

## UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

## RESEARCH TRIANGLE PARK, NC 27711

NOV 1 6 2009

OFFICE OF AIR QUALITY PLANNING AND STANDARDS

## **MEMORANDUM**

TO:

Kishor Fruitwala, Chief

RCRA Facility Assessment Section

FROM:

Conniesue Oldham, Group Leader

Measurement Technology Group (E143-02)

**SUBJECT:** 

Dow Request for Method Modifications

This is in response to an e-mail message dated September 1, 2009, from Dow to you asking for approval of a number of sampling and analytical method deviations that have been proposed for use during the upcoming 40 CFR Part 63 Subpart EEE (Hazardous Waste Combustor MACT) Comprehensive Performance Tests of hazardous waste combustors at numerous Dow facilities located in Texas and Louisiana. Based on our discussions with you, we have decided that some of the modifications are not minor and under EPA's delegation of approval authority should be reviewed by my office. I am attaching a table summarizing all of the requested modifications. The modifications that my office is reviewing are items 7, 10, 13, 14, 15, 16, 17, 18, 19, 21, 25, 27, 28, 29, 30, 33, 34, 35, and 38.

Items 7 and 10 are modifications to the analytical procedures in Method 29 for measuring metal emissions. Item 7 requests that we allow the use of laboratory reagent water rather than American Society for Testing and Materials (ASTM) Type II water as required by the method. The laboratory reagent water is certified to meet the ASTM Type II specifications for electrical conductivity, which is the important parameter for metals analysis, but is not tested to determine if it meets other Type II specifications such as total organic carbon content. We agree that this is an acceptable modification because the laboratory reagent water will meet the pertinent specifications for ASTM Type II water. Item 10 requests that we allow the laboratory to add boric acid to the front half portion of the Method 29 samples after they have been digested in a microwave oven with hydrofluoric acid. The boric acid will sequester the hydrofluoric acid and prevent it from damaging the laboratory glassware. We agree that it is acceptable to add boric acid to the digested samples because it will not adversely affect the Method 29 analytical results.

Items 13, 14, 15, and 16 are modifications to the analytical procedures in Method 6010 for analysis of metal samples from Method 29 by inductively coupled argon plasma. Items 13 and 14 request that we allow the laboratory to adopt the procedure in EPA CLP ILM4.0 for determining the "specified concentration range around the calibration blank" that is required in

Section 4.2.8 of Method 6010 because there is no definition or procedure specified in Section 4.2.8. We agree that the procedure in EPA CLP ILM4.0 is an acceptable procedure for defining the "specified concentration range around the calibration blank." Item 15 requests that we allow the laboratory calibration blank to be prepared in a matrix of 5% nitric acid and 5% hydrochloric acid rather than 10% hydrochloric acid and 2 % nitric acid as specified by the method. We agree that a matrix of 5% nitric acid and 5% hydrochloric acid would better represent the range of sample matrices that arise from the preparation procedures in Method 29 than the specified matrix of 10% hydrochloric acid and 2 % nitric acid from Method 6010. Item 16 requests that we allow the laboratory to consider method blanks acceptable if they are below the reporting limit for the analysis rather than below the method detection limit. In the context of the air samples taken for compliance purposes, having method blank values below the laboratory reporting limit is an acceptable alternative to having method blank values below the method detection limit.

Items 17, 18, 19, and 21 are modifications to the analytical procedures in Method 8260B for the analysis of volatile organic compounds by gas chromatography/mass spectrometry. Item 17 requests that we allow the laboratory to use ion 119 as the quantitation ion for the internal standard chlorobenzene-d<sub>5</sub> for the 25-ml purge tests rather than ion 117 as specified in Method 8260. We agree that it is acceptable to use ion 119 as the quantitation ion for the 25-ml purge tests because it will improve the sensitivity of the analysis. Item 18 requests that we allow an absolute retention time window of 0.2 minutes around the expected retention time for components in the sample rather than a relative retention time (RRT) window of 0.06 RRT units. We agree that setting an absolute retention time window of 0.2 minutes is an acceptable alternative because we do not expect that retention times would shift significantly using the columns and conditions specified in Method 8260B. Item 19 requests the use of alternate ions in the mass spectrum of 12 target analytes to identify and measure those target analytes. These alternate ions are either the base ions in the mass spectrum or replace ions that have interferences. We agree that the alternate ions are acceptable alternatives to the specified ions to identify and measure the 12 target analytes. Item 21 requests that we allow the analyst to substitute a single 30-ml aliquot of methylene chloride to rinse the filter sample container or the front-half rinse sample container when transferring the shipped samples for analysis as a substitute for the three 10-ml aliquots specified by the method. While we believe that the three 10-ml aliquots would be better laboratory practice for transferring sample, we agree that a single 30-ml aliquot would provide adequate recovery of the sample and is an acceptable alternative.

Item 25 requests that we allow continuous liquid-liquid extraction of the combined condensate and condensate rinse as an alternative to the separatory funnel extraction specified in Method 3542. We agree that continuous liquid-liquid extraction is a better extraction procedure than using a separatory funnel and is an acceptable modification to Method 3542.

Items 27, 28, and 29 are modifications to the Method 23 sampling procedure. Together they request that we approve the use of acetone and toluene as solvents for rinsing the sample

train components to recover any sample on the glassware surface, and that we allow the solvents to be analyzed together as an alternative to using acetone, methylene chloride, and toluene as the recovery solvents with the toluene rinse analyzed separately as specified in Method 23. We already have data to indicate that omitting the methylene chloride and combining the toluene rinse with the other solvents will not affect the measured emissions, so this is an acceptable modification to the Method 23 sampling procedures.

Items 30, 33, 34, and 35 are modifications to the analytical procedures in Method 23. Items 30, 33, 34, and 35 are modifications to the extraction and preliminary clean-up procedures. Because Method 23 uses isotopically labeled internal standards for calibration, and the proposed modification to the extraction and clean-up procedures occurs after the addition of the internal standards, the calibration procedure will automatically compensate for any modifications to these procedures. Therefore, these are acceptable modifications provided that the results of the analysis meet all of the quality assurance limits in Method 23. Item 38 requests that we allow an alternate acceptable ion abundance ratio range for pentachlorodibenzodioxin. The proposed modification is to allow an ion abundance ratio range of 0.55 to 0.75 for the M/M+2 ratio rather than 1.32 to 1.78 for the M+2/M+4 ratio. We agree that it is acceptable to monitor the M/M+2 ratio as an alternative to the M+2/M+4 ratio and that the range of 0.55 to 0.75 is comparable to the range of 1.32 to 1.78.

We believe that these modifications are acceptable for use at any hazardous waste combustor subject to the emission limits in 40 CFR Part 63, Subpart EEE. Therefore, we will announce on EPA's web site (at <a href="http://www.epa.gov/ttn/emc/tmethods.html#CatB">http://www.epa.gov/ttn/emc/tmethods.html#CatB</a>) that our approval of these modifications is broadly applicable to all hazardous waste combustors.

If you need further assistance, please contact Gary McAlister at (919) 541-1062.

Attachment

B. The matrix m standards for H <sub>2</sub> : described in EP/ performed. The diluted and neutr collection. Therefore acid and base match the initial therefore not pos	A. EPA Method calibration curve sample analysis. perform a single analysis, as descr 9056.	1. HCl/Cl <sub>2</sub> Ana			
B. The matrix matching of calibration standards for H <sub>2</sub> SO <sub>4</sub> and NaOH impingers described in EPA Method 26A will not be performed. The impinger solutions are diluted and neutralized during sample collection. Therefore, the concentration of the acid and base in the impingers does not match the initial matrix. Matrix matching is therefore not possible in the final matrix.	A. EPA Method 26A states to analyze a calibration curve both before and after sample analysis. The laboratory will perform a single calibration prior to sample analysis, as described in SW-846 Method 9056.	lysis Modifications – KNOX	Modification		
The impinger solutions are difured and neutralized during sample collection.  Therefore, the concentration of the acid and base in the impingers does not match the initial matrix. Matrix matching is therefore not possible in the final matrix.	The laboratory will perform a single calibration prior to sample analysis, as described in SW-846 Method 9056.	1. HCVCl <sub>2</sub> Analysis Modifications – KNOX-WC005 based on EPA METHOD 26A (TestAmerica, Knoxville, TN <sup>16</sup> )	Justif	ication	
Intermediate	Intermediate	America, Knoxy	Modification Category <sup>15</sup>		
<	4	⁄іllе, TN <sup>i</sup>	B-901/2/3 <sup>1</sup>		
<	٠ ٧	9	B-824 <sup>2</sup>		
۷.	٠.		F-210 <sup>3</sup>	Dow	
<	۷.		FTB-603⁴	Freeport	
۷.			F-2820 <sup>5</sup>		
٧	√		B-33 RKI <sup>6</sup>		
۷,	<b>√</b> ×		F410/420 <sup>7</sup>		
<	4		R-4 <sup>8</sup>	Dow Plaquemin e	
4	٧		R-750 <sup>9</sup>		
۷.	٧ -		B-53 <sup>10</sup>	UCC	
4,	٧.		V-A5 <sup>11</sup> Texas Ci		
fa			6 & 712	Angus	
			MN-460 <sup>13</sup>	Dow Clear Lake	
			HT-1 <sup>14</sup>	Rohm & Haas	

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B. Approximate rinse volumes will be used in the recovery of the Method 29 sampling train versus the exact volumes prescribed in Method 29.  The method modifications proposed include:  —Use of approximately (versus "exactly") 100 ml ± 25 ml of 0.1 N HNO <sub>3</sub> to rinse the probe nozzle and liner and front half of the filter housing;  —Use of approximately (versus "exactly") 100 ml ± 50 ml of 0.1 N HNO <sub>3</sub> to rinse the transfer line, the HNO <sub>3</sub> to rinse the empty impinger; and —Use of approximately (versus "exactly") 100 ml ± 25 ml of 0.1 N HNO <sub>3</sub> to rinse the empty impinger; and —Use of approximately (versus "exactly") 100 ml ± 50 ml of deionized water to rinse the acidic KMnO <sub>4</sub> impingers.	A. A Teflon* transfer line will be used between the filter and the first impinger of the sampling train.	II. Metals Sampling Modifications – EPA M	Modií	ication
EPA Method 29 states that exactly 100 ml of 0.1 N HNO <sub>3</sub> is to be used to recover the probe nozzle and liner and front half of the filter holder; exactly 100 ml of 0.1 N HNO <sub>3</sub> , is to be used to recover the first three impingers (a moisture knock-out if used and two impingers (a moisture knock-out if used and two impingers containing HNO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> ); exactly 100 ml of 0.1 N HNO <sub>3</sub> is to be used to recover the empty impinger between the two HNO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> impingers and the two mpingers containing acidic KMnO <sub>4</sub> ; exactly 100 ml of the acidic KMnO <sub>4</sub> solution and 100 ml of water to recover the impingers of acidic KMnO <sub>4</sub> ; and 25 ml of 8N HCl if visible deposits remain in the acidic KMnO <sub>4</sub> impingers. The rinse volumes in the method are 1) overly prescriptive, and 2) may be inadequate for sample recovery. The rationale for the method specification to use exactly 100 milliliters of nitric acid in recovery is to ease the blank corrected; therefore the use of exactly 100 milliliters is not necessary.	This is done to address space limitations on the stack, to allow for ease in probe moving and to minimize potential hazards moving the very large and heavy impinger box.	II. Metals Sampling Modifications – EPA METHOD 29 (URS Corporation, Austin, TX <sup>17</sup> )	Justifi	ication
Minor	Minor		Modif Categ	ication gory <sup>15</sup>
۷.	۷		B-901/2/3 <sup>1</sup>	
۷.	124		B-824 <sup>2</sup>	
<	۷ .		F-210 <sup>3</sup>	Dow
<	4		FTB-603 <sup>4</sup>	Freeport
<	1		F-2820 <sup>5</sup>	
<	\ 		B-33 RKI <sup>6</sup>	
<	~		F410/420 <sup>7</sup>	.,
<	<b>V</b>		R-4 <sup>8</sup>	Dow Plaquemin e
<	<b>~</b>		R-750 <sup>9</sup>	
×			B-53 <sup>10</sup>	ucc
	<b>√</b>		V-A5 <sup>11</sup>	Texas City
			6 & 7 <sup>12</sup>	Angus
۷.	<u> </u>		MN-460 <sup>13</sup>	Dow Clear Lake
٠,	۷.		HT-1 <sup>14</sup>	Rohm & Haas

D. The initial measurement of impinger samples from nitric acid/hydrogen peroxide can be made by weighing to ± 0.5 grams or measuring volume to ± 2.5 mL (± 5 mL for large volume samples).	C. Laboratory reagent water is used rather than ASTM Type II water.	B. The digestate for the front-half fraction uses 0.4% HCl. The use of HCl is not specified in EPA Method 29, but is necessary to achieve maximum mercury recovery during the microwave extraction.	A. The digestates from each fraction will be reduced to final volumes that are lower than the volumes specified in EPA Method 29. This is done to achieve lower reporting limits. The concentrations of the reagents will be maintained at the same concentrations as stated in EPA Method 29.	III. Metals Analysis Modifications - KNO?	Modi	lication
This information is not used by the laboratory to calculate sample results and is recorded on the laboratory benchmark and provided to the client for information only.	The laboratory reagent water meets the ASTM criteria for electrical conductivity, but is not tested for all ASTM Type II criteria. The laboratory uses the term reagent water rather than ASTM Type II water since not all ASTM Type II criteria are evaluated. For example, the reagent water is not tested for Total Organic Carbon since this parameter is not tested for Total Organic Carbon since this parameter is not relevant to the analytical method.	The use of HCl is not specified in EPA Method 29, but is necessary to achieve maximum mercury recovery during the microwave extraction.	This is done to achieve lower reporting limit.  A lower acid volume is added to a lower final volume to keep the acid concentration constant.	III. Metals Analysis Modifications - KNOX-MT-0006 based on EPA METHOD 29 (TestAmerica, Knoxville, TNito)	Justif	ication
Minor	Minor	Intermediate	Minor	America, Knox	Modil Cates	ication gory <sup>15</sup>
\ \	۷	~		ville, TN <sup>10</sup>	B-901/2/3 <sup>1</sup>	
٠	<	~	ζ,	٥	B-824 <sup>2</sup>	
٧	<b>~</b>	٧	۷,		F-210 <sup>3</sup>	Dow
۷	~	٧	۷,		FTB-603 <sup>4</sup>	Freeport
۷.	۷.	4	4,		F-2820 <sup>5</sup>	
۷,	Ž,	\ \	~		B-33 RKI <sup>6</sup>	5
۷	\ \	٧	۷		F410/420 <sup>7</sup>	
ځ.	#   <b>&lt;</b>	√	4		R-48	Dow Plaquemin e
٧	. <	1	' <		R-750°	
					B-53 <sup>10</sup>	UCC
۷.,	۷.		۷.		V-A5 <sup>11</sup>	Texas City
					6 & 7 <sup>12</sup>	Angus
<b>4</b>	۷,		۷,		MN-460 <sup>13</sup>	Dow Clear Lake
٧	, Ž 98.	۷.	~		HT-1 <sup>14</sup>	Rohm & Haas

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	E. The samples are not analyzed in duplicate. Instrument and method precision are measured by analyzing the LCS/LCSD.	(Continued) III. Metals Analysis Modificat	Modifi	ication
	TestAmerica Knoxville does not require the reporting of separate duplicate analyses for mercury as specified in Section 9.2.3 of EPA Method 29. Method 29 was written allowing the use of an Atomic Absorption  Spectrometer with a CVAAS attachment using a BOD bottle for sample analysis.  The reference to this older style instrumentation may have required the duplicate analysis of mercury samples due to the use of BOD bottles for sample preparation and analysis.  The use of automated instrumentation used for mercury analysis is referenced in section 11.1.3. Note 2. Is states that "Optionally, Hg can be analyzed by using the CVAAS analysis procedures given by some instrument manufacturer's directions. Upon completion of the digestion described in (1), analyze the sample according to the instrument manufacturer's directions. This approach allows multiple (including duplicate) automated analyses of a digested sample aitquot."  The use of automated instrumentation allows for multiple automated analyses and processes the results of multiple readings for each sample to provide a final averaged result for mercury. For example, during a ten second period, the instrument takes a reading every 0.1 second for a total of 100 replicate measurements. The average of these replicate readings to used to determine the absorbance and resulting sample	(Continued) III. Metals Analysis Modifications – KNOX-MT-0006 based on EPA METHOD 29 (TestAmerica, Knoxville, TN <sup>16</sup> )	Justifi	cation
	Minor	OD 29 (TestA	Modifi Categ	ication cory <sup>15</sup>
	4	merica, K	B-901/2/3 <sup>1</sup>	
Ī	۷,	noxville,	B-824 <sup>2</sup>	
ľ	۷,	TN16	F-210 <sup>3</sup>	Dow
Ī	· · · · · · · · · · · · · · · · · · ·		FTB-603 <sup>4</sup>	Freeport
	«		F-2820 <sup>5</sup>	
ŀ	۷.		B-33 RKI <sup>6</sup>	
-	<		F410/420 <sup>7</sup>	
-	<		R-4 <sup>8</sup>	Dow Plaquemin
ŀ	4		R-750 <sup>9</sup>	e
-		-	B-53 <sup>10</sup>	
ŀ	۷.		V-A5 <sup>11</sup>	UCC Texas City
-			6 & 7 <sup>12</sup>	Angus
-	. * 4		MN-460 <sup>13</sup>	Dow Clear Lake
	4		HT-1 <sup>14</sup>	Rohm & Haas

B. SW-846 Method 6010B states that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. In determining inter-element correction factors, the laboratory uses the procedure in EPA CSP ILMO4.0.	A. Mixed calibration standard solutions are purchased from approved vendors.	IV. Metals Analysis Modifications - KNOX	G. The aliquot for mercury analysis of the nitric acid/hydrogen peroxide impingers is taken from the sample after it is reduced in volume to 100 mL. This is done to provide lower reporting limits.	F. Bonc acid is added after the HF microwave digestion of the front-half samples. Hydrofluoric acid is sequestered by the addition of boric, acid, protecting glassware and instrumentation.		(Continued) III. Metals Analysis Modificat	Modi	fication
In determining IEC's, because of lack of definition in Method 6010B, the laboratory has adopted the procedure in EPA CLP ILM4.0 for the "concentration range around the calibration blank."	For ICP Atomic Emission Spectroscopy, a vendor prepared mixed standard containing the analytes of interest is used to calibrate the instrument rather than using individual solutions of the elements.	IV. Metals Analysis Modifications – KNOX-MT-0007 based on SW-846 METHOD 6010B (TestAmerica, Knoxville, TN <sup>16</sup> )	This is done to provide lower reporting limit for mercury by taking an aliquot after sample concentration.	Hydrofluoric acid is sequestered by the addition of boric acid, protecting glassware and instrumentation.  Do you have any data showing that the Boric acid addition does not negatively impact the metals analysis?  Yes, We have MDL data and Demonstration of capability Data.	TestAmerica Knoxville provides relevant mercury precision data for the method by performing one of the following depending on the train fraction: LCS/LCSD, MS/MSD or PDS/PDSD.	Metals Analysis Modifications - KNOX-MT-0006 based on EPA METHOD 29 (TestAmerica, Knoxville, TN-16)	Justi	lication
Minor	Minor	3 (TestAmerica.	Minor	Minor		ЮD 29 (TestAп	Modi Cate	fication gory <sup>15</sup>
۷_	۷	Knoxvill	4	۷,		nerica, K	B-901/2/3 <sup>1</sup>	
<	۷ .	le, TN <sup>16</sup> )	1	۷,		noxville,	B-824 <sup>2</sup>	
۷,	۷,		۷	۷,		(N16)	F-210 <sup>3</sup>	Dow
۷.	- <b>- - -</b>		۷,	4			FTB-603 <sup>4</sup>	Freeport
۷,	4		4	۷.			F-2820 <sup>5</sup>	
۷.	4		۷.	<	*		B-33 RKI <sup>6</sup>	
۷.	4		۷,	<			F410/420 <sup>7</sup>	
4	۷ .		7	۷,			R-48	Dow Plaquemin e
٧	۷.		À	۷,			R-750 <sup>9</sup>	
E)							B-53 <sup>10</sup>	UCC
<	. <		۷.	۷,			V-A5 <sup>11</sup>	Texas City
							6 & 7 <sup>12</sup>	Ąngus
۷,			۷	۷.			MN-460 <sup>13</sup>	Dow Clear Lake
	۷.		٧.	<		73	HT-1 <sup>14</sup>	Rohm & Haas

B. A retention time window of 0.2 minutes is used for all components, since these alternate ions data systems do not have the capability of using the relative retention time units specified.	A. Ion 119 is used as the quantitation ion for chlorobenzene-d <sub>s</sub> , for 25-ml purge tests.	V. Volatile POHC Analysis Modifications –	E. Method blanks are considered acceptable if they are below the reporting limit, rather than the method detection limit.	D. The calibration blank is prepared in 5% nitric acid and 5% hydrochloric acid, rather than 2% nitric acid and 10% hydrochloric acid.	C. ICSA (interference check sample A) results from the non-interfering elements must fall within ± 1 RL from zero. If this is not achieved the field sample data must be evaluated.	(Continued) IV. Metals Analysis Modificati	Modif	ication
0.2 minutes was chosen to reflect a window comparable to the Method Specified 0.06 RRT window specified in Method 8260B. The use of capillary column chromatography provides reliable and reproducible target analyte retention times	This alternate ion is used for quantitation to provide improved relative response of associated target analytes when a larger purge volume is required.	V. Volatile POHC Analysis Modifications - KNOX-MS-0015 based on SW-846 METHOD 8260B (TestAmerica, Knoxville, TN16)	Method 6010B does not list air as one of the applicable matrices although method 29 references 6010. The method blank criteria have been set to support the reporting limits provided for the air matrix and is qualified to the laboratory MDL.	The marrix used by the laboratory provides for improved performance relative to the wide variety of digestate acid matrices which result from the various EPA preparation protocols applied.	This is a clarification of the criteria used by the laboratory since it is not specified in the reference method.	(Continued) IV. Metals Analysis Modifications - KNOX-MT-0007 based on SW-846 METHOD 6010B (TestAmerica, Knoxville, TN-16)	Justifi	cation
Minor	Minor	8260B (TestA	Minor	Minor	Minor	HOD 6010B (	Modif Categ	ication tory <sup>15</sup>
		merica, k	۷,	√	Ý	TestAmer	B-901/2/3 <sup>1</sup>	
٨	٧	inoxville,	٧	√	7	ica, Knox	B-824 <sup>2</sup>	
۷,	۷.	TN16)	۷.	4	۷	ville, TN¹	F-210 <sup>3</sup>	Dow
۷	٧		۷	√	7	٥	FTB-603 <sup>4</sup>	Freeport
4	۷,		Ý	4	Ý		F-2820 <sup>5</sup>	
			4	4	٨		B-33 RKI <sup>6</sup>	
۷,	4		4	<b>V</b>	٧		F410/420 <sup>7</sup>	
۷,	۷		۷,	√	۷.		R-48	Dow Plaquemin e
4	۷,		<b>V</b>	4	<b>~</b>		R-750 <sup>9</sup>	
٧	۷.						B-53 <sup>10</sup>	UCC
			۷.	4	٧		V-A5 <sup>11</sup>	Texas City
							6 & 712	Angus
,			٠ ٧	¥	4		MN-460 <sup>13</sup>	Dow Clear Lake
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W.			
A. The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846.  The following is a list of the analytes that have different quantitative ions assigned in the laboratory SOP than those ions listed in Method 8260B.  The order is presented as analyte name, Method 8260B quantitative ion, and TestAmerica Knoxville quantitative ion, respectively.  1. 1,2-dichloroethane-44 (surrogate), 102, 65, (65 is the base ion)  2. Trichlorothoromethane, 151, 101, (151 does not exist, so we use the base)  3. Acetone, 58, 43, (43 is the base)  4. 2-butanone, 72, 43, (43 is the base)  5. Trichlorothoromethane, 85, 97, (97 is the base)  5. Trichlorothoromethane, 87, 10, (interferences with 95)  6. 1,1,2-trichloroethane, 83, 97, (97 is the base)  7. Tolume, 92, 91, (91 is the base)  8. 4-methyl-2-pentamone, 100, 43, (43 is the base)  9. Ethylbenzene, 91, 106, (106 is used to be consistent with xylenes)  10. 1,2-dichoron-3-chloropropane, 75, 157, (157 is the base)  9. Ethyloropropane, 75, 188 (interferences with 75)  11. Cis-1,4-dichloro-2-butene, 75, 110	VI. Volatile POHC Analysis Modifications -	Modif	ication
Except where otherwise noted, where the base ion is used, these alternate ions provide for greater sensitivity for the target analyte.	- KNOX-MS-0011 based on SW-846 METHOD 8260B (TestAmerica, Knoxville, TN <sup>16</sup> )	Justifi	cation
Minor	D 8260B (Test	Modif Categ	ication tory <sup>15</sup>
×	America,	B-901/2/3 <sup>1</sup>	
<	Knoxville	B-824 <sup>2</sup>	
خ, ی	TN <sup>16</sup> )	F-210 <sup>3</sup>	Dow
۷,		FTB-603 <sup>4</sup>	Freeport
* 4		F-2820 <sup>5</sup>	
n		B-33 RK1 <sup>6</sup>	
- <-		F410/420 <sup>7</sup>	
. <		R-48	Dow Plaquemin e
٠. ٠. ٠. ٠. ٠. ٠. ٠. ٠. ٠. ٠. ٠. ٠. ٠. ٠		R-750 <sup>9</sup>	
<u>د</u>		B-53 <sup>10</sup>	UCC
DE LA CONTRACTOR DE LA		V-A5 <sup>11</sup>	Texas City
a k B		6 & 7 <sup>12</sup>	Angus
#		MN-460 <sup>13</sup>	Dow Clear Lake
۷.		HT-1 <sup>14</sup>	Rohm & Haas

D. If the sample is not concentrated immediately after extraction, it is stored at 4°C in the dark, and not transferred to another container.	C. The front-halfrinse is not filtered as specified; the use of continuous extraction on the filter and liquid portion of the sample eliminates the need for filtering the particulate material.	B. A single 30-mL aliquot of methylene chloride may be used to rinse the Petri dish containing the filter or the container holding the front half rinse; the method specifies the use of 3 rinses with 10 mL.	A. Katter than spiking the litter in a petri- dish on the bench, the filter will be transferred to the soxhlet extraction apparatus, and all spiking material will be added there.	VII. Semivolatile POHC Analysis Modifica	Modification		
The elimination of an additional container reduces the chance for sample contamination.	The use of continuous extraction on the filter and liquid portion of the sample eliminates the need for filtering the particulate material.	The same volume of methylene chloride is used with fewer transfers resulting in greater efficiency and equivalent rinsing.	Spiking the filter in the Petri dish on the bench results in the loss of the more volatile components present in the spike solution for this semivolatile organic analysis. The filter is spiked in the soxihet apparatus providing improved recovery of the more volatile spiked analytes.	VII. Semivolatile POHC Analysis Modifications - PREP METHOD SW-846 METHOD 3542 (TestAmerica, Knoxville, TN <sup>16</sup> )	Justi	lication	
Minor	Minor	Minor	Minor	542 (TestAmer	Modi Cate	fication gory <sup>15</sup>	
4	۷,	<b>~</b>	~	іса, Клох	B-901/2/3 <sup>1</sup>		
				wille, TN	B-824 <sup>2</sup>		
				ڻ	F-210 <sup>3</sup>	Dow	
					FTB-603 <sup>4</sup>	Freeport	
					F-2820 <sup>5</sup>		
			8		B-33 RKI <sup>6</sup>		
					F410/420 <sup>7</sup>		
					R-48	Dow Plaquemin e	
		la .			R-750 <sup>9</sup>		
					B-53 <sup>10</sup>	UCC	
			-		V-A5 <sup>11</sup>	Texas City	
۷.	4	<	٧.		6 & 712	Angus	
					MN-460 <sup>13</sup>	Dow Clear Lake	
					HT-1 <sup>14</sup>	Rohm & Haas	

rinse, the laboratory will have the flexibility to select whether to raise or lower the pH first. rinse is being eliminated. the acetone, methylene chloride, and toluene rinses in the field. The methylene chloride A. Method 0023A calls for a combination of VIII. PCDDs/PCDFs Sampling Modifications - SW-846 METHOD 0023A (URS Corporation, Austin, TX<sup>1</sup>) G. The final extracts may be concentrated to 1 milliliter before analysis, rather than the 5 extraction specified in the method. is used rather than the separatory funnel combined condensate and condensate rinse (continued) VII. Semivolatile POHC Analysis Modifications – PREP METHOD SW-846 METHOD 3542 (TestAmerica, Knoxville, TN<sup>th</sup>) milliliters specified in the method. F. Continuous liquid-liquid extraction of the Modification methylene chloride is supported by guidance documentation from EPA for the These changes will ease compliance with shipping regulations, and the elimination of technique provides improved recoveries of sensitivity of the method target analytes. The continuous liquid-liquid extraction is adjusted to both a low and a high pH as indicated in the method, and this pH adjustment order works well for this this extraction technique provides a longer solvent/sample contact time. The sample pH adjustment of the condensate fraction. As SOP actually concerns the order of pH This modification listed in the laboratory alternate extraction technique. liquid extraction provides for improved mentioned below, the continuous liquiddetermination of PCDDs/PCDFs by EPA The use of a 1 mL final volume improves recoveries of target analytes as the use of Justification Minor Minor Minor Minor Modification Category 15 B-901/2/31 4 4 4 < B-8242 4 4 F-210<sup>3</sup> Dow Freeport FTB-6034 ۷ F-2820<sup>5</sup> 4 B-33 RKI6 F410/4207 4 Dow R-48 Plaquemin R-7509 4 B-53<sup>10</sup> 4 UCC Texas City V-A511 4  $6 & 7^{12}$ Angus 4 ۷ ۷, Dow MN-460<sup>13</sup> 4 Clear Lake Rohm & HT-1<sup>14</sup> Haas

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fication	Modif	IX. PCDDs/PCDFs Sampling Modification:	A. EPA Method 23 calls for the use of acètone, methylene chloride, and toluene rines in the field. Only acetone and toluene	rinses in the field. Only acetone and toluene will be used to recover the train.	<b>B.</b> EPA Method 23 calls for separate analysis of the toluene rinse fraction. This	fraction will be combined with all other fractions for extraction and analysis.	X. PCDDs/PCDFs Analysis Modifications -	A. No silica gel will be added to the soxhlet apparatus.	B. All provided solvent rinses are combined concentrated, and added to the resin/filter components before soxhlet extraction.	C. Prior to clean-up, the extract is dried with sodium sulfate and cleanup recovery standard is added.	D. The extract is split for archiving. Tetradecane is added to the remaining half and the extract is concentrated to the tetradecane.	E. The extract undergoes acid/base silica gel column and florisil column clean-up. Basic alumina and AX-21 carbon/celite 545 columns are not used.
ücation	Justifi	PCDDs/PCDFs Sampling Modifications - EPA METHOD 23 (URS Corporation, Austin, TX <sup>17</sup> )	This is considered a minor deviation to a method and is explicitly discussed on EPA's	website (www.epa.gov/ttn/emc/methods/method23.h tml).	-		PCDDs/PCDFs Analysis Modifications - SW-846 METHOD 8290 (Vista Analytical Laboratories, El Dorado, CA 18)	Modifications have been made to reduce interference and/or improve sensitivity		,		į.
fication gory <sup>15</sup>	Modif Cates	stin, TX <sup>17</sup> )	Minor	Minor		Minor	aboratories, El	Minor	Minor	Minor	Minor	Minor
	B-901/2/3 <sup>1</sup>						Dorado,	4	۷.	۷	4	٧
	B-824 <sup>2</sup>						CA <sup>18</sup> )	۷	۷,	4	~	4
Dow	F-210 <sup>3</sup>							1	V	٧	٧	4
Freeport	FTB-603 <sup>4</sup>							V	1	4	7	7
	F-2820 <sup>5</sup>							4	4	٧	ν.	<b>خ</b> ر
	B-33 RKI <sup>6</sup>		4		<			<b>~</b>	۷.	¥	~	۷,
	F410/420 <sup>7</sup>							۷	۷	٧	~	۷.
Dow Plaquemin e	R-4 <sup>6</sup>					3		<b>~</b>	۷,	۷	۷.	۷.
	R-750 <sup>9</sup>							√ 	۷.	۷.	۷.	۷.
UCC	B-53 <sup>10</sup>							۷	۷.	۷,	12	۷.
Texas City	V-A5 <sup>11</sup>		4		۷			1	<b>\</b>	۷	۷.	۷,
Angus	6 & 712							< −	۷.	۷.	۷.	۷.
Dow Clear Lake	MN-460 <sup>13</sup>					-		۷,	۷,	۷	~	۷.
Rohm & Haas	HT-1 <sup>14</sup>			۷		۷		ζ,	۷,	۷,	٠,	۷.

I. For pentachlorodibenzodioxin, the acceptable range for abundance ratios is as follows: Use M+2/M+4, the theoretical ration is 0.65, and the control limits are 0.55 and 0.75.	H. The initial calibration curve includes six levels; the concentration of the lowest level is at one half the low point of the curve specified in Table 23-2 of EPA Method 23.	G. The internal standard mix includes <sup>12</sup> C-OCDF. The concentration of the <sup>13</sup> CC-OCDF is 200 pg/ul. OCDF is quantified against <sup>13</sup> CC-OCDF.	F. After clean-up, the clate is concentrated, added to a conical vial containing tetradecane and recovery standard solution, and concentrated again to a final volume 20 ul.	(continued) X. PCDDs/PCDFs A	Modification				
e os is as ical are 0.55	ides six ist level rve hod 23.	ified C	ntrated, olution, lume 20	nalysis Modific	i				
				(continued) X. PCDDs/PCDFs Analysis Modifications – SW-846 METHOD 8290 (Vista Analytical Laboratories, El Dorado, CA <sup>18</sup> )	Justification				
Minor	Minor	Minor	Minor	Analytical Labo	Modification Category <sup>15</sup>				
۷.	۷.	4	4	oratories,	B-901/2/3 <sup>1</sup>				
۷.	۷,	۷,	4	El Dorad	B-824 <sup>2</sup>				
Ţ	۷	٧	۷,	3, CA <sup>18</sup> )	F-210 <sup>3</sup>	Dow			
✓	۷	۷,	۷.		FTB-603 <sup>4</sup>	Freeport			
4	۷.	4	۷.		F-2820 <sup>5</sup>				
~	۷,	<b>ا</b>	ν.		B-33 RKI <sup>6</sup>				
√ 	۷.	٤	<b>خ</b> رو		F410/420 <sup>7</sup>				
۷,	۷,	<b>خ</b> ر	۷,		R-4 <sup>6</sup>	Dow Plaquemin e			
۷.	٠,	۷,	۷.		R-750 <sup>9</sup>				
۷,	اکر	۷,	4	×	B-53 <sup>10</sup>	UCC Texas City			
۷,	: <	۷,	۷.		V-A5 <sup>11</sup>	TEARS CITY			
۷.	۷,	٧	٨		6 & 712	Angus			
۷	۷,	4	۷,		MN-460 <sup>13</sup> Dow Clear Lal				
					HT-1 <sup>14</sup>	Rohm & Haas			

<sup>&#</sup>x27;Phase II (Boilers) Units: B-901, B-902, and B-903, Dow, Freeport, Texas.

<sup>&</sup>lt;sup>3</sup> Phase II (HAF) Unit: F-210, Dow, Freeport, Texas.

<sup>&</sup>lt;sup>5</sup> Phase II (Boiler) Unit: F-2820, Dow, Freeport, Texas.

<sup>&#</sup>x27;Phase II (Boilers) Units: F-410 and F-420 (Vinyls), Dow Plaquemine, Louisiana.

<sup>&</sup>lt;sup>9</sup>Phase II (Boilers) Units: R-750 (Chlorinated Methanes [CMP]), Dow, Plaquemine, Louisiana.

<sup>&</sup>lt;sup>11</sup>Phase I (Incinerator) Unit: VA-5, UCC, Texas City, Texas

<sup>&</sup>lt;sup>13</sup>Phase I (Incinerator) Unit: MN-460, Dow (formerly Celanese), Clear Lake, Texas.

<sup>&</sup>lt;sup>2</sup>Phase II (HAF) Unit: B-824, Dow, Freeport, Texas.

<sup>&</sup>lt;sup>4</sup>Phase II (HAF) Unit: FTB-603, Dow, Freeport, Texas.

<sup>&</sup>lt;sup>6</sup>Phase I (Incinerator) Unit: B-33 Rotary Kiln Incinerator, Dow, Freeport, Texas.

<sup>&</sup>quot;Phase II (Boiler) Unit: R-4 (Glycols), Dow Plaquemine, Louisiana.

<sup>&</sup>lt;sup>10</sup>Phase II (Boiler) Unit: B-53, UCC, Texas City, Texas.

<sup>&</sup>lt;sup>12</sup>Phase II (Boilers) Units: Unit 6 & 7, Angus, Sterlington, Louisisana.

<sup>&</sup>lt;sup>14</sup>Phase II (Boiler) Unit: HT-1, Rohm & Haas, Deer Park, Texas.

<sup>&</sup>lt;sup>15</sup> Deviations labeled as "Minor" have been submitted to EPA Region 6 for approval. Deviations labeled as "intermediate" have been submitted to EPA RTP for approval and approval was received via a letter for B-33 RKI that was applicable for all other similar facilities in this source category. See http://www.epa.gov/ttn/emc/approal/ALT053.pdf for a copy of the approval letter.

<sup>16</sup> TestAmerica Laboratories, Knoxville, TN maintains the following certifications, approvals, and accreditations: Louisiana DEQ Cert. #03079 and Texas CEQ

<sup>17</sup> URS Corporation, Austin, TX (Austin General Engineering) sampling laboratory maintains the following accreditation: Louisiana DEQ Cert. #84341.

<sup>18</sup> Vista Analytical Laboratories, El Dorado, CA maintains the following certifications, approvals, and accreditations: Louisiana DEQ Cert. #01977 and Texas CEQ T104704189-08-TX.