kg) with the 3 different types of sampling used.

Table 5. Experiment 1, Analytical Results

Sample	recovery (TCDD) %	TCDD's[1], detection limits	OCDD[2], detection limits
Stack emission	10-30	< 1 ng/m^3	< 1 ng/m^3
Wash water	5-10	< 2 ng/kg	< 0.2 ng/kg

1) Recovery rate controlled with $^{13}C_{12}$-2,3,7,8-TCDD

2) Calculated with 80% recovery; this recovery rate was determined in earlier experiments by external calibration

The incinerator described performed according to the preset conditions (see Table 3) and did not show any significant deviation of the stack gas values during the test series. During two runs (experiments 1 and 2b) a waste with 9% chlorine content was incinerated separately (exp. 1) and together with a chlorine-free waste, thus lowering the average chlorine feed to the kiln to 3.5% (exp. 2b). A blank run (exp. 2a) was done with the same batch of chlorine-free material used in experiment 2b. Three different sampling techniques were used to assure that sampling of the PCDD's was essential. For experiments 2a and 2b the sampling procedures were improved by using specially constructed water separators, working according to the impinger-jet principle. By separating most of the moisture (about 90% rel. humidity at 50°C in the stack) the porosity and good extractive characteristics of the PU foam and the performance of the impingers could be maintained during the full sampling period and the losses of solvent in the impingers were negligible. Minor amounts of moisture do not affect the good adsorption quality of PU foam for chlorinated hydrocarbons (Moody and Thomas 1982).

Table 6. Experiment 2a, 2b, Analytical Results

Sample	recovery %	2,3,7,8-TCDD[1] internal standard	2,3,7,8-TCDD[1] external standard	PCDD[2]	HCDD[2]	H_7CDD[2]	OCDD[3]
Experiment 2a							
Stack emission							
Impinger absorption		ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³
Determination A	37	<1	<1	<1	<1	<1	(2.3)[4]
Determination B	48	<6	<6	<1	<2	<1	<1
PU foam absorption	32	<1	<1	<1	<1	<1	<1
Wash water		ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
Determination A	43	<1	<1	<1	<1	<1	<1
Determination B	60	<1	<1	<1	<1	<1	<1
Experiment 2b							
Stack emission							
Impinger absorption		ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³
Determination A	34	<1	<1	<1	<2	<2	<1
Determination B	26	<1	<1	<1	<1	<1	<2
PU foam absorption	20	<1	<1	<1	<1	<1	<1
Wash water		ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
Determination A	53	<1	<1	<1	<1	<1	<1
Determination B	46	<1	<1	<1	<1	<1	<1

[1] Recovery determined by $^{13}C_{12}$-2.3.7.8-TCDD.
No other TCDD's detectable. This was controlled by a standard mixture containing all the 22 TCDD isomers.

[2] Calculated with 50% recovery.
External standards: 1,2,3,7,8-penta-CDD (for PCDD), 1,2,3,4,7,8-hexa-CDD (for HCDD), 1,2,3,4,6,7,8-hepta-CDD (for H_7CDD). No peaks observable in a retention time window of ± 4 min.

[3] Calculated with 80% recovery; this recovery rate was determined in earlier experiments by external calibration.

[4] See text

Experiment 1 was a preliminary test which gave data on the stack and wash water emissions for tetra- and octachlorodibenzo-dioxins and served to test our sampling techniques and analytical procedures. The low recovery rates of 5 to 10%, due to the very difficult standardization of the complicated clean-up procedure could be improved, although it only somewhat affects the reproducibility (Ryan et al., 1983). No TCDD's or OCDD could be detected in the stack emissions and wash water circuit. The blank experiment 2a proved the validity of the experimental set up and the established detection limit of about 1 ppt. During experiment 2b, a modification of experiment 1, chlorine-containing and chlorine-free wastes were incinerated simultaneously, feeding the chlorine-free waste to the burners in the kiln, thus creating a preheating effect. In this run the emissions were tested for the homologs from tetrachloro- to octachlorodioxins.

Again no 2,3,7,8-TCDD or other TCDD's, PCDD's, H_6CDD's, H_7CDD's and OCDD were detected at the detection limit of 1 ppt (ng/m^3 or ng/kg) in the stack and wash water circuit. The incineration of wastes containing 9% chlorine without or with additional firing of chlorine-free material in a rotary kiln at 1000°C with a residence time of the gases ranging from 3 to 7 seconds did not cause emissions of chlorinated dioxins. This means that even at temperatures of 1000°C a 3-second residence time of the combustion gases together with the preheating and diluting effect of the chlorine-free waste is enough for dioxin-free incineration. Comparing the EPA claims (des Rosiers, 1983) of 2 sec dwell time at 1200°C or 1.5 sec dwell time at 1500°C with the conditions described above we feel that the kiln temperatures can be lowered to 1000°C if a dwell time of 3 sec and effective spraying of the waste are guaranteed (see also Karasek and Viau, 1983). In our opinion incineration under suitable conditions like those described above is a practical and acknowledged technique for the disposal of chlorine-containing wastes, as other processes (des Rosiers, 1983) have not yet been approved or installed.

REFERENCES

Bontoyan, WR (ed 1979)
CIPAC Proceedings 1; Symposium Papers
Collaborative International Pesticides Analytical Council Publications, 1979

Cattabeni F, Cavallaro A, Galli G (1978)
Dioxin
Toxicological and Chemical Aspects
SP Medical and Scientific Books

Choudhry GG, Hutzinger O (1982)
Part I-VI; Mechanistic aspects of the thermal formation of halogenated organic compounds including polychlorinated dibenzo-p-dioxins
Toxicol Environ Chem 5 : 1 ff

Henschler D (ed 1982)
Analyt. Methoden zur Prüfung gesundheitsschädlicher Arbeitsstoffe
Bd. 1, Luftanalysen
Verlag Chemie, Weinheim

Hutzinger O, Frei RW, Merian E, Pocchiari F (editors 1982)
Chlorinated Dioxins and Related Compounds; Impact on the Environment;
Pergamon Press
Proceedings of a Workshop held in Rome, Italy, 22-24 Oct. 1980

Hutzinger O, Frei RW, Merian E, Reggiani G (ed 1983)
Proceedings of the 3rd. International Symposium on Chlorinated Dioxins and Related Compounds;

Salzburg, October, 12.-14. 1982
Chemosphere 12 (4/5) : 425-790
Pergamon Press, Oxford

Karasek FW, Viau AC (1983)
Gas chromatographic-mass spectrometric analysis of polychlorinated dibenzo-p-dioxins and organic compounds in high-temperature fly ash from municipal waste incineration.
J Chromatogr 265 : 79-88

Kimbrough RD (ed 1980)
Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products
Elsevier/North-Holland Biomedical Press.

Lamparski LL, Nestrick TJ (1980)
Determination of tetra-, hexa-, hepta- and octachlorodibenzo-p-dioxin isomers in particulate samples at parts per trillion levels.
Anal Chem 52 : 2045-2054

Lamparski LL, Nestrick TJ, Stehl RH (1979)
Determination of part-per-trillion concentrations of 2,3,7,8-tetrachlorodibenzo-p-dioxin in fish.
Anal Chem 51 : 1453-1458

Little AD, Inc. (1981)
Dioxin from Combustion Sources, Study on State-of-the-Art
The American Society of Mechanical Engineers

Millard BJ (1978)
Quantitative Mass Spectrometry,
Heyden & Son, London, Philadelphia, Rheine

Moody GJ, Thomas JDR (1982)
Chromatographic Separation and Extraction with Foamed Plastics and Rubbers
Chromatographic Science Series, Vol 21
Marcel Decker, Inc., New York; Basel

Oehme M, Stray H (1982)
Quantitative determination of ultra-traces of chlorinated compounds in high-volume air samples from the arctic using polyurethane foam as collection medium.
Fresenius Z Anal Chem 311 : 665-673

Des Rosiers PE (1983)
Remedial measures and disposal practices for wastes containing dioxins and furans.
Chemosphere 12 : 727-744

Ryan JJ, Pilon JC, Conacher HBS, Firestone D (1983)
Interlaboratory study on determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin in fish.
J Assoc Off Anal Chem 66 : 700-707

Turner BC, Glotfelty (1977)
Field air sampling of pesticide vapors with polyurethane foam.
Anal Chem 49 : 7-10

Womann H (1979)
Neue Rückstandsverbrennungsanlage mit nasschemischer Rauchgasreinigung.
Chemie-Technik 8 : 487-492

Received November 15, 1983; Accepted November 25, 1983