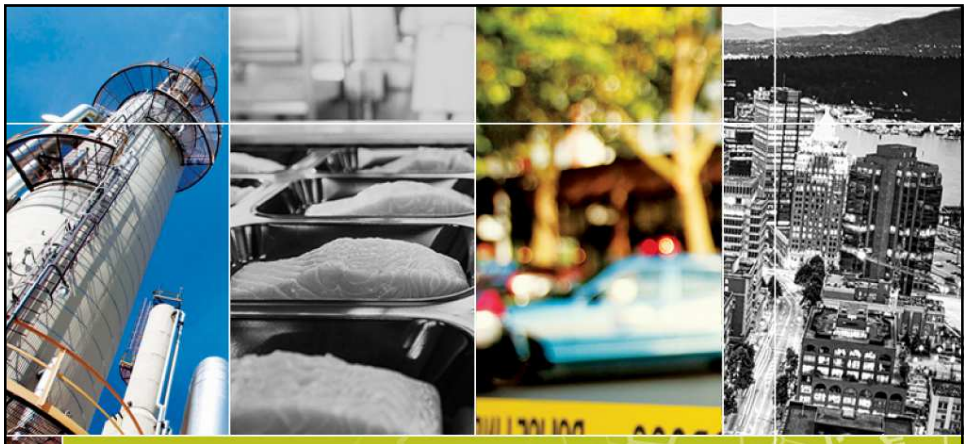

Stack Emission Services from the Laboratory's View

October 28, 2016

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Air Sampling Purpose

- Define Purpose and Objectives for Sampling
- What parameters and detection limits?
- These define Sampling and Analytical Methods

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Stack (Source Emissions) Sampling and Analysis

- Sources
- Stack Sampling Train
- Particulates and Inorganics testing
- Organics testing

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Maxxam's experience with Stack Testing

- Maxxam has worked on multiple projects where the USEPA data validators have reviewed project data and verified Maxxam's ability to generate acceptable packages of legally defensible data.
- Maxxam has been involved in the testing of over 8000 stack-related projects during the past 20 years.
- Maxxam presently handles 400-500 stack projects per year

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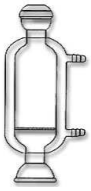
Customer Service and Communication

Much time is spent setting up each project (especially stack related):

- Project scope is defined (parameters and methods)
- About two weeks before the start date, stack sampling glassware is cleaned and proven
- Chemicals needed in the field are prepared
- Sampling media (filters, XAD-2 traps, sorbents, etc) are prepared
- Sampling material is picked up or delivered



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Sources Requiring Stack Testing

- trial burns
- annual permit resampling events
- sludge incinerators
- cement kiln annual programs
- hospital incinerators
- municipal waste incinerators (could be EFW)
- aluminum smelters
- a host of other manufacturing and service industries that thermally treat materials containing chlorine, heavy metals and inorganic or organic priority pollutants.

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Stack (Source Evaluation) from….

- Coal fired plants (not in Ontario)
- Process vents

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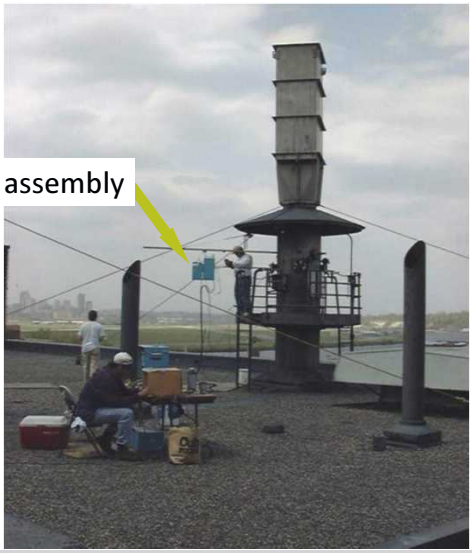
Iso-kinetic Stack Gas Sampling



- Before sampling, there are many steps required
- Laboratory activities are coordinated with the Stack Tester

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Stack Emission – Inorganics and Organics

- Particulates by filter and probe rinse
- Metals by filter and acidic impingers
- Ammonia by acidic impinger
- Hexavalent chromium by hydroxide solution
- Acid gases and halogens by impinger
- VOCs by VOST plus condensate
- Dioxins/furans/SVOCs by XAD trap (plus filter and rinses)

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Stack Emission Tests – Organics and Inorganics

Stack emission testing include:	
EPA Method 5 Total Particulate	Particulates – variations on Method 5
EPA Method 6 SO2	EPA 201/201A PM10
EPA Method 8 H2SO4 mist and SO2/SO3	EPA 202 Condensable Particulate Matter
EPA method 12 Total Lead	EPA 306, 0061 Hexavalent Chromium by IC/PCR
EPA Method 15/16 Sulfurs & Mercaptans	EPA 308 Methanol by GC/FID
EPA Method 18 VOCs by GC/FID	EPA 316 Formaldehyde
Canadian EPS 1/RM/2, 1/RM/3 and 1/RM/23 Dioxins & Furans by HRMS, SVOCs by LR-GC/MS	EPA 0010 SVOCs and PCBs
EPA Method 23 /23A Dioxins & Furans by HRMS	EPA 0011 Aldehydes and Carbonyls
EPA Method 24 Volatile Matter	EPA 0030/0031 VOST
EPA Method 26/26A HCl, HBr, HF, Cl2, Br2, F2	EPA 0060 Multimetals by ICP/MS
EPA Method 29 Multimetals by ICP/MS, ICP/AES plus Mercury	EPA 1668A PCB Congeners by HRMS
EPA CTM-027 Ammonia by IC	ASTM D 6784-02 Ontario Hydro Mercury Speciation
EPA 101A Mercury	CARB methods - many California Air Resources Board methodologies

Particulates and Metals by EPA Methods 5 and 29

- Laboratory is called upon to prepare and supply media, reagents and solvents
- Pre-weighed quartz filters
- Low particulate residue acetone
- High quality nitric acid for cleaning / recovery
- Nitric acid/peroxide mixture
- Permanganate/sulphuric acid for mercury



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Particulates and Metals by EPA Methods 5 and 29

After sampling, all filters, rinses, and impinger contents are submitted to the lab:

- Particulates are captured on the filter and also deposits on the probe – both fractions are critical – reported as total mass.
- Particulate-bound-metals will also be found on the filter and probe rinse.
- Each of the impinger contents and rinses are vital – every volume must be recorded to determine total mass of metals.

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Metals by EPA Method 29

Metals is Sum of Masses =

- Mass on filter + mass in acetone rinse
- Mass in nitric/peroxide impinger
- Mass in nitric rinse
- Mass in permanganate impinger (Hg)
- Mass in HCl rinse (Hg)

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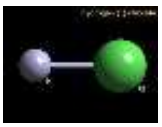
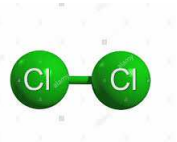
Acid Gases (HCl, HF, HBr) plus Halogens (Cl2, F2, Br2) by EPA Method 26A

- Acid gases are captured in the 0.1 N sulphuric acid impinger (which lets the halogens go through)
- Halogens are captured in the 0.1 N NaOH solution
- Each of the impinger contents and rinses are vital – every volume must be recorded to determine total mass of acids or halogens





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Acid Gases (HCl, HF, HBr) plus Halogens (Cl2, F2, Br2) by EPA Method 26A

The impinger contents are measured for anions by ion chromatography first reported in mg/L – as a liquid

Mass = concentration x volume of liquid

(mg) (mg/L) (L)

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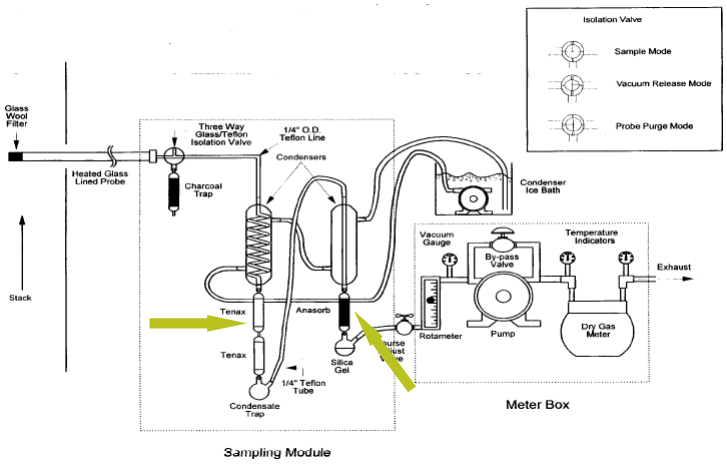
VOCs by VOST EPA 0031 - schematic



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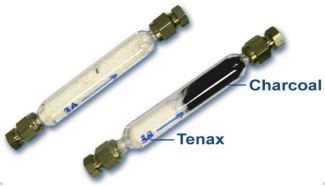
VOCs by VOST

- VOST tubes capture most of the analytes – reported as total mass.
- Some liquid will condense from wet sources in the first impinger.
- This condensate is tested for the same VOCs as the VOST in the same manner as a water sample – the volume of liquid is critical to determine total mass of VOCs.



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VOCs by VOST

Parameter	MDL (ug)
1,1,1,2-Tetrachloroethane	0.01
1,1,1-Trichloroethane	0.01
1,1,2-Trichloroethane	0.02
1,1-Dichloroethane	0.01
1,1-Dichloroethylene	0.01
1,2-Dichloroethane	0.01
1,2-Dichloropropane	0.01
Acetone (2-Propanone)	0.05
Benzene	0.01
Bromodichloromethane	0.01
Bromomethane	0.02
Carbon Disulfide	0.03
Carbon Tetrachloride	0.02
Chlorobenzene	0.01
Chloroethane	0.01
Chloroform	0.01
Chloromethane	0.02
cis-1,2-Dichloroethylene	0.01
cis-1,3-Dichloropropene	0.01
Dibromochloromethane	0.01
Dibromomethane	0.01
Dichlorodifluoromethane	0.02
Ethylene Dibromide	0.01

Parameter	MDL (ug)
Iodomethane	0.02
Methyl Butyl Ketone (2-Hexanone)	0.03
Methyl Ethyl Ketone (2-Butanone)	0.04
Methyl Isobutyl Ketone	0.02
Methylene Chloride	0.02
Tetrachloroethylene	0.02
Toluene	0.01
trans-1,2-Dichloroethylene	0.01
trans-1,3-Dichloropropene	0.01
Trichloroethylene	0.01
Trichlorofluoromethane (FREON 11)	0.01
Vinyl Chloride	0.01
Vinyl Acetate	0.02
1,1,2,2-Tetrachloroethane	0.01
1,2,3-Trichloropropane	0.02
1,2-Dichlorobenzene	0.02
1,3-Dichlorobenzene	0.02
1,4-Dichlorobenzene	0.02
Bromoform	0.01
Ethylbenzene	0.01
m / p-Xylene	0.02
o-Xylene	0.02
Styrene	0.01

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General Dioxins/Furans and SVOC Train – example

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Dioxins/Furans and SVOCs using XAD Trap - Based on EPS 1/RM/2, 3, and 23 – lab preparation

- XAD-2 resin is cleaned and proofed
- pre-filters are cleaned
- Train components received from stack tester are cleaned; final solvent rinse of glassware is saved and analysed (proof) for the analytes of concern
- All solvents to be used in the field are proofed
- In high profile cases, all bottles to be used for sample recovery, are proofed

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Dioxins/Furans and SVOCs using XAD Trap - Based on EPS 1/RM/2, 3, and 23 – after sampling

- XAD trap and pre-filter capture most of the analytes
- Train components are also rinsed so any residual analytes are dissolved in the solvent rinses
- The volumes of these rinses are not critical in the calculation of mass, but total mass contained must be included, i.e. no volume of solvent lost during the extraction process
- Total mass = sum [XAD + filter + impinger contents + rinses]

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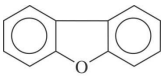
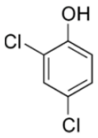
Dioxins/Furans and SVOCs using XAD Trap - Based on EPS 1/RM/2, 3, and 23 – after sampling

Extracts can be tested for a number of SVOC parameters including:

- Dioxins/furans
- PCBs (as congeners or homologue groups
- Chlorobenzenes
- PAHs
- Chlorophenolics



Dibenzofuran



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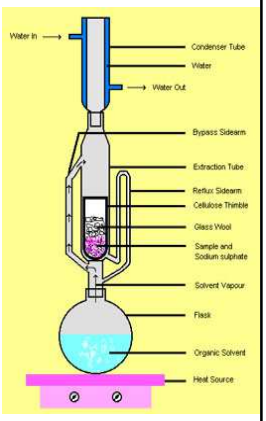
Dioxins/Furans - Based on EPS 1/RM/2, 3, and US EPA Method 23 - extraction

- This method is used to measure polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) emissions from combustion sources at low pg to ng levels.
- The PCDDs and PCDFs are extracted from the sampling train apparatus with toluene. Following extraction, the samples are cleaned up and passed through a series of columns that remove, by reaction and/or selective adsorption, the bulk of the organic matrix co-extracted with the PCDDs and PCDFs.



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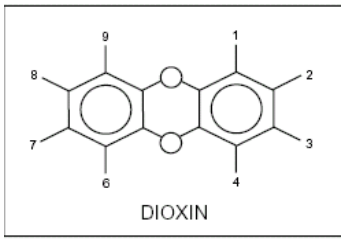
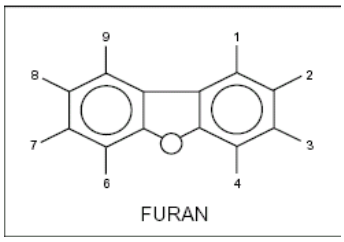
Structure of Dioxins and Furans



DIOXIN



FURAN

General chemical structures of dioxins and furans are depicted.

Congeners with chlorine in the 2, 3, 7 and 8 positions are considered toxic.

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Dioxins/Furans - Based on EPS 1/RM/2 & 3, and US EPA Method 23

- The resulting fraction is concentrated to a known volume for analysis. Qualitative/quantitative analysis for PCDDs and PCDFs are separated by high-resolution capillary gas chromatography (HRGC) and measured by high-resolution mass spectrometry (HRMS).
- PCDDs and PCDFs are identified by comparing gas chromatographic (GC) retention times and the ion abundance ratios of the m/z's with the corresponding values obtained for authentic standards.

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Dioxins/Furans - Based on EPS 1/RM/2 & 3, and US EPA Method 23

- The resulting fraction is concentrated to a known volume
- The HRGC/HRMS system is calibrated and the analyte concentration is determined using an isotope dilution technique.
- Quantitation is based on the use of internal standards and relative response factors (RRFs). Total PCDDs and PCDFs are reported as the sum of the individual isomers, corrected for internal standard recoveries.

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Dioxins/Furans - Based on EPS 1/RM/2 & 3, and US EPA Method 23

Capillary Columns:

- the primary column for the analysis of dioxins and furans is a fused silica column, Varian CP-Sil 8 CB
- If the 2,3,7,8-TCDF congener is suspected of being present then……
- the confirmation column is a fused silica column, Restek, Rtx-Dioxin2 for the specific quantification of 2,3,7,8-TCDF (secondary column)

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Dioxins/Furans - Based on EPS 1/RM/2 & 3, and US EPA Method 23 – clean-up procedures

- PCDDs and PCDFs are often associated with other chlorinated organics, which may potentially interfere with the analysis.
- These include PCBs, polychlorinated methoxybiphenyls, polychlorinated hydroxy diphenylethers, polychlorinated benzylphenyl ethers, polychlorinated diphenyl ethers (DPEs), polychlorinated naphthalenes, polychlorinated xanthenes, polynuclear aromatics, and pesticides.

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Dioxins/Furans - Based on EPS 1/RM/2 & 3, and US EPA Method 23

The following clean-up procedures can be used:

- Extract Preparation is completed then…..

- Mixed Bed Silica Gel Column Clean-Up
- Secondary H_2SO_4 Acid/Silica Gel Clean-Up – if required
- Basic Alumina Column Clean-Up
- Carbon/Celite Column Clean-Up

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Dioxins/Furans - Based on EPS 1/RM/2 & 3, and US EPA Method 23 – clean-up procedures

Mixed Bed Silica Gel Column Clean-Up

- The acid silica gel removes any oxidizable contaminants including PAHs and some organochlorine pesticides, many of which are oxidized to acids.
- The basic silica gel removes any acids and phenols. The high water content of the acid and base silica gel deactivates the silica to the point where the silica gel acts only as a support for the acid and base.
- The $AgNO_3$/Silica gel reacts with organic thio-compounds, molecular sulphur and olefins, complexing them and retaining them on the column.

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Dioxins/Furans - Based on EPS 1/RM/2 & 3, and US EPA Method 23 – clean-up procedures

Basic Alumina Column Clean-Up:

- Alumina is slightly basic, so will retain acidic compounds more strongly.
- It is good for separation of components that are weakly or moderately polar and the purification of amines.

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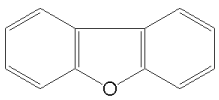
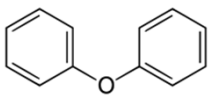
Dioxins/Furans - Based on EPS 1/RM/2 & 3, and US EPA Method 23 – clean-up procedures

Carbon/Celite Column Clean-Up:

- Final clean-up step routinely used at Maxxam
- Primary benefit is (partial) removal of chlorinated diphenylethers, which could positively enhance furan result(s)



Dibenzofuran



Diphenylether

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Customer Service and Communication

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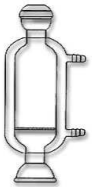
- About two weeks before the start date, stack sampling glassware is cleaned and proven
- Chemicals needed in the field are prepared
- Sampling media (filters, XAD-2 traps, sorbents, etc) are prepared
- Sampling material is picked up or delivered



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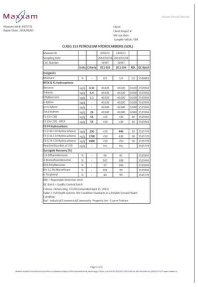
Customer Service and Communication

Laboratory reports include the following as a minimum:



a. Date sample
b. Sample location and field ID
c. Date of sample receipt
d. Parameter results of analysis
e. Field QC results (and recovery)
f. Lab QC results (and recovery)
g. Date of sample analysis
h. Lab analyst who performed the extraction or analysis
i. Any notes concerning the processing of the samples; difficulties encountered, if any
j. An electronic file as well as PDF version

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Customer Service and Communication

Laboratory reports can include, as options at extra charge, the following:

a. All raw instrument output to allow a third party data validator to verify calculations and interpretations
b. Database file

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Customer Service and Communication

When issues are identified….Maxxam has an internal protocol whenever an unusual set of circumstances are observed.

- This process begins with the review of the scope of work
- Continues with sample receipt and inspection
- Once sample tests are approved for every sample
- Any difficulties encountered during sample preparation or analysis
- Unusual QC results

The customer is notified as soon as possible to discuss the issues, solutions and next steps.

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