High Moisture Sources And Stack Testing

Jerry Winberry

Sampling Methods For Stacks With High Moisture Content

High moisture sources:

- Ammonium nitrate prilling facilities
- Lime hydrators
- Evaporators
- Coke oven quench towers

The Problem

$$\Delta H = D_n^4 \left[\frac{\pi K_p C_p}{4K_m}\right]\left[\frac{M_d(1-B_{ws})^2}{M_d(1-B_{ws})+18(B_{ws})}\right]\left[\frac{T_m P_s}{T_s P_m}\right]\Delta P$$

Sampling Problems

- Erroneous readings due to low flow rate through orifice
- Inaccurate control of sampling rate due to small volume of gas passing through control valves
- Non-isokinetic sampling due to fluctuations in moisture content of stack gas

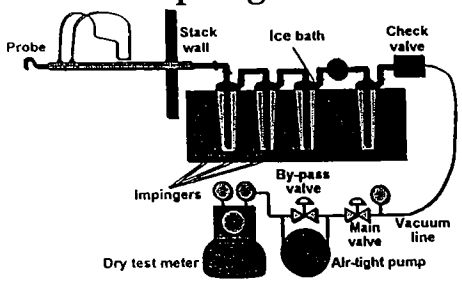
Solution

- Place orifice meter before impingers
- Total sample volume passes through orifice meter
- Moisture content measurement unnecessary
- Isokinetics not affected by moisture changes

JACA Corporation Method

- Advantages
- Prevention of condensation at orifice
- Protection from particulate fouling
- Disadvantages
- Orifice meter pressure does not remain constant

EPA High Moisture Sampling Train



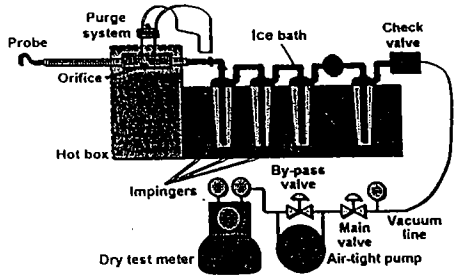
EPA Method

- Developed for use at ammonium nitrate facilities
- Consists of an in-situ orifice with a changeable orifice plate
- Filter located before silica gel impinger
- Probe heated to prevent condensation

EPA Method Isokinetic Sampling Rate Equation

$$\Delta H = D_n^{\,4}\left[\frac{K_p C_p}{4K_m}\right]^2 \Delta P$$

High Moisture Sampling Train



Problems Common To All Three Methods

- Entrained water droplets
- Condensation in manometer lines
- Improper condensation in impingers

SW-848, Method 0023A

Sampling and Analysis for Polychlorinated DiBenzo-p-Dioxins (PCDDs) and Polychlorinated Dibensofurans (PCDFs)

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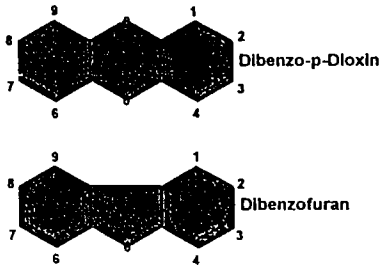
Applicability

- This method is applicable to the determination of PCDDs and PCDFs from stationary sources
- Simultaneous sampling and analysis for polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), and semi-volatile organic compounds (SVOCs) can also be performed

What Are Dioxins?

- Dioxin is a family of 210 different molecules with one or two basic structure:
  - The dioxin structure with two oxygen atoms
  - The furan structure with one oxygen atom

Structures Of Dioxins And Furans



Differences Between Molecules

- The differences between the molecules lie in the number and attachment positions of chlorine atoms.

Chlorinated Dioxins And Furans

- 7-2,3,7,8-substituted chlorinated dioxins
- 75 Total chlorinated dibenzo-p-dioxins

Chlorinated Dioxins And Furans

- 10-2,3,7,8-substituted chlorinated furans
- 135 Total chlorinated dibenzofurans

Congeners

- Molecules with different chemical formulas and the same basic structure are referred to as congeners. Generally, the most common one is octachlorodibenzo-p-dioxin (OCDD), with chlorine in all eight available positions.

Interference's

- If not using high resolution GC/MS, then interferences from polychlorinated biphenyls and polychlorinated diphenyl ethers could effect low resolution techniques.

Interference's

- Very high amounts of other organics compounds in the matrix will interfere with the analysis
- Contamination in solvents, reagents, glassware, and other sampling processing hardware (all glassware must be cleaned thoroughly before use)

Method 0023A Design Requirements

- Gas flow measurement system (EPA Methods 2-4)
- Modified Method 5 sampling train, retaining heated filter
- Addition of condenser and XAD-2 resin trap

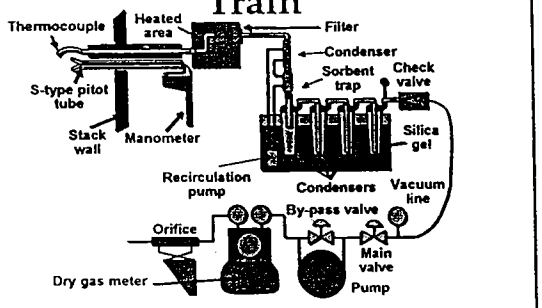
Method 0023A Sampling Train

- Probe with nozzle
- Pitot tube/temperature sensor array
- Heated filter assembly
- Condenser/XAD-2 resin trap assembly

Method 0023A Sampling Train

- Condensing impingers
- Silica gel
- Pump/dry gas meter/orifice assembly

Method 0023A Sampling Train



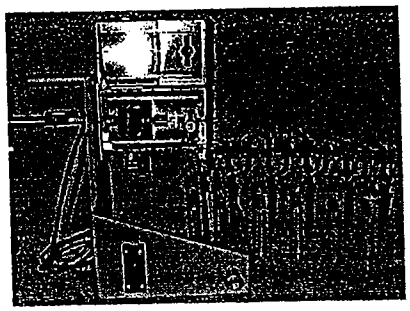
XAD-2 Resin Trap

- XAD-2 is a cross-linked styrene-divinylbenzene(-CH_2-CH-CH_2-CH-CH_2)-Organic Polymeric Adsorbent
- Amberlite XAD-2 physical characteristics:

  Mesh Size: 20-60
  Bulk Density: 1.08 g/mL
  Surface Area: 300 m2/g
  Temp. Max: 190° C

Demo

Method 0051 Sample Train



Method 0051 Sample Train

Operational Requirements

- Single point (> 1 meter) integrated sampling
- Purging of probe for 5 minutes prior to sampling
- Probe/filter at 120° C (248° F)
- Sampling at 2 L/min for 60 minutes

Operational Requirements

- Leak-free system
- Performance evaluation (PE) sample

Method 0051 Chemistry

- Impingers 2 & 3 remove HCl from sample gas stream by the following equation:

  $HCl + Water(Acidic) = H_3O + Cl^-$

Method 0051 Chemistry

- Impingers 4 & 5 remove Cl_2 from the stack gas stream by the following reaction:

  $Cl_2 + H_2O(Basic) = H^+ + Cl^- + HClO$

Method 0051 Impinger Arrangement

- 1st impinger (Optional)
  - empty
- 2nd and 3rd impingers
  - 15 mL of 0.05 M H_2SO_4

Method 0051 Impinger Arrangement

- 4th and 5th Impingers
  - 15 mL of 0.1 M NaOH
- 6th Impinger/drying tube
  - 30 g silica gel

Method 0051 Operation

- Preliminary field determination (sample location, recovery area) same as FRM 6
- Sample train preparation (charging of filter and impingers) same as FRM 6

Method 0051 Operation

- Pre-leak check (-10 " Hg) stopcock, probe, and filter prior to inserting probe into stack
- Pre-leak check (-10 " Hg) impinger and meter box assembly before testing

Method 0051 Operation

- Purge probe/filter assembly at 2 L/min for 5 minutes
- Position probe/Teflon-elbow pointing downstream
- Sample collection in general accordance with FRM 6
- Sample at 2 L/min for 60 minutes

Method 0051 Operation

- The last impinger of the 0.1 M NaOH must be maintained strongly basic during sampling. Monitor pH of solution frequently. To resolve:
  - Use stronger base (0.5M)
  - Add volume to impinger (30 mL)
  - Recharge impinger during sampling

Method 0051 Operation

- Leak check before/after component changes during sample run
- Post-leak check in accordance with FRM 6

Sample Train Recovery Containers

- 1- Combined impingers 1,2 and 3 (measured) and water rinses
- 2- Combined impingers 4 and 5 (measured) and water rinses (add 2 mL of $Na_2S_2O_3$)
- 3- Silica gel contents (note color,weigh)

Sample Train Recovery

- (Overhead of Method 0051 Sample Train Recovery Scheme)

Analysis

- Analysis of recovery reagents for Cl- by SW-846, Method 9057, Ion Chromatography

Method 0051 QA/QC Requirements

- (Overhead of Method 0051 QA/QC Requirements)

Method 0051 Key Points

- System uses a modified FRM 6 sampling train
- Sampling is performed at 2 L/min for 60 minutes

Method 0051 Key Points

- Methodology quantitates HCl from Cl_2 emissions
- Must maintain last impinger of NaOH strongly basic

Method 0051 Key Points

- Two tier pre-test leak check (-10 " Hg):
  - Stopcock, probe, and filter
  - Impinger and meter box assembly
- Can also determine moisture of stack gas

Method 0051 Key Points

- Glass lined probe/Teflon elbow and Teflon filter assembly only
- Methodology limited to relatively dry, particulate-free gas streams

Method 0051 Observer Checklist

- (Overhead of Method 0051 Observer Checklist)

Sample Train Recovery Containers

- 5A- Impinger 4 (measured) and HNO_3 rinse of impinger 4 (100 mL)
- 5B- $KMNO_4$ impingers contents (measured) and $KMNO_4$ (100 mL) + water (100 mL)
- 5C- 8 M HCl (25 mL) rinse of the two impingers and transferred to container containing water (200 mL)

Sample Train Recovery Containers

- 6- Silica gel contents (note color, weigh)
- 7- Acetone blank (100 mL)
- 8A- HNO_3 reagent blank (300 mL)
- 8B- Water reagent blank (100 mL)
- 9- 5 % HNO_3/10% H_2O_2 reagent blank (200 mL)

Sample Train Recovery Containers

- 10- $KMNO_4$ reagent blank (100 mL)
- 11- 8 M HCl reagent blank (200 mL of water + 25 mL of 8 M HCl)
- 12- Filter blank