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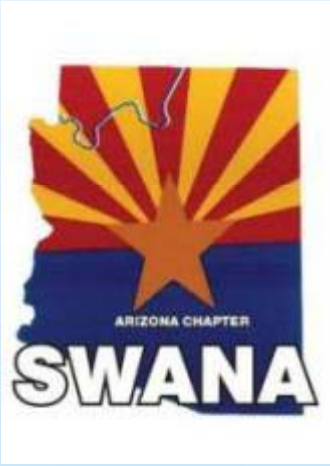
Test Methods to Evaluate Landfill Gas

Jim Cetrullo

Landfill Programs



Arizona Chapter of the Solid Waste Association of North America

2010 Twentieth Annual Arizona Solid Waste Management Seminar

http://www.azswana.org/

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Landfill Gas Emissions

……..Attracting more regulatory attention:

- Local Odor & Nuisance
- Fire and Explosive Potential
- Contribute to Ground Level Ozone
- Health Risks from hazardous air pollutants, both carcinogens and non-carcinogens
- Green House Gases –Methane and CO2 Emissions
- Use for Gas to Energy Projects
- Carbon Credits for renewable energy source

Federal Regulations

In March 1996, the EPA promulgated Clean Air Act (CAA) regulations for MSW landfills because of the concern to public health and the environment (EPA, 1996, EPA 1998).

Regulations require that large MSW landfills

2.5 million megagrams (Mg) and 2.5 million cubic meters or more of waste - must collect and control if their estimated emissions of NMOCs are 50 megagrams per year or more.

Subsequent updates to

40 CFR Part 60, 61, and 63 Amendments for Testing and Monitoring

40 CFR Part 63 National Emission Standards for Hazardous Air Pollutants: Municipal Solid Waste Landfills

- **Methane used as a surrogate for NMOC Control Tier II Testing**

Federal Register / Vol. 71, No. 174 / Friday, September 8, 2006 / Proposed Rules 40 CFR Parts 60, 62, and 63

- **Standards of Performance, Emission Guidelines, and Federal Plan for Municipal Solid Waste Landfills and National Emission Standards for Hazardous Air Pollutants: Municipal Solid Waste Landfills**
- **Allows combustion of Landfill Gas as an accepted control technology for NMOC reduction**
- **New Source Performance Standards NSPS Rules; AP-42 in works**

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Landfill Gas Composition

Typical Composition

Component	Percent by Volume	Atmosphere Concentration
Methane CH4	45 to 60	Colorless odorless gas 0.0002%
Carbon Dioxide CO2	40 to 60	Atmosphere 0.03%
Nitrogen N2	2 to 5	Atmosphere 79%
Oxygen	0.1 to 1.0	Atmosphere 21%
Ammonia	0.1 to 1.0	Pungent Odor Atmosphere 0.0001%
NMOC's	0.01 to 0.6	Organic Compounds
Sulfides	0 to 1.0	Unpleasant odors 0.001%
Hydrogen	0 to 0.2	Atmosphere 0.00005%
Carbon Monoxide	0 to 0.2	Colorless odorless gas

LFG contains significant volume of methane that can be used as a fuel.
LFG is dried, compressed, and chemicals removed that cause operational or emissions concerns; sulfide, halides, siloxanes
Carbon dioxide can be removed to upgrade BTU content of gas.

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Landfill Gas Composition

Volatile compounds:	**Volatile compounds (continued):**	
Methane	Methyl isobutyl ketone	
Ethane	Methylene chloride	PCBs
Propane	Propylene dichloride	
Butane	t-1,2-Dichloroethene	Mercury:
Pentane	Tetrachloroethene	Organo-mercury compounds
Hexane	Toluene	Total
Carbonyl sulfide	Trichlorethylene	Elemental
Chlorodifluoromethane	Vinyl chloride	
Chloromethane	Vinylidene chloride	Gases:
Dichlorodifluoromethane	Ethanol	CO2
Dichlorofluoromethane	Methyl ethyl ketone	O2
Ethyl chloride	2-Propanol	
Fluorotrichloromethane		Moisture
1,3-Butadiene	**Semi-volatile compounds:**	
Acetone	1,4-Dichlorobenzene	Reduced-sulfur compounds:
Acrylonitrile	Ethylbenzene	Hydrogen sulfide
Benzene	Xylenes	Methyl mercaptan
Bromodichloromethane		
Carbon disulfide	Polycyclic aromatic hydrocarbons (PAHs)	
Carbon tetrachloride		
Chlorobenzene		
Chloroform	Total - NMOC (Method 25C)	
Dimethyl sulfide		
Ethyl mercaptan	**Carbonyls:**	
Ethylene dibromide	Acetaldehyde	
Ethylene dichloride	Formaldehyde	
Methyl chloroform		

Landfill Gas Constituents; combined represent Non Methane Organic Compounds “NMOC’s”

Hydrogen Sulfide
Halides
Metals: Mercury

Pending Air Toxics regulations AP 42

U.S. **EPA’s Field Test Programs to Update Data on Landfill Gas Emissions Susan A. Thorneloe** *Air Pollution Prevention and Control Division, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 27711, USA*

Flare Testing

U.S. EPA's Field Test Programs to Update Data on Landfill Gas Emissions

Sampling LFG Flare

Flare compounds of interest

Gases:	Dioxins/Furans
O2	
CO2	PAHs
CO	
NOx	Mercury
SOx	
Total Hydrocarbons	Metals:
	Pb, As, Cd, Cr, Mn, Ni
HCl	

CAA & Amendments & MACT Rules

Method 26/26A or Method 0050 for HCl and Cl2
Method 29 or Method 0060 for Metals and Mercury
Method 0023A for Dioxins and Furans
Method 0010 for TCO/GRAV Unspeciated Mass
Method 0030 or Method 0031 for Volatile Organics
Method 0010 for Semivolatile Organics
Method 0010 for PAH in Stack Gas Emissions

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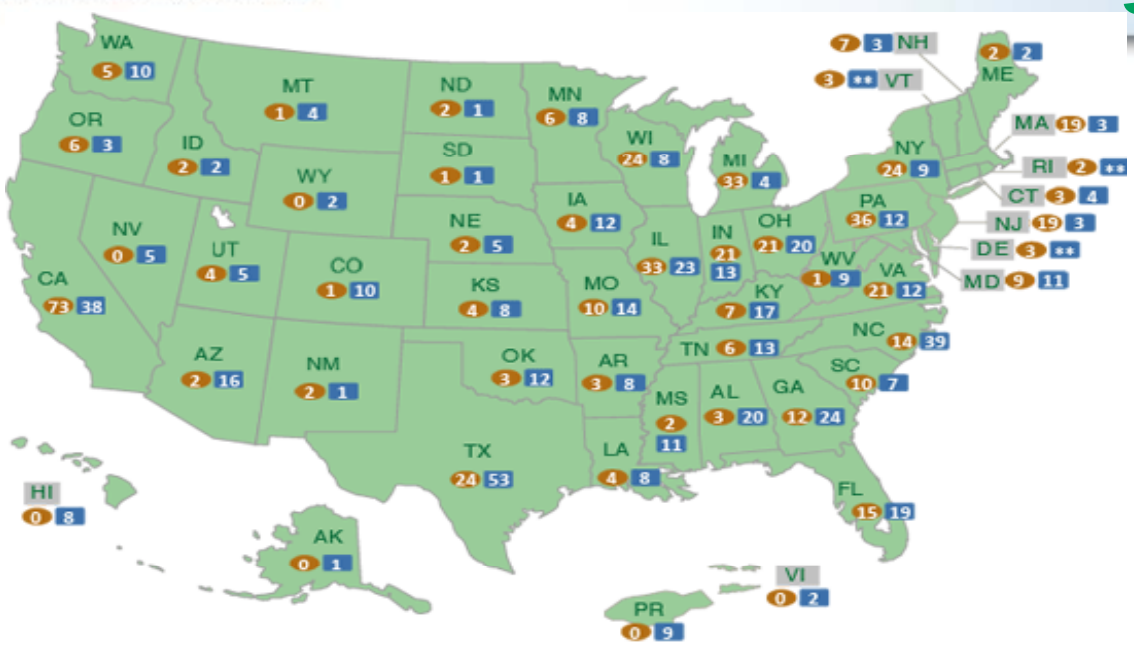
EPA Landfill Methane Outreach Program



http://www.epa.gov/lmop/index.htm

Nationwide Summary
509 OPERATIONAL Projects (1,563 MW and 304 mmscfd)
~530 CANDIDATE Landfills (1,170 MW or 600 mmscfd, 13.5 MMTCE Potential)

OPERATIONAL PROJECTS

CANDIDATE LANDFILLS*

* Landfill is accepting waste or has been closed for 5 years or less has at least 1 mmtons of waste and does not have an operational/under construction LFGE project; or is designated based on actual interest/planning.

These data are from LMOP's database as of December 16, 2009.

** LMOP does not have any information on candidate landfills in this state.

Extension of Tax credits for LFG to Energy projects

On October 3, 2008, the President signed into law H.R. 1424 - The Emergency Economic Stabilization Act of 2008 The bill included a two year extension of the production tax credit for WTE and LFG as well as other renewable sources of energy. The placed in service date is now December 31, 2010.

Landfill Gas Data Collection

Components of Landfill Gas can have effects on;

- Operation and performance issues
- Emissions considerations - Title V permitting

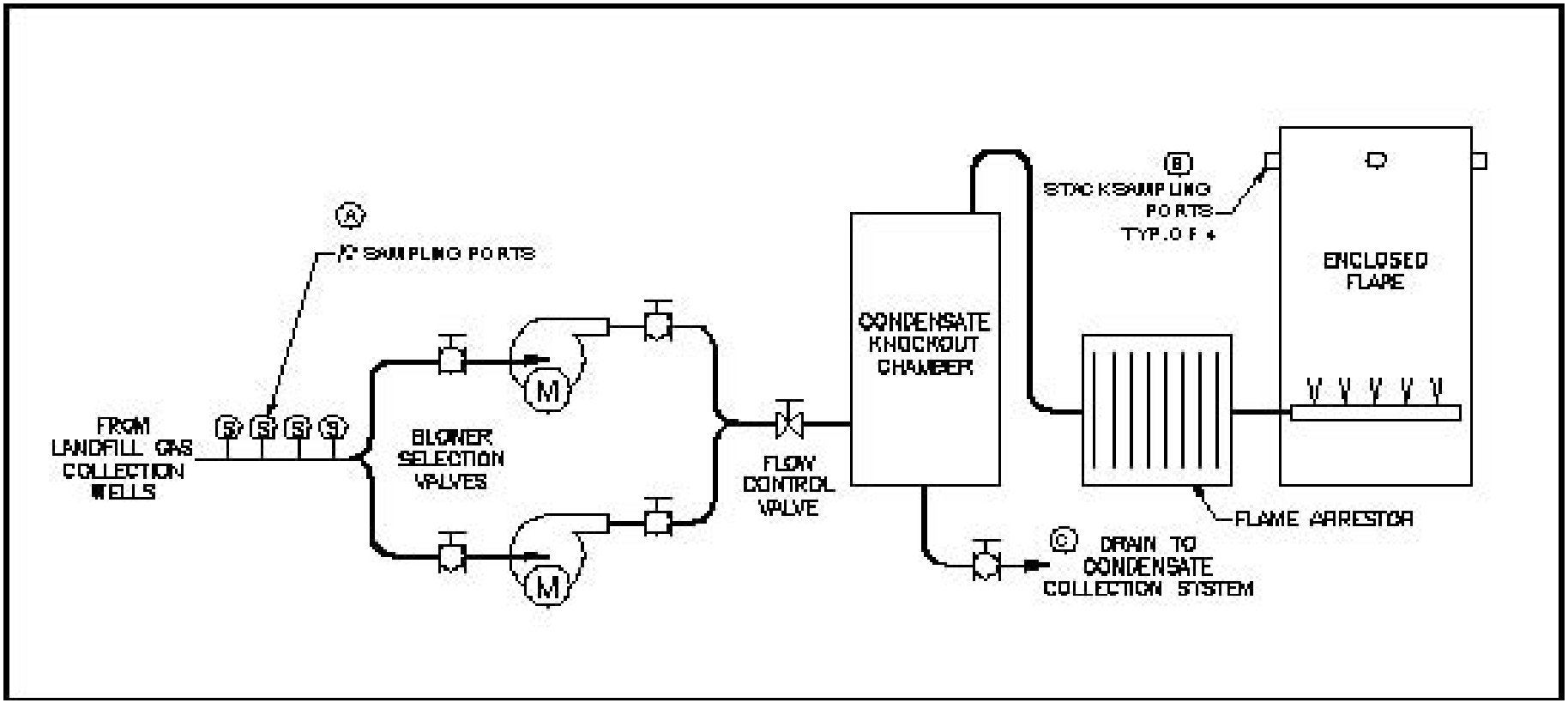
Landfill Gas Analysis offers unique challenges

- Testing protocols, shipping and handling are critical.
- Landfill Gas contains compounds that are very reactive
- High moisture content can have an impact on final data

Data Quality Considerations before sampling

- What am I going to use the data for? Regulatory or informational
- Is there operational variability; What is the range?
- Is the data going to be representative, and representative of what?
- Is the laboratory certified, qualified, and notified?

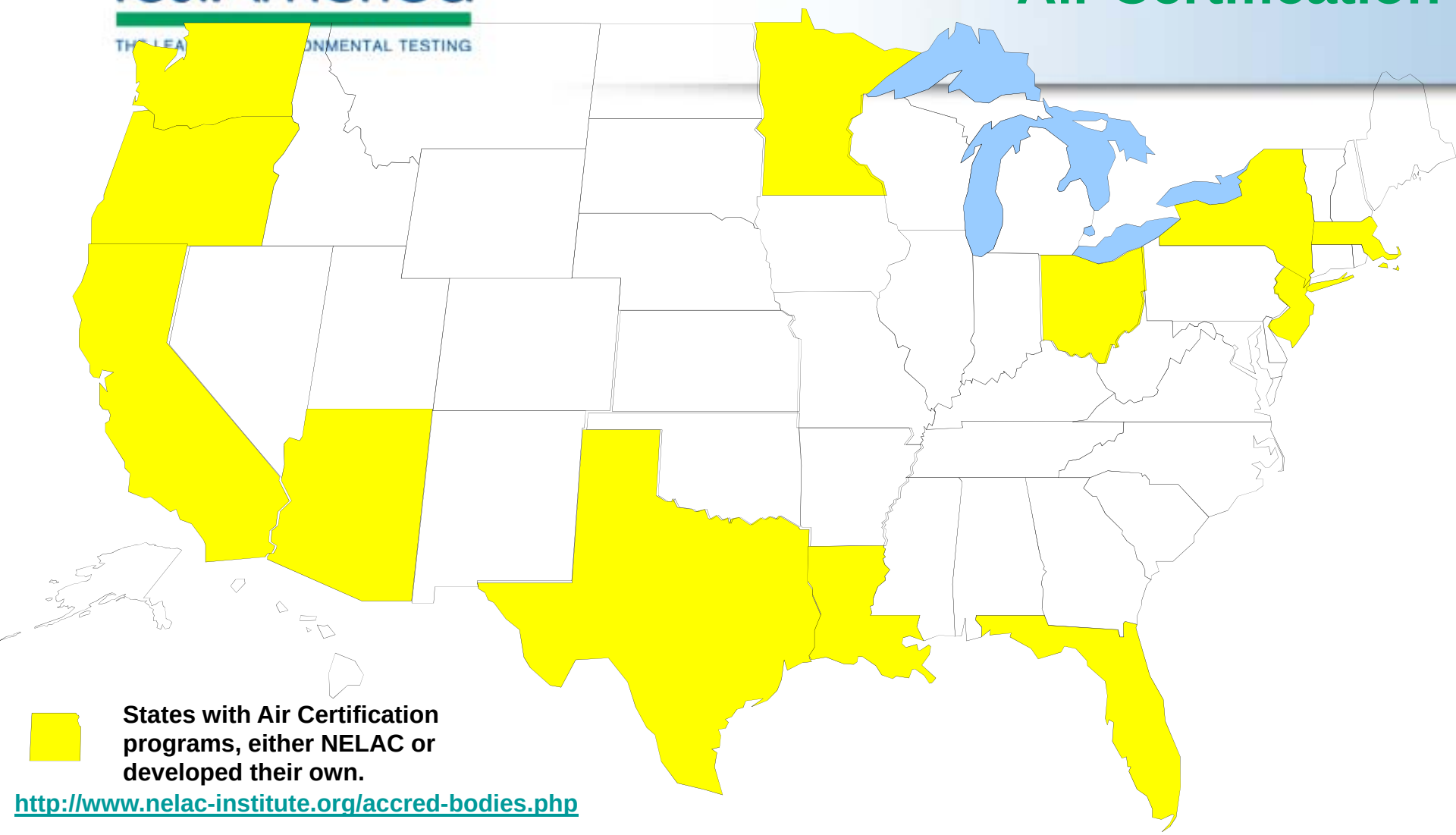
Landfill Gas System - Sampling



www.**erefdn.org**/rpts_summary_ordrs/Landfillgas.pdf

U.S. EPA's Field Test Programs to Update Data on Landfill Gas Emissions
Susan A. Thorneloe
Air Pollution Prevention and Control Division, Office of Research and Development,
U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 27711, USA

Air Certification



States with Air Certification programs, either NELAC or developed their own.

http://www.nelac-institute.org/accred-bodies.php

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Typical Test Methods

Analytes	Method	Detector	Comments
Permanent Gases CO2, CH4, O2, N2	ASTM D1946	TCD	Performance monitoring
Permanent Gases CO2, CH4, O2, N2	Method 3C	TCD/FID	
BTU Content	GPA 2172-92 ASTM D3588	Calculation TCD/FID	Wet & Dry BTU
Non-Methane Organic Carbon (NMOC's)	Modified EPA 25 C (TO3)	FID	Required for Emissions compliance Tier II
Speciated VOC's	TO14/15	GC/MS	Used for screening composition of NMOC's Halides by Calculation
Hydrogen Sulfide, Mercaptans & Total reduced Sulfur	Method 15/16	FPD	Method ASTM 5504 Very sensitive
SILOXANES	Mod TO15 /Mod 8260	GC/MS	Two Methods Whole Gas/Impinger

Test Methods

Regulations, State Certification, and QA/QC define Test Method Selection

Is the Method and testing application defined in Promulgated Regulation? If so, the referenced method should be performed.

Key Method: NMOC *Non-Method Organic Carbon*

EPA 25C and EPA Method 18 are the methods referenced in the Federal Register. NMOC is defined by the method(s) and is a term used only in regards to Landfills

Many methods used in Chemical Testing Landfill Gas not listed in the FR. US EPA Compendium Methods, TO & IO are Guidance methods and should not be used for regulatory compliance unless written into a permit; but are generally accepted for informational testing.

We see State authorities & EPA approve, permit or accept these and other methods. It is important that the method is applicable to matrix of the sample being analyzed.

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A recent case

- Client was asked to perform analysis for VOC's by Method 320 FTIR for a permit.
- The method is in regulation to measure VOCs for stack emissions but not for LFG.
- The FTIR detection system uses infra-red whose performance is significantly affected by the presence of water & carbon Dioxide. Both are present in LFG and can vary over time.
- The best practice for Method 320 analysis of LFG is that the testing needs to be done in real time on site with a complex set up to allow for the potential variability in water (& carbon dioxide) content in the gas stream.
- Method 320 is difficult to perform in the field on LFG, very expensive, low confidence in the resulting data

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Alternate Method TO 15

ANALYTE	Result	Result	Result	Result	Result	Result	UNITS
Acetone	7800	5900	9500	6400	13000	5600	ppbv
Benzene	1100	950	1400	1100	1900	1300	ppbv
cis-1,2-Dichloroethene	880	660	1000	600	1100	720	ppbv
Dichlorodifluoromethane	ND	870	1300	870	930	ND	ppbv
Ethylbenzene	5500	4300	6400	4400	7700	5800	ppbv
Methylene chloride	800	790	1200	830	1600	920	ppbv
Styrene	710	560	860	500	980	670	ppbv
Tetrachloroethene	910	610	900	600	1000	690	ppbv
Trichloroethene	380	330	420	330	510	370	ppbv
Trichlorofluoromethane	450	430	640	450	820	ND	ppbv
Vinyl chloride	ND	720	950	720	1000	ND	ppbv
Xylenes, total	13000	10000	15000	10000	19000	14000	ppbv
1,4-Dichlorobenzene	460	ND	510	ND	550	ND	ppbv

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Sulfur Testing In Landfill Gas

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Sulfur in Landfill Gas

- Sampling and Analysis:
  - Regulatory monitoring requirements
  - Potential Health and Safety Risks
  - Impacts on equipment – engines, turbines
  - Treatment Processes
- Hydrogen Sulfide as primary reduced sulfur component in LFG (typically 90% or more)
- Identified Large Variability in Testing results
- Concern about shipping LFG

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Variables in Sampling and Analysis

- H_2S is highly reactive (also light sensitive)
- Sampling containers may contain “active” sites that catalyze reactions
- Sampling Methods – (raw gas, post compression or other sample “handling”)
- Hold Time Prior to Analysis
- Analytical Methods (field vs lab)
  - ~ Lab methods typically EPA 15/16 or ASTM D5504

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Investigation at Two Landfills

Container	Sampling Approach	Analytical Method	Comments
None	Raw Gas	Electrochemical cell	Field meter
Tedlar Bag	Raw Gas and Raw Gas with container flush	EPA 15/16	Also looked at effect of hold times
Tedlar Bag	Raw Gas with container flush	EPA 15/16	Also looked at effect of hold times
SUMMA Canister	Raw Gas	EPA 15/16	Also looked at effect of hold times
Impinger	Raw gas – calibrated pump	EPA 300	Used as a cross-check on H2S concentrations and to assess viability to eliminate shipping concerns.
Charcoal Tube	Raw Gas – calibrated pump	NIOSH 6013	Used as a cross-check on H2S concentrations and to assess viability to eliminate shipping concerns.

Typical Sample Containers for Landfill Gas Collection

SUMMA Canister

Tedlar bag

SUMMA Canisters are generally pre-filled with He to dilute the methane and make them easier to ship

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Shipping Challenges

Sampling Overseas
Setting up sampling point
Connecting to SUMMA Canister
Sampling done; tightening dust cap
Ready to return!

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SUMMA's vacationing in Morocco

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Impingers in the Field

Hydrogen Sulfide Test Results – Site 1

		24hrs	48hrs	72hrs	1 week
Sample ID	Container	ppmv	ppmv	ppmv	ppmv
Raw Gas #1	SUMMA	81	79	68	64
Raw Gas #2	SUMMA	30	12	5.2	ND
Raw Gas #3	SUMMA	ND	ND	ND	ND
Raw Gas #1	Tedlar	130	97	91	82
Raw Gas #2	Tedlar	110	100	94	64
Raw Gas #3	Tedlar	110	100	99	72
Feed Gas	Tedlar	110		100	80

Raw Gas #1	Charcoal	98.3
Raw Gas #2	Charcoal	72.7
Raw Gas #3	Charcoal	91.1

Field measured Concentration ~200ppmv

Tedlar (flushing technique) 150ppmv

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Using a "Flushing" Technique

Different site with 2 Landfill Gas Flares, (different feeds)

		24hrs	72hrs
		ppmv	ppmv
Flare A #1	Tedlar (Flushing)	2600	3000
Flare A #2	Tedlar (Flushing)	2500	2600

Next day

Flare A #3	Tedlar (Flushing)	2500	

Flare B #1	Tedlar (Flushing)	1200	1300
Flare B #2	Tedlar (Flushing)	1300	1400

H_2S Concentrations verified by alternate impinger technique and subsequent analysis of sulfate by EPA 300

Sampling for Sulfur Compounds

Recommend sampling Protocol

Flush Bag

- Immediately protect from light
- Ship over night to Laboratory for analysis

Sulfur Data EPA Method 15/16

Sulfur data over 4 month period, using the sampling approach described

ANALYTE	Result	Result	Result	Result	Result	Result	UNITS
Carbon disulfide	0.29	0.29	0.27	0.27	0.32	0.20	ppmv
Carbonyl sulfide	0.92	0.89	0.84	0.87	0.89	0.83	ppmv
Dimethyl disulfide	ND	ND	ND	ND	ND	ND	ppmv
Dimethyl sulfide	1.2	1.2	1.2	1.2	1.2	1.0	ppmv
Ethyl mercaptan	0.25	0.27	0.25	0.25	0.28	0.25	ppmv
Methyl mercaptan	1.6	1.5	1.5	1.6	1.7	1.3	ppmv
Hydrogen sulfide	190	180	200	180	240	240	ppmv

Siloxanes

Siloxanes: ***Compounds used in many consumer products***

Siloxanes bad news for engines & turbines and emissions control of post combustion catalytic converters

List compounds

Decamethylcyclopentasiloxane (D5)
Octamethylcyclotetrasiloxane (D4)
Hexamethylcyclotrisiloxane (D3)
Octamethyltrisiloxane (MDM or L3)
Hexamethyldisiloxane (MM or L2)
Trimethylsilanol Si(CH3)3OH
Tetramethylsilane Si(CH3)

Target Concentration < 0.05 mg/m3

For LFG to energy technology

Manufacturers Maximum Siloxane concentrations

Engine Type	**Siloxane, mg/m3**
Reciprocating engines	<28
Micro turbines	0.03 - 0.06

Methods of collection, Whole Gas or Impinger, Analysis is by GC/MS

Equipment manfacturers have their preferences: Total Inorganic silica

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Conclusion

Landfill Gas Testing represents a Challenge

- Good science is critical to reflect the Landfill Gas Composition
- Sample scheduling, operational changes can have impact on Gas Composition
- Sampling Protocols & Containers should be selected with care
- Address shipping concerns and timelines to maintain sample integrity
- Important to engage experienced laboratories and consultants to ensure that the data reported meets expectations
- NELAC Accredited Laboratory using appropriate methods

Questions

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