GENERAL ELECTRIC
GENERAL ELECTRIC COMPANY
FAIRFIELD, CONNECTICUT 06431

STEPHEN B HAMILTON, JR
MANAGER - ENVIRONMENTAL SCIENCE AND TECHNOLOGY

(203) 373-3316

July 2, 1985

Dr. J. G. Wirth
General Manager
Plastics Technology Department
1 Plastics Avenue
Pittsfield, MA 01201

Dear Joe:

As you can see from the attached, I have been asked to comment on EPA's draft of proposed controls on the inadvertent manufacture of halogenated dibenzofurans and dioxins as contaminants during the manufacture of other chemicals. I was requested to review this because EPA is aware of the development work done at CRD on quantitative analytical techniques for chlorinated dibenzofuran congeners.

I am enclosing a copy of the questions on which EPA requests advice, the proposed listing, the guidelines for sampling and the quality assurance plan. I have sent the guidelines for the analytical testing to CRD for their comments.

I would appreciate your comments on how important an issue this is to PBG and any other comments you consider relevant.

Please note the request that comments be sent to EPA by July 19, 1985 in order to be used in the proposal.

Sincerely,

S. B. Hamilton

SBH:ls

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GENP 010500

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

RECEIVED
JUN 24 1985
S. B. HAMILTON

Dr. Steve Hamilton
General Electric Corporation W-1B2
3135 Easton Turnpike
Fairfield, Connecticut 06431

Dear Dr. Hamilton:

The Environmental Defense Fund (EDF) and the National Wildlife Federation (NWF) petitioned the Environmental Protection Agency (EPA) under Section 21 of the Toxic Substances Control Act (TSCA) to immediately impose controls on the inadvertent manufacture of dibenzofurans and dioxins as contaminants during the manufacture of other chemicals. EPA, in its response to the petition, agreed to initiate an administrative proceeding to determine whether additional regulatory action was warranted. EDF/NWF have subsequently filed suit challenging EPA's decision to initiate an administrative proceeding in lieu of immediately issuing controls on the inadvertent manufacture of dibenzofurans and dioxins.

The Office of Pesticides and Toxic Substances (OPTS), in co-operation with the Office of Solid Waste and Emergency Response, has developed a list of chemicals which, based primarily on theoretical assessments, may have the potential to produce chlorinated and/or brominated dibenzofurans and dioxins as contaminants. OPTS intends to require analysis of the chemicals on the list (1) which are prioritized as 1, 2 or 3, and (2) with routes of contamination shown as S or FS, (and F in those cases where the feedstock is not listed), and (3) which show uses other than as a pesticide only. The analysis will be used to determine whether dioxins and dibenzofurans are present, at what levels, and under what process conditions dioxins and furans are formed in these chemicals.

Mike Dellarco, Program Manager for Environmental Monitoring Systems Division, Research and Development, and Dr. Don Barnes, Senior Science Advisor to the Assistant Administrator for

Pesticides and Toxic Substances, suggested that we ask you to review the preliminary list of chemicals to be tested, the rationale for selection of chemicals to be tested and the preliminary analytical guidelines for testing. We have included a copy of the list, a detailed description of how it was compiled, and a preliminary copy of the analytical guidelines, along with a copy of the preliminary sampling plan and QA plan. To help direct your review, we have attached a page of questions and issues we have identified thus far. We would very much appreciate any comments you can give us on these issues, and on any problems you see that we may have missed. We are soliciting these comments prior to proposing the rule, so that we need your comments by July 19, 1985, to use them in the proposal. I have enclosed a postage-paid, self-addressed envelope for your use in sending us your comments.

Let me thank you in advance for your time in responding to this request.

Sincerely,

Suzanne Rudzinski

Suzanne Rudzinski, Chief
Chemical Regulation Branch

Enclosures

cc: Don Barnes
Mike Dellarco

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GENP 010511

Questions/Issues on the Dioxin/Furan List and Methodology

1. Is the rationale for developing the list of chemicals to be tested a reasonable one? What problems, if any, do you see with it?

2. Are there other candidate chemicals that fit the rationale but are not on the list? If so, what are they?

3. What types of problems are there with the scheme of providing only a skeleton of the analytical method and relying on industry to fill in the gaps?

   - Can they develop analytical standards? How easily?
   - Can they do the appropriate cleanup? How easily?
   - Will we be able to get reliable data and compare results?
   - If the answer to any of the above is no, what more do we need to provide?

4. Is 1 part per billion a practicable limit of detection using this method? If not, why? What limit is more appropriate? Why?

5. Are there laboratories available to perform these tests? If so, please provide a qualitative sense of how many.

6. Is the sampling plan and the Quality Assurance plan adequate? If not, what needs to be added?

7. Are any available methodologies not addressed? If so, please identify them and their strengths and weaknesses.

8. Do you know of any available biological testing systems which could serve as a screen for the chemicals to be tested? If so, please identify them and provide information you may have concerning sensitivity of the test and the rate of false positives/false negatives found.

Table 1. Summary of Current Commercial Status and Use

PRIORITY	CAS NUMBER	CHEMICAL NAME	CURRENT COMMERCIAL STATUS PROD	CURRENT COMMERCIAL STATUS IMPT	USE PEST ONLY	USE PEST INTM	CR
1	58-89-9	1,2,3,4,5,6-Hexachlorocyclohexane, gamma isomer	n	y	n	n	F
1	70-30-4	2,2'-Methylenebis(3,4,6-trichlorophenol)	y	n	n	n	FS
1	87-86-5	Pentachlorophenol and salts	y	y	y	n	S
1	93-72-1	2,4,5-Trichlorophenoxypropanoic acid, all esters & salts	n	n	y	n	FS
1	93-76-5	2,4,5-Trichlorophenoxyacetic acid, all esters & salts	n	n	y	n	FS
1	94-75-7	(2,4-Dichlorophenoxy)acetic acid, all salts & esters	y	y	y	n	FS
1	94-82-6	2,4-Dichlorophenoxybutyric acid, all salts & esters	y	y	y	n	FS
1	95-77-2	3,4-Dichlorophenol	y	n	n	n	S
1	95-95-4	2,4,5-Trichlorophenol	n	n	n	y	I
1	118-74-1	Hexachlorobenzene	n	n	n	n	I
1	120-36-5	2-[2,4-(Dichlorophenoxy)]-propionic acid, all salts & esters	y	y	y	n	S
1	120-83-2	2,4-Dichlorophenol	y	y	n	y	S
1	131-52-2	Sodium pentachlorophenate	y	n	y	n	FS
1	136-25-4	2,2-Dichloropropanoic acid, 2-(2,4,5-trichlorophenoxy)-ethyl ester	n	n	y	n	FS
1	136-78-7	2-(2,4-Dichlorophenoxyethyl sulfate), sodium salt	n	n	y	n	FS
1	299-84-3	Phosphorothioic acid, O,O,-dimethyl O-(2,4,5-trichlorophenyl) ester	n	n	y	n	FS

GENP 010513

Table 1. Summary of Current Commercial Status and Use

PRIORITY	CAS NUMBER	CHEMICAL NAME	CURRENT COMMERCIAL STATUS		USE		
			PROD	IMPT	PEST ONLY	PEST INTM	CR
1	576-24-9	2,3-Dichlorophenol	y	n	n	n	S
1	583-78-8	2,5-Dichlorophenol	y	n	n	y	S
1	25167-83-3	2,3,4,6-Tetrachlorophenol	n	n	y	n	S
2a	--	Tetrabromobisphenol-A diacrylate (V)	y	n	n	n	S
2a	--	Tetrabromobisphenol-B	n	n	n	n	S
2a	79-94-7	Tetrabromobisphenol-A	y	y	n	n	S
2a	79-95-8	Tetrachlorobisphenol-A	n	n	n	n	S
2a	87-10-5	3,4,5-Tribromosalicylanilide	n	n	n	n	FS
2a	87-65-0	2,6-Dichlorophenol	y	n	n	y	S
2a	95-94-3	1,2,4,5-Tetrachlorobenzene	y	y	n	y	I
2a	99-28-5	2,6-Dibromo-4-nitrophenol	n	n	n	n	FS
2a	118-79-6	2,4,6-Tribromophenol	y	n	n	n	FS
2a	344-07-0	Chloropentafluorobenzene	n	n	n	n	I
2a	392-56-3	Hexafluorobenzene	n	n	n	n	I
2a	488-47-1	Tetrabromocatechol (V)	n	n	n	n	S
2a	608-71-9	Pentabromophenol	y	n	n	n	FS
2a	615-58-7	2,4-Dibromophenol	y	n	n	n	FS
2a	632-79-1	Tetrabromophthalic anhydride	y	n	n	n	P
2a	771-60-8	Pentafluoroaniline	n	n	n	n	I
2a	1689-84-5	3,5-Dibromo-4-hydroxybenzonitrile	y	y	n	y	F
2a	2577-72-2	3,5-Dibromosalicylanilide	n	n	n	n	FS

GENP 010514

Table 1. Summary of Current Commercial Status and Use

PRIORITY	CAS NUMBER	CHEMICAL NAME	CURRENT COMMERCIAL STATUS PROD	CURRENT COMMERCIAL STATUS IMPT	USE PEST ONLY	USE PEST INTM	CR
2a	21850-44-2	Tetrabromobisphenol-A-bis-2,3-dibromopropylether (V)	y	n	n	n	S
2a	25327-89-3	Allyl ether of tetrabromobisphenol-A	n	y	n	n	S
2a	37853-61-5	Bismethylether of tetrabromobisphenol-A	n	n	n	n	S
2a	55553-62-3	Tetrabromobisphenol-A-bis-ethoxylate (V)	y	n	n	n	S
2b	1163-19-5	Decabromophenoxybenzene	y	y	n	n	S
2b	32534-81-9	Pentabromodiphenyloxide	y	y	n	n	S
2b	32536-52-0	Octabromodiphenyloxide	y	n	n	n	S
2b	42576-02-3	Methyl-5-(2,4-dichlorophenoxy)-2-nitrobenzoate	y	n	y	n	F
2b	42874-03-3	2-Chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene	n	n	y	n	I
2c	--	ALKYLAMINE TETRACHLOROPHENATE	N	N	--	--	FS
2c	--	2-Chloro-1,4-diethoxy-5-nitrobenzene	n	n	--	--	F
2c	82-68-8	Pentachloronitrobenzene	n	n	y	n	I
2c	88-06-2	2,4,6-Trichlorophenol	n	n	y	n	S
2c	92-04-6	2-Chloro-4-phenylphenol (V)	n	n	n	y	P
2c	95-88-5	4-Chlororesorcinol	y	y	n	n	P
2c	97-17-6	O-(2,4-Dichlorophenyl) O,O-di-ethylphosphorothioate	n	n	y	n	F
2c	97-50-7	5-Chloro-2,4-dimethoxyaniline	y	n	n	n	P
2c	116-29-0	4-Chlorophenyl-2,4,5-trichlorophenyl sulfone	n	n	y	n	P

GENP 010515

Table 1. Summary of Current Commercial Status and Use

PRIORITY	CAS NUMBER	CHEMICAL NAME	CURRENT COMMERCIAL STATUS PROD	CURRENT COMMERCIAL STATUS IMPT	USE PEST ONLY	USE PEST INTM	CR
2c	299-85-4	O-(2,4-Dichlorophenyl)-O-methylisopropylphosphoramidothioate	n	n	y	n	F
2c	320-72-9	3,5-Dichlorosalicyclic acid	n	n	--	--	S
2c	470-90-6	2-Chloro-1-(2,4-dichlorophenyl) vinyl diethyl phosphate	n	y	y	n	F
2c	500-28-7	O-(3-Chloro-4-nitrophenyl)-O,O-dimethylphosphorothioate	n	n	y	n	F
2c	615-67-8	Chlorohydroquinone	n	n	n	n	P
2c	933-75-5	2,3,6-Trichlorophenol	n	n	n	n	S
2c	961-11-5	2-Chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate	y	n	y	n	F
2c	1757-18-2	O-(2-Chloro-1-(2,5-dichlorophenyl)vinyl) O,O-diethyl phosphorothioate	n	n	y	n	F
2c	1836-75-5	2,4-Dichlorophenyl-p-nitrophenyl ether	n	n	y	n	F
2c	1940-42-7	4-Bromo-2,5-dichlorophenol	n	n	n	y	FS
2c	1982-47-4	3-(4-(4-Chlorophenoxy) phenyl)-1,1-dimethylurea	n	n	y	n	P
2c	2104-96-3	O-(4-Bromb-2,5-dichlorophenyl) O,O-dimethyl phosphorothioate	n	n	y	n	F
2c	2300-66-5	3,6-Dichloro-o-anisic acid, dimethylamine salt (V)	y	n	y	n	FS
2c	2463-84-5	O-(2-Chloro-4-nitrophenyl) O,O-dimethylphosphorothioate	n	n	y	n	F
2c	2675-77-6	1,4-Dichloro-2,5-dimethoxybenzene	y	n	y	n	P

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GENP 010516

Table 1. Summary of Current Commercial Status and Use

PRIORITY	CAS NUMBER	CHEMICAL NAME	CURRENT COMMERCIAL STATUS		USE		
			PROD	IMPT	PEST ONLY	PEST INTM	CR
2c	3380-34-5	5-Chloro-2-(2,4-dichlorophenoxy)phenol	y	n	n	n	FS
2c	3772-94-9	Pentachlorophenyl laurate	n	n	n	n	FS
2c	5736-15-2	2,2'-Methylenebis(3,4,6-trichlorophenol), monosodium salt	n	n	y	n	FS
2c	19666-30-9	2-tert-Butyl-4-(2,4-dichloro-5-isopropoxyphenyl) delta-1,3,4-oxadiazolin-5-one	n	y	y	n	I
2c	37853-59-1	1,2-Bis(tribromophenoxy)-ethane	y	n	n	n	FS
2c	41198-08-7	O-(4-Bromo-2-chlorophenyl) O-ethyl S-propyl phosphorothioate	n	y	y	n	F
2c	43121-43-3	1-(4-Chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone	n	y	y	n	P
--	21923-23-9	Chlorthiophos	n	n	y	n	—
3	--	3-Chloro-4-fluoronitrobenzene	y	n	n	n	I
3	--	2-Chloro-4-fluorophenol	n	n	--	--	F
3	--	3-Chloro-4-fluorophenol	n	n	--	--	F
3	—	N-2-Chloro-4-trifluoromethyl phenyl-DL-valine(+)-cyano-(3-phenoxyphenyl)methyl ester	y	n	y	n	I
3	Class	Phthalocyanine dyes and pigments	y	y	n	n	I
3	50-31-7	2,3,6-Trichlorobenzoic acid	n	n	n	y	I
3	56-23-5	Carbon tetrachloride	y	y	n	n	I
3	75-01-4	Vinyl chloride	y	y	n	n	—
3	76-13-1	1,1,2-Trichloro-1,2,2-trifluoroethane	y	n	n	n	I
3	78-88-6	2,3-Dichloropropene	y	n	n	y	I

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ENP 010517

Table 1. Summary of Current Commercial Status and Use

PRIORITY	CAS NUMBER	CHEMICAL NAME	CURRENT COMMERCIAL STATUS		USE		
			PROD	IMPT	PEST ONLY	PEST INTM	CR
3	79-00-5	1,1,2-Trichloroethane	y	n	n	n	I
3	79-01-6	1,1,2-Trichloroethylene	y	y	n	y	I
3	79-27-6	1,1,2,2-Tetrabromoethane	y	n	n	n	—
3	79-28-7	1,1,2,2-Tetrabromoethylene	y	n	n	n	I
3	79-34-5	Tetrachloroethane	n	y	n	n	I
3	85-22-3	Pentabromoethylbenzene	y	n	n	n	I
3	87-61-6	1,2,3-Trichlorobenzene (V)	y	y	n	n	I
3	87-68-3	Hexachlorobutadiene	n	n	n	n	I
3	87-83-2	Pentabromotoluene	y	n	n	n	I
3	87-84-3	Pentabromochlorocyclohexane	y	n	n	n	P
3	89-61-2	1,4-Dichloro-2-nitrobenzene	y	n	n	n	I
3	89-64-5	4-Chloro-2-nitrophenol	n	y	n	n	P
3	89-69-0	2,4,5-Trichloronitrobenzene	n	n	—	—	I
3	91-08-7	Toluene-2,6-diisocyanate	y	y	n	n	—
3	93-65-2	2-(4-Chloro-2-methylphenoxy) propionic acid	y	y	n	y	F
3	94-74-6	4-Chloro-o-toloxy acetic acid	y	y	n	y	P
3	94-81-5	4-(2-Methyl-4-chlorophenoxy) butyric acid	n	n	n	y	P
3	95-50-1	o-Dichlorobenzene	y	y	n	y	I
3	95-56-7	o-Bromophenol	y	n	n	n	P
3	95-57-8	o-Chlorophenol	n	y	n	y	P
3	95-76-1	3,4-Dichloroaniline	y	y	n	y	I
3	96-18-4	1,2,3-Trichloropropane	y	n	n	n	I
3	96-19-5	1,2,3-Trichloro-1-propene	y	n	n	n	I

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CFNP 010518

Table 1. Summary of Current Commercial Status and Use

PRIORITY	CAS NUMBER	CHEMICAL NAME	CURRENT COMMERCIAL STATUS PROD	CURRENT COMMERCIAL STATUS IMPT	USE PEST ONLY	USE PEST INTM	CR
3	97-23-4	2,2'-Methylenebis(4-chlorophenol)	y	y	n	n	I
3	99-30-9	2,6-Dichloro-4-nitroaniline	y	y	n	n	P
3	99-54-7	1,2-Dichloro-4-nitrobenzene	y	y	n	y	I
3	102-36-3	3,4-Dichlorophenylisocyanate	y	n	n	y	I
3	106-37-6	p-Dibromobenzene	y	y	n	n	I
3	106-46-7	p-Dichlorobenzene	y	n	n	y	I
3	107-05-1	3-Chloropropene	y	n	n	y	I
3	107-06-2	1,2-Dichloroethane	y	y	n	y	—
3	108-70-3	1,3,5-Trichlorobenzene (V)	y	y	n	n	I
3	108-90-7	Chlorobenzene	y	n	n	y	I
3	117-08-8	Tetrachlorophthalic anhydride	y	n	n	n	I
3	117-18-0	1,2,4,5-Tetrachloro-3-nitrobenzene	y	n	n	n	I
3	117-80-6	2,3-Dichloro-1,4-naphthalenedione	n	y	y	n	P
3	118-75-2	2,3,5,6-Tetrachloro-2,5-cyclohexadiene-1,4-dione	n	y	n	n	S
3	120-82-1	1,2,4-Trichlorobenzene	y	y	n	y	I
3	127-18-4	1,1,2,2-Tetrachloroethylene	y	y	n	n	I
3	147-82-0	2,4,6-Tribromoaniline (V)	y	n	n	n	I
3	320-60-5	2,4-Dichlorobenzotrifluoride	y	y	n	y	I
3	328-84-7	3,4-Dichlorobenzotrifluoride	n	y	n	y	I
3	330-54-1	3-(3,4-Dichlorophenyl)-1,1-dimethylurea	y	y	y	n	I

Table 1. Summary of Current Commercial Status and Use

PRIORITY	CAS NUMBER	CHEMICAL NAME	CURRENT COMMERCIAL STATUS		USE		CR
			PROD	IMPT	PEST ONLY	PEST INTM	
3	348-51-6	o-Chlorofluorobenzene	y	n	n	n	I
3	367-12-4	o-Fluorophenol	y	n	n	n	P
3	513-31-5	2,3-Dibromopropylene	n	n	--	--	I
3	527-20-8	Pentachloroaniline	n	n	--	--	I
3	542-75-6	1,3-Dichloropropene	y	n	y	n	I
3	555-37-3	1-Butyl-3-(3,4-dichlorophenyl)-1-methylurea	n	y	y	n	--
3	558-13-4	Carbon tetrabromide	y	n	n	n	I
3	584-84-9	Toluene-2,4-diisocyanate	y	y	n	n	--
3	608-93-5	Pentachlorobenzene	n	n	n	y	I
3	626-39-1	Tribromobenzene	y	n	n	n	I
3	709-98-8	3,4-Dichloropropionanilide	y	n	y	n	I
3	827-94-1	2,6-Dibromo-4-nitroaniline	y	n	n	n	P
3	1194-65-6	2,6-Dichlorobenzonitrile	n	y	y	n	I
3	1344-32-7	Trichlorobenzyl chloride	n	n	n	y	I
3	1435-53-6	2,4-Dibromofluorobenzene	n	n	--	--	I
3	1861-32-1	Dimethyl tetrachloroterephthalate	y	n	y	n	I
3	1897-45-6	Tetrachloroisophthalonitrile	y	y	y	n	I
3	13041-24-9	3,4-Dichlorobenzotrichloride	n	n	n	y	I
3	13463-67-7	Titanium dioxide	y	y	n	n	I
3	15086-94-9	Tetrabromofluorescein and disodium salt	y	y	n	n	S
3	20925-85-3	Pentachlorobenzonitrile	n	n	--	--	I
3	35915-19-6	Dichlorobenzoic acid	n	n	n	n	I

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GENP 010520

Development of the List of Chemicals to be Proposed for Testing

OPTS began by compiling existing lists of chemicals potentially contaminated with chlorinated and/or brominated dibenzo-p-dioxins and/or dibenzofurans (DBDs/DBFs). The "working" list was created from several published and unpublished existing lists. They are:

- Dioxins (Esposito et.al. 1980) EPA 600/2-80-197.
- Dioxin Strategy (USEPA 1983).
- Informal list prepared by Office of Pesticide Programs (OPP).

Literature searches were made for all known reaction conditions uder which DBDs/DBFs have been formed. These reaction conditions were checked against chemicals with known contamination, and mechanisms of formation were described as diagrammed on the following page.

Based on its assessment of reaction conditions and mechanisms of reaction for the formation of halogenated furans and dioxins for chemicals knowmm to be contaminated with these materials, it became clear that DBDs/DBFs share most of the same "precursor" compounds. The exceptions are: chlorinated/ brominated 2-hydroxyphenyl ethers which form only dioxins, and chlorinated/ brominated biphenyls which form only dibenzo-furans. The other precursor compounds identified are: ortho-Chlorophenols, Chlorinated benzenes, Polychlorinated phenyl ethers, Chlorinated phenoxyphenols and Polychlorinated hydroxydibenzofurans. Although brominated compounds are not listed or specifically discussed, the same type of chemical reactions, generally requiring less severe reaction conditions, will occur with brominated compounds.

Using these theories on the mechanism of formation of halogenated furans and dioxins, OPTS reviewed all chemicals on the "working" list for which actual monitoring data do mot exist to determine whether the theories would apply and indicate that there is a potential for formation of DBDs/DBFs. The theories were also used to review each chemical listed in the Directory of Chemical Producers (SRI 1984), and additional chemicals potentially contaminated with DBDs/DBFs were added to the "working" list. Chemicals believed to be precursors to DBD/DBF formation were also added.

To prioritize the list of chemicals according to probability of DBD/DBF contamination, those chemicals with actual monitoring data showing contamination were designated group 1.

Group 2 chemicals are listed because the theories apply. Generally these chemicals have molecular structures similar to the chemicals known to be contaminated and are known to be processed under conditions most favorable to dioxin/furan formation. The favorable conditions include (1) chlorination or bromination at elevated temperatures (i.e., >100°C) or pressures

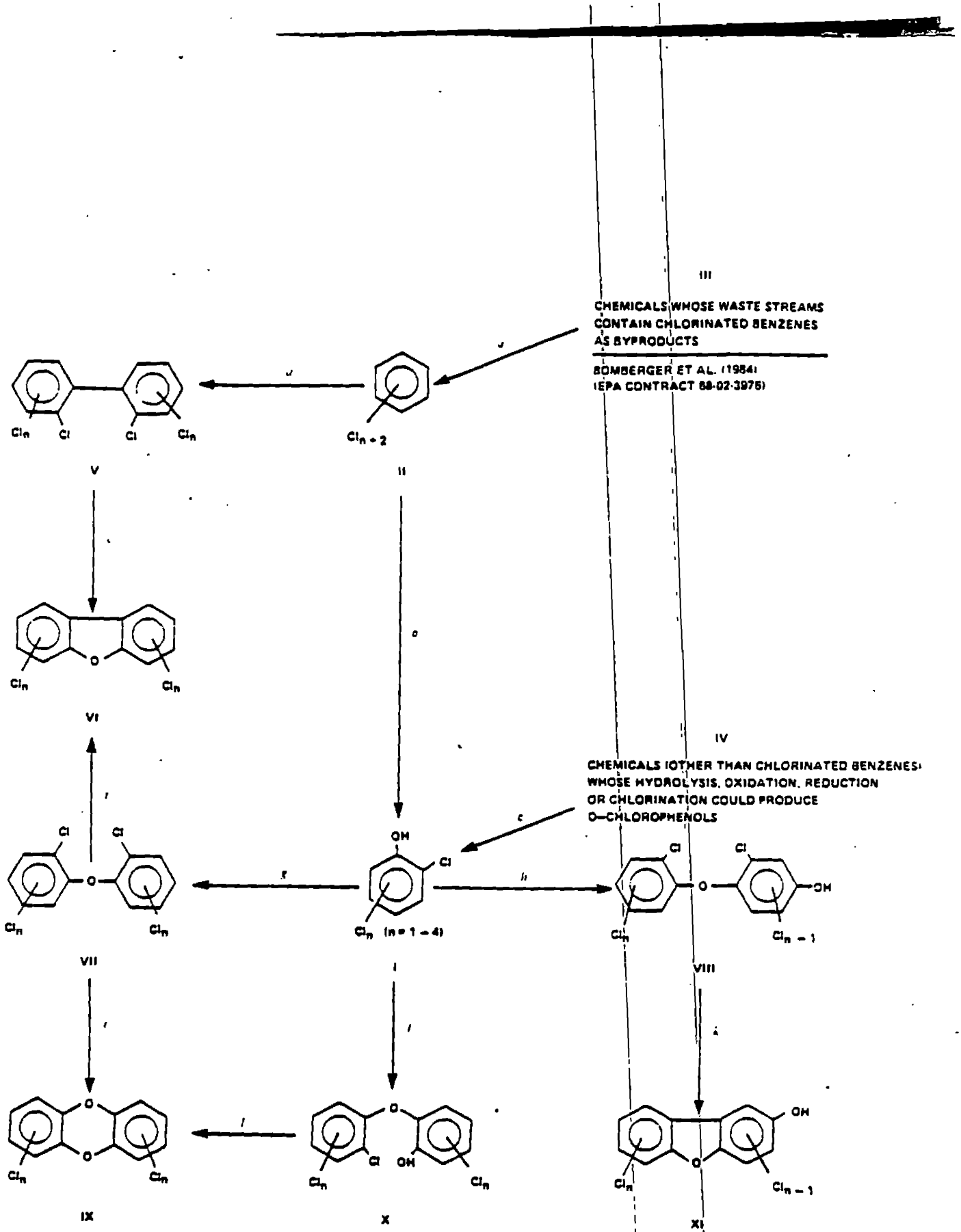

FIGURE 1. RATIONALE FOR FORMATION OF PCDDs AND PCDFs

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GENP 010522

and (2) subsequent alkaline treatment of the chemical intermediate formed (e.g., for product washing this treatment results in the addition of oxygen to the phenyl molecule which in turn leads to the formation of dioxins/furans). This large group of chemicals has been subdivided as follows:

2a Polybrominated phenols and derivatives. These chemicals are prepared under the same conditions as the chlorophenols where dioxin contamination has been documented.

2b Polybrominated phenyl ethers and derivatives. These chemicals are prepared by bromination of diphenyl ether under vigorous conditions.

2c Chlorophenol pesticide derivatives similar in structure to di- and trichlorophenols and derivatives, and di- and trichlorophenyl ethers and derivatives for which dioxin contamination has been documented. These chemicals are prepared under conditions very similar to those used for the chlorophenols for which dioxin contamination is documented.

2d Compounds produced from hexachlorobenzene which is known to be contaminated and other fully halogenated benzenes and any chemical that may contain hexachloro- or hexabromobenzene as an impurity.

Group 3 chemicals are those potentially contaminated or that may lead to contamination according to theories on the formation of PBDs/PBFs. They have structures similar to chemicals known to be contaminated, but without significantly more process data the probability of contamination cannot be ascertained.

For group 4 chemicals the probability of contamination is highly speculative and for many chemicals, improbable. These chemicals appeared on other published lists; however, existing theories do not apply. Some of these chemicals are structurally similar to chemicals known to be contaminated, but process information indicates that formation of PBDs/PBFs is unlikely.

For chemicals in groups 1, 2 and 3, and where possible in group 4, the route of contamination (CP) was identified. Unlike the contamination pathway, which is a chemical reaction sequence, the route of contamination is the physical mechanism or source of contamination. The route of contamination is designated and defined as follows:

- P This chemical is a precursor to PBD/PBF contamination; the chemical itself, as produced, is not contaminated. Industrial use of the compound, under the proper PBD/PBF formation conditions, could result in the formation of PBDs/PBFs in final products.

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- F This chemical is contaminated only as a result of a contaminated feedstock chemical (i.e., either the raw starting material or an unisolated intermediate). The chemical's synthesis does not lead to further DBD/DBF formation.

- S This chemical is contaminated as a result of DBD/DBF synthesis during the chemical's production. This chemical may in turn be a feedstock for further chemical production.

- FS This chemical is contaminated as a result of both a contaminated feedstock and further synthesis of DBDs/DBFs during production.

- I This chemical contains an impurity that may be contaminated or lead to contamination with DBDs/DBFs. The possible level of contamination is expected to be very low.

The complete list of chemicals was reviewed within OPTS and chemicals in groups 3 and 4 were eliminated from consideration because OPTS believes they have a very low probability of contamination.

From the remaining group of chemicals, those believed to be contaminated via a contaminated impurity (I) were carefully examined. As discussed above in the definition of impurity (I), the contamination of these chemicals is expected to be very low compared to chemicals contaminated via other routes. Therefore the chemicals marked I were dropped from consideration.

The group of chemicals marked P (for precursor to dioxin/furan contamination) were further examined. As discussed under the definition of precursor (P), these chemicals are not themselves contaminated, but may lead to dioxin/furan contamination. Therefore they were removed from the list designated for testing, but were placed on a separate list for which process and use information will be required.

Coordination with OSW followed and chemicals listed by OSW as "good" or "possible" candidates for wastestreams contaminated with DBDs/DBFs were added to the OPTS list, and duplicates were eliminated.

This consolidated list contains chemicals known to be contaminated with DBDs/DBFs (1), chemicals with molecular structures and process conditions favorable to DBD/DBF formation, but without actual monitoring data (2), and chemicals with molecular structures favorable to DBD/DBF formation, but not enough process data to make a determination (3). This list was examined for those chemicals used only as pesticides (PO), since TSCA has no jurisdiction over these. The chemicals marked with a "Y" in the "PO" column are used only as pesticides. They will be

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eliminated from the OTS list and picked up by OPP in their data call-in program.

Some chemicals on the list are not currently in production, but could come into production at any time. While they have not been removed from the list, manufacturers will not be required to test a chemical not currently in production at the time the rule is promulgated. He will, however, be required to test that chemical should he ever resume production.

GUIDANCE FOR A SEQUENTIAL APPROACH TO THE SAMPLING OF DIBENZODIOXINS AND DIBENZODIOXINS

INTRODUCTION

This is the sequential sampling scheme referred to in the Proposed Rule for Processing, Distribution, and Use of Certain Designated Chemical Substances Suspected to Produce and/or Be Contaminated with Dioxins and Furans (49 FR 28172, 28182, July 10, 1984).

For this proposed rule, dioxins and furans are in reality four classes of compounds: brominated dibenzofurans, brominated dibenzodioxins, chlorinated dibenzofurans, and chlorinated dibenzodioxins, and specifically within these classes the compounds substituted with from four to seven chlorine and/or bromine atoms per molecule. Hereafter these particular compounds will collectively be referred to as polyhalgenated dibenzofurans (PHDFs) and polyhalogenated dibenzodioxins (PHDDs). Specific subgroups within the collective group addressed by the regulation will be more specifically named.

This document contains a statement of the sequential decision scheme, the rationale for its use, the details of sample selection (how much, when and where), and the statistical properties of the sequential decision scheme. This scheme is part of an overall activity to provide guidance to those who are in a position to respond to the proposed regulations.

PROPOSED TRUNCATED SEQUENTIAL DECISION SCHEME

For a given material at the production/formulation site, select a sample and measure the concentration of PHDFs and PHDDs. The sampling scheme must be used for all tests and analytical evaluations for determination of PHDFs and PHDDs. A measurement may be obtained by a screening method which has been demonstrated by the tester to a documented degree of sensitivity and specificity. The confirmatory method for identifying the PHDFs and PHDDs and the concentrations of these compounds is high resolution gas chromatography / high resolution mass spectrometry (HRGC/HRMS).

The product sample selection procedure is repeated until either a product sample is found to contain PHDFs and/or PHDDs or seven samples have been processed, in which case declare the production of the sampled material to be free from PHDFs and PHDDs. If any of the concentrations of PHDDs in a single product sample exceeds 0.1 parts per billion (ppb) and/or the concentrations of PHDFs in a single sample exceeds 1.0 parts per billion (ppb), the product will be deemed to contain PHDDs and PHDFs respectively. In HRGC/HRMS a resolvable chromatographic peak is

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considered a single brominated dibenzofuran compound, a single chlorinated dibenzofuran compound, an single brominated dibenzodioxin compound, or a single dibenzodioxin compound. The number of samples, N, required is not to exceed seven.

REASON FOR NOT USING A SINGLE SAMPLE TO DETERMINE COMPLIANCE

Analysis of a material is subject to two main sources of PHDFs and PHDDs being generated as byproducts or impurities may vary over time and/or location at the site. Secondly, the measured concentration of PHDFs and PHDDs will vary among repeated measurements on the same sample. Therefore, the measured concentration of a particular single screening test or single gas chromatographic peak will vary among samples selected randomly in time and space so that a single sample would not be representative of the underlying process except for the extreme cases.

In the following paragraphs the variable nature of observations will be expressed by the symbol e, the probability that a sample will have a measured concentration below 0.1 ppb for PHDDs and 1.0 ppb for PHDFs in a particular gas chromatographic peak.

JUSTIFICATION FOR USING SEQUENTIAL SAMPLING

Given the analytical costs associated with HRGC/HRMS, it is important to utilize statistical procedures which minimize the number of samples which need to be analyzed. Sequential monitoring of a material allows a determination of the presence of PHDFsand/or PHDDs to be based on fewer samples, on the average, than would be required under an equivalent fixed sample size decision rule because of the large number of samples required to descibe a production having undemonstrated variablity of PHDF and PHDD content. For each such screening test or HRGC/HRMS analysis this efficiency increases with the number of potential PHDFs and PHDDs in the material and decreases as the magnitude of e increases. For materials containing sufficiently high concentrations of even a single PHDF or PHDD compound (i.e., e is close to zero for its associated screening test or peak) only one sample will be required to declare the presence of PHDFs or PHDDs. For most multiple congener materials, the use of the proposed scheme would probably result in the analysis of only 4 or 5 samples to identify materials containing PHDFs at 1.0 ppb and PHDDs at 0.1 ppb. Even for materials containing a single congener at levels above the 0.1 ppb, the application of the scheme would probably result in the analysis of fewer than 7 samples to declare the presence of PHDFs and PHDDs when e is no larger than 0.7.

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TIMES, LOCATIONS, AND QUANTITIES

A material may be produced through a group of activities, within one or more locations at a site. The production of the material is assumed to be cyclic in nature and that within each cycle the distribution and concentration range of brominated and chlorinated dibenzofurans and dibenzodioxins is consistent. Each cycle, then, is a time interval representing a period within which the activity mix of the production of the material is essentially repeated, such as a batch, shift, or day.

Samples under the proposed sequential sampling plan will be selected from separate cycles of the production process. Further description of sample selection appears in "Guidance for Sampling Brominated and Chlorinated Dibenzofurans and Dibenzodioxins." It is important to randomly select the sampling time and location independently for each cycle. Any deviations from this random selection must be documented and justified. As many as seven cycles will be required under tne proposed procedure. Changes in the production process, especially changes judged to potentially affect brominated and chlorinated dibenzofuran and dibenzodioxin levels, require that the entire sequential testing effort be redone. If a single production process is the potential source of brominated and chlorinated dibenzofuran and dibenzodioxin exposure through several media, each medium should be separately tested by the sequential sampling.

The size of a sample to be chemically analyzed depends on the medium of the sample and the intended analytical method. Sample sizes are recommended in the "Guidance for Sampling Brominated and Chlorinated Dibenzofurans and Dibenzodioxins."

STATISTICAL PROPERTIES OF THE PROPOSED DECISION SCHEME

In general, two decision errors are possible: (1) declaring materials in compliance to be not in compliance, and (2) declaring processes which are not in compliance to be in compliance. Choice of the 0.1 ppb as the test threshold and requiring two samples to exceed it eliminates any significant likelihood of committing an error of the first type. The probability of committing an error of the second type decreases with the number of potential brominated and chlorinated dibenzofurans and dibenzodioxins congeners present in the process and the maximum number of required samples, and increases with the magnitude of e for each such peak. The proposed maximum number of seven samples was chosen because it results in an acceptable probability of the second error without the requirement of an excessive amount of samples to be analyzed to determine the presence of PHDFs and PHDDs. For the seven samples, the error of the second type will be less than 0.25 for a typical process (i.e., one having 5 or more peaks) provided the e-values for the process are all no larger than 0.92 (assuming unconditional independence or complete gas chromatographic resolution of individual PHDF and PHDD concentrations).

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GUIDANCE FOR SAMPLING BROMINATED AND CHLORINATED DIBENZOFURANS AND DIBENZODIOXINS

The following are recommended steps for collecting samples the following four classes of compounds: brominated dibenzofurans, brominated dibenzodioxins, chlorinated dibenzofurans, and chlorinated dibenzodioxins. Of specific interest within these classes are the compounds substituted with from four to seven chlorine and/or bromine atoms per molecule. Hereafter these compounds will collectively be referred to as polyhalgenated dibenzofurans (PHDFs) and polyhalogenated dibenzodioxins (PHDDs). Specific subgroups within the collective group addressed by the regulation will be more specifically named. All of the following steps should be carefully recorded.

1. Determine the Objectives of the Sampling Exercise.

In the case of this proposed rule, some objectives might be (1) to measure PHDF and PHDD levels occuring as byproducts or impurities in a product to determine compliance with the rule, and (2) to know the limitations of these measurements.

2. Describe the System or Production Process from Which the Sample Materials Will Be Collected.

The samples collected can only provide information about the product from which they have been collected and the completeness of this information depends on how, at what time(s), where, and for wnat duration the samples are collected. Of particular importance in determining a sampling plan for the process are the continuity, homogeneity, and cyclic characteristics of the production process. Compositing of samples for chemical analysis has benefits in reducing analytical costs but risks in requiring lower instrument quantification levels and reducing the ability to identify whether PHDFs and PHDDs are from uniform concentrations in all members of a composite or high concentrations in one member and no concentrations in the other members of the composite. Each of the seven samples described in the "Guidance for a Sequential Approach to the Sampling of Dibenzofurans and Dibenzodixins" may be a randomly selected composite, but the seven may not be composited unless the level of concern is revised to be one seventh of the currently proposed levels, i.e. 0.1/7 or 0.014 ppb fo PHDDs and 1.0/7 or 0.14 ppb for PHDFs.

3. Prepare for Sample Collection Operations.

For this section and the following section it is important to first read the appendices from the document "Analytical Methods for Brominated and Chlorinated Dibenzofurans and Dibenzodioxins"

a. Methods and Equipment

Sample collection methods, to be applied here, depend on the nature of the material to be screened or chemically analyzed and the screening or chemical analytical procedure, which for high resolution mass spectrometer detector (HRGC/HRMS), here is assumed to include extraction. Proper guidance, such as sample preparation, extraction, and brominated and chlorinated dibenzofuran and dibenzodioxin measurement by high resolution gas chromatography with a HRGC/HRMS, for collected samples appears in "Analytical Methods for Brominated and Chlorinated Dibenzofurans and Dibenzodioxins"

b. Accounting for Potential Sources of Contamination or Loss During Sampling.

Sample collection containers, sample collection equipment, and chemical analytical equipment are common sources of contamination. Rigorous cleaning of containers and equipment coming in contact with samples and sample extracts decreases the possibility of contamination. The use of method blanks and field blanks evaluates the entire collection and extraction procedures for contamination. Field spikes should be used to determine the possibility of losses of brominated and chlorinated dibenzofurans and dibenzodioxins between collection and actual screening or chemical analysis.

Coordination among the sampling plan designers, the sample collectors, and the screening testers or chemical analysts is a useful way to obtain information on accounting for potential contamination or loss during sampling.

c. Preparing an Operational Plan Which Describes the Details of the Proposed Sample Collection Procedures.

The actual sample collection operational procedures may differ from the proposal and the differences and reasons for the differences must be recorded. A Sampling Plan which describes the sample size, location selection and time selection procedures, and quality assurance guidance, appears in the next section.

4. Prepare a Sampling Plan and Collect Samples.

Professional judgement is very important in sampling. Frequently using such judgement can isolate a worst-case situation, sample the situation, and determine that the magnitude of the worst-case situation is below the stated level of concern. Professional judgement may provide information to more completely sample a system by focusing attention on steps in a process which potentially produces PHDFs and PHDDs. For these complex systems

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professional judgement must be assisted by proven sampling methods. To make a complete analysis, sampling should also determine the presence or absence of PHDFs and PHDDs in locations or situations not necessarily judged to be most important.

The proposed rule requires random sampling. A random sample selection system includes all possibilities and systematically chooses from among a list or compilation of those possibilities. The way of choosing from among the possibilities is the use of a random number table or through an automated random number generator. A haphazard selection system, the result of selection through convenience and/or purposeful neglect, includes only a portion of all possibilities, has very little estimating power, and should not be considered a random selection procedure.

For the purpose of incorporating this sampling plan with the EPA "Guidance for a Sequential Approach to the Sampling of Brominated and Chlorinated Dibenzofurans and Dibenzodioxins" the sampling unit for each process will be a cycle. A cycle is defined as the time interval representing a period within which the activity mix of a process is essentially repeated. This cycle may be a batch, a shift, a day, or some other time period.

It is important to use random selection procedures in determining the sampling time and location for each individual cycle (the details for these determinations are given below in parts b and c). Cycles should be sampled, one at a time, until as many as seven cycles have been sampled. If two samples from any of the seven or fewer cycles are analyzed and show measurement levels of PHDFs and PHDDs above the limit of quantitation, the material is not in compliance with the rule. If none of the seven cycles show PHDDs above the 0.1 parts per billion (ppb), or PHDFs above 1.0 ppm, no further sampling is necessary until there are changes in the process as described below.

If there are changes known or suspected to change the generation of PHDFs and PHDDs as byproducts or impurities in a process or a cycle, the seven cycles sampling exercise must be done again. For each defined process and independent cycle:

a. The size of a sample of a material to be analyzed or sample will be determined by the kind of material to be sampled and the sensitivity of the analytical method. If the material is gaseous, a sample size of ten cubic meters is usually sufficient for analysis. If the material is aqueous or liquid, the sample size of one liter is usually sufficient for analysis. If the material is a solid, the sample size of one hundred grams is usually sufficient for analysis. Any sample size must have proper documentation demonstrating capability to measure PHDDs at 0.1 ppo and PHDFs at 1.0 ppb.

b. Location(s) of sample collection are defined as a subset of all possible locations of storage of a given material.

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Physically possible sample collection sites are listed and chosen through random selection procedures.

c. In processes where over seven batches of a material are produced in a year, sample collection times must be selected from a random time period within each individual batch production cycle. The cycle time is completely segmented into intervals long enough to collect a sample and one interval is randomly selected for the actual collection. For processes where under seven batches of material are produced, random selection of seven samples from a list of production time segments for all batches.

d. Quality assurance of the sampling and actual sample collection exercise includes documentation of: the sampling plan, sample collection procedures, and any chain of custody records. Special notation should be made of any deviations from orginal plans and projections recorded at an earlier stage of the sampling exercise. Especially:

i. dates and times of sample collection and chemical analysis of samples.

ii. exact location and time of sample collection.

iii. process or product batch or lot identification

iv. chain of custody records employed in the sample collection and ultimate disposition of the samples.

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QUALITY ASSURANCE PLAN FOR MEASUREMENT OF BROMINATED AND CHLORINATED DIBENZOFURANS AND DIBENZODIOXINS

For quality assurance (QA) to be an effective method of measurement validation of qualification, a Quality Assurance Plan (QAP) must be prepared and should include the following: history and disposition of samples; sampling and sample collection procedures; and extraction and instrumental analysis procedures. The QAP documents how a laboratory intends to demonstrate its capability to produce data of acceptable quality. The proposed rule is concerned with the following four classes of compounds: brominated dibenzofurans, brominated dibenzodioxins, chlorinated dibenzofurans, and chlorinated dibenzodioxins. Of specific interest within these classes are the compounds substituted with from four to seven chlorine and/or bromine atoms per molecule. Hereafter these compounds will collectively be referred to as polyhalgenated dibenzofurans (PHDFs) and polyhalogenated dibenzodioxins (PHDDs)

An accurate trace or history of the life of a sample (to be chemically analyzed for PHDFs and PHDDs must be assembled and should contain information beginning with a description of the system, scheme, or survey design for sample collection. A written record, sometimes called a chain of custody form, shall follow the sample. Necessary contents of the record are written general descriptions of what happens to the sample, schedules and timetables, disposition, and handling. Following final chemical analysis, the last entry in this trace should be the disposition of the sample. Any further use (particularly for another activity), movement, or examination of the sample should be added to the history.

Details of the sampling or sample collection procedure are the second section of the QAP. Since the history describes handling disposition, schedules, and general descriptions of what happens in sampling, the requirement here is a detailed description of sampling and sample collection. Reasons for using a specific or general sample selection process and reasons for not using other processes must be included here. Estimates of how well the selected samples represent the material to be characterized is an essential part of quality assurance. The greater the variability of composition of a material, the more frequently sampling is required for estimation and characterization purposes. In determining or estimating errors generated in sample collection, control samples or blanks, and PHDFs and PHDDs (native compounds or, preferably isotopically labelled compounds) reinforced controls or standards, must be sent to the collection site(s) and returned with the samples for identical handling and treatment. Duplicate samples, which are collected, documented, and handled the same as other samples, are necessary for recovery, precision, and accuracy determinations.

The third section of the QAP is a description of the extrac-

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tion and chemical analysis or screening test procedures. To determine both extraction efficiency and measurement efficiency, it is necessary to use chemical standards of PHDF and PHDD mixtures or individual PHDFs and PHDDs compounds in control samples. Once capabilities have been established, the operator must determine precision and accuracy must be determined and use those determination to designate acceptable bounds for analytical performance. The operator must keep control chart records to assure that instrument readings of standards fall within the range of acceptable performance. The operator must establish and describe the quantitative range of an instrument and analytical procedure. Specific requirements are as follows:

For chemical analysis, these procedures must be demontrated capable to reproducibly and repeatedly quantitate PHDDs at 0.1 parts per billion (ppb) and 1.0 ppb of PHDFs. Quality control check sample analysis begins the determination of system capabilities.

For PHDDs, at least two analyses of the same spiked standard (instrument standard) at 0.1 ppb must be quantifiable to within $\pm$10% of 0.1 ppb. The recovery of standard spiked into a product material at 0.1 ppb and run through the entire chemical analysis must be within 80-120% of the amount spiked, with reference to the instrument standard, ninety-nine percent (99%) of the time.

For PHDFs, at least two analyses of the same spiked standard (instrument standard) at 1.0 ppb must be quantifiable to within $\pm$10% of 1.0 ppb. The recovery of standard spiked into a product material at 1.0 ppb and run through the entire chemical analysis must be within 80-120% of the amount spiked, with reference to the instrument standard, ninety-nine percent (99%) of the time.

Qualitative requirements include: response factors for PHDFs and PHDDs to be measured, instrument hardware and operating conditions (including type and source of columns, carrier gas and flow rate, operating temperature range, and ion source temperature), and structural assignment and/or library matching of mass spectra. For both qualitative and quantitative measurements, the instrument operator should be blind to the nature or source of samples, particularly to duplicates, blanks, and brominated and chlorinated dibenzofuran and dibenzodioxin reinforced samples. The limit of detection (LOD) and limit of quantitation (LOQ) shall be described for each material. Tentative LOD and LOQ definitions are greater than or equal to three times background noise and greater than or equal to ten times background noise, respectively. Details of quantitative calibration procedures for the known and/or expected range of the PHDF and PHDD levels in actual samples complete this section of the QAP.

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The last section of the QAP must include the results of laboratory participation in round robin analytical programs, the results of performance audits, the results of systems audits, analytical result of performance audit samples, persons responsible for all aspects of sampling, chemical analysis, data analysis, corrective actions, and quality assurance/quality control. This section also must include a description of how problems are handled and documented, and how corrections in working level notebooks are indicated and explained.

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