AP42 Ref 62
EFD Ref. 96
(A-L)

via overnight mail

29 May 1996

GSF Energy
7201 Hamilton Boulevard
Allentown, PA 18195-1501
Telephone (610) 481-4911

Susan A. Thorneloe
Senior Environmental Engineer
Global Emissions & Control Division
U.S. Environmental Protection Agency
Air & Energy Engineering Research Laboratory (MD-63)
Research Triangle Park, NC 27711

Dear Susan:

Per our phone conversation yesterday, attached are the following documents for your review:

✓ A	Nov 10, 1995	Fax from George Sherer, Brooklyn Union to Morry Kapitan, APCI - Results of Trace Constituent Analysis and Measurement of the Nation's Gas Stream.
✓ B	Dec 4, 1995	Fax from George Sherer, Brooklyn Union to Morry Kapitan, APCI - Results of mercury testing at Fresh Kills on November 16, 1995.
✓ C	Dec 4, 1995	Letter from Mike Sauers, APCI to Kenneth Eng, U.S. EPA - Follow-up to the November 9, 1995 meeting at EPA.
✓ D	Dec 7, 1995	Letter from Kenneth Eng, U.S. EPA to Mike Sauers, APCI - Testing for Mercury at the Fresh Kills landfill.
✓ E	Dec 14, 1995	Fax from Ted Nabavi, NYC Department of Sanitation to Mike Sauers, APCI - Press Release EPA Report.
✓ F	Dec 14, 1995	Fax from Mike Sauers, APCI to Ted Nabavi, NYC Department of Sanitation - Arizona Instruments information on Interferences for Jerome meter - Results of comparison between a Jerome 431-X Gold Film Mercury Vapor Analyzer and a UV mercury vapor detector, as performed by an independent company.
✓ G	Jan 24, 1996	Letter from Kenneth Eng, U.S. EPA to Mike Sauers, APCI - to confirm the conversation Mike had with Yue On Chiu on January 12, 1996.

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To Morry KapitAN	From George Schera
Co. ARC	Co.
Dept.	Phone # 718-403-2919
Fax # 610-481-5318	Fax #

ERD ref 96ⓐ

RESULTS OF TRACE CONSTITUENT ANALYSIS AND MEASUREMENT OF THE NATION'S GAS STREAM

Amir Attari
Sherman Chao 708 768-0587

Institute of Gas Technology (IGT)
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ABSTRACT

Major and minor components of natural gas are routinely analyzed by gas chromatography (GC), using a thermal conductivity (TC). The best results obtained by these methods can report no better than 0.01 mole percent of each measured component. Even the extended method of analysis by flame ionization detector (FID) can only improve on the detection limit of hydrocarbons. The gas industry needs better information on all trace constituents of natural gas, whether native or inadvertently added during gas processing that may adversely influence the operation of equipment or the safety of the consumer. The presence of arsenic and mercury in some gas deposits have now been documented in international literature as causing not only human toxicity but also damaging to the field equipment. Yet, no standard methods of sampling and analysis exist to provide this much needed information.

In this paper we report the results of a three-year program to develop an extensive array of sampling and analysis methods for speciation and measurement of trace constituents of natural gas. A cryogenic sampler operating at near 200K (-99°F) and at pipeline pressures up to 12.4×10^6Pa (1800 psig) has been developed to preconcentrate and recover all trace constituents with boiling points above butanes. Specific analytical methods have been developed for speciation and measurement of many trace components (corresponding to US EPA air toxics) by GC-AED and GC-MS, and for determining various target compounds by other techniques. Moisture, oxygen and sulfur contents are measured on site using dedicated field instruments. Arsenic, mercury and radon are sampled by specific solid sorbents for subsequent laboratory analysis.

✓ H	Jan 25, 1996	Letter from Mike Sauers, APCI to Kenneth Eng, U.S. EPA - Follow-up to the November 8, 1995 meeting and letter of December 7, 1995 regarding mercury testing at the Fresh Kills landfill (transmitted test results performed by TRC).
✓ I	Feb 6, 1996	Letter from Kenneth Eng, U.S. EPA to Mike Sauers, APCI - Deficiencies found in the January 25, 1996 TRC Test Report.
✓ J	May 15, 1996	Letter from Kenneth Eng, U.S. EPA to Mike Sauers, APCI - Permission to Test at Fresh Kills.
✓ K	May 16, 1996	Letter from Mike Sauers, APCI to Kenneth Eng, U.S. EPA - with an attached copy of the letter from James Canora, TRC - dated April 11, 1996 (responds to EPA's February 6, 1996 letter which lists deficiencies).
✓ L	May 21, 1996	Fax from Yue On Chiu, U.S. EPA to Mike Sauers, APCI - Agenda - Fresh Kills Test Protocol Development Teleconference on May 23, 1996.

I also have attached the following older test report which summarizes results of mercury (and other metals) testing performed at our Mountaingate landfill gas recovery facility located in Los Angeles, CA.

- Report by Horizon - Air Measurement Services, Inc.
  Landfill Gas Particulate and Metals Concentration and Flow Rate
  Mountaingate Landfill Gas Recovery Plant - May 1992

I hope this information helps with your review, if you have any questions please call me at (610) 481-4317.

Sincerely,

Michael J. Sauers/kar

Michael J. Sauers
Environmental Activities, Manager

attachments

RESULTS AND DISCUSSION

Many types of selected target components listed below are routinely measured in this program. However, the characterization and quantitation is not limited to those components in the list. Any other component found in the screening analysis, which is conducted first, will also be characterized and its concentration measured.

- Non-hydrocarbons: He, H_2, O_2, N_2, CO, CO_2, H_2O, As, Hg
- Hydrocarbons: C_1-C_{14} paraffins, C_2-C_3 olefins, BTEX, PAH
- Oxygenated compounds: Acetone, methanol, glycols, aldehydes, phenols, cresols
- Nitrogen compounds: NH_3, NO/NO_x, amines, N-heterocycles
- Halocarbons: Freons and landfill gas components (C_1-C_3, cyclic, aromatic), PCBs
- Sulfur compounds: H_2S, SO_2, COS, CS_2, mercaptans and derivatives
- Organometallics: Volatile compounds of As,Co,Cu,Fe,Ge,Hg,Ni,P,Pb,Sb,Se,Si,Sn
- Others: NORM (Naturally Occurring Radioactive Materials including Radon)

Processed gases from various gas producing areas, representing different single or mixed geological formations in the United States are sampled at either the inlet or the terminus of NG pipelines.

The following types of samples are collected at each site:

- Whole gas samples
- Liquefied fractions (cryogenic sampling train at 200K)
- Lean gas (after the cryogenic sampler)
- Particulate samples (if present on the sampling train filter up-stream of sampler)
- Pipeline condensate (when available)
- Pipeline deposits (from brush-piggings, if available)

Samples are collected using different sampling techniques to preserve and/or preconcentrate the compounds of interest for later analysis in laboratory. An automatic insertion probe from Welker Engineering is used to place the tip of the probe at the center third of the pipeline to assure representative sampling. A proportional sampler from Welker Engineering is also used to sample pipeline gas over a long span of time to collect a representative whole gas sample. Gas cylinders internally coated with phenolic resin are used to collect gas samples, insuring the integrity of the reactive components of the gas sample, such as sulfur compounds.

For trace organic constituents a cryogenic system, which operates at 200K (-99°F) and at line pressures up to 12.4×10^6 Pa (1800 psig) has been employed. The system is designed to condense, preconcentrate and recover all components that boil above butane's boiling point. This cryogenic sampler uses a heat exchange coil made of approximately 10 feet of 1/4 inch O.D. 316 S.S. tubing wound in a helical form, which is attached to a single ended 150-ml 316 S.S. sample cylinder through a Tee connector. The gas flows downward through the coil and cylinder and exits through a straight S.S. tubing. Two shut-off valves are installed at either end of each tubing above the level of chilling fluid.

INTRODUCTION

The deregulation of the gas industry in the United States has caused some concern over the uniformity of gas quality and their environmental and processing implications. Contaminations from various sources may occur and transport through pipeline systems may cause a wider spread of the existing problems. In order to prevent these potential problems from happening the pipeline natural gas from various sources should be surveyed to assess the current situation and to predict and prevent the unforeseen difficulties.

Routine analysis of processed natural gas for calculation of heating value, specific gravity and compressibility (compression factor) has now been established as an ordinary and necessary measurement practice by the gas industry world-wide. Automated gas chromatographs, which are now a shelf item from many manufacturers, provide the needed gas composition with acceptable precision (repeatability) and even good accuracy if calibration gas of known uncertainty is used. These routine analyses, however, provide information only on major and minor components, i.e. N_2, CO_2, paraffins from C_1 through C_5 and all other hydrocarbons above C_6 (C_6 plus) as if they were a single component. The lowest level of concentration afforded by this routine analysis is about 0.01 mole percent.

Below this 0.01 mole % may lurk a whole population of gas components collectively classified as trace constituents. The major portion of trace constituents are naturally occurring species such as traces of paraffinic and aromatic hydrocarbons, H_2S, organic sulfur compounds (the natural odorants), and traces of H_2 and He. Among them, the increasing levels of carbon dioxide, water content, O_2 and heavy hydrocarbons are presenting clean-up problems for LNG plant operators. Arsenic and mercury have been found in some natural gas deposits. The presence of arsenic was noted when trialkylarsine sulfides, as a white deposit, was found on pressure regulation devices in natural gas distribution lines. Mercury was detected in Groningen gas after having accumulated in natural gas liquids recovery vessels and again, in Algeria because of the extensive damage it caused to the aluminum heat exchangers of Skikda LNG plant. There are also other trace species in processed natural gas which are inadvertently added by gas processing operations such as traces of various amines, ammonia, NO_x, formaldehyde, halocarbons, mercury (from mercury spills), etc. Formaldehyde and oxides of nitrogen were detected after they were related to odor fading in odorized natural gas.

Whatever the sources of these components, it is to the benefit of the gas industry to obtain the required information on the quality of gas to avoid any potential problems. To provide this type of information, in August of 1989 the Gas Research Institute (GRI) sponsored a program at IGT to develop a safe sampling scheme and necessary analytical methods to survey the concentration of all constituents of natural gas, specifically those compounds likely to be found in natural gas that also appear on the EPA list of air toxic substances. This survey sought to provide comprehensive gas quality information on processed natural gas from several important gas producing areas of U.S. and Canada.

The work of this trace constituents survey include formulating a list of target trace components required for this program in reference to the list of hazardous air pollutants, devising a natural gas sampling train and sampling procedures to preserve and preconcentrate trace constituents in natural gas for subsequent analyses, developing analytical methods for both field and laboratory applications, and finally collecting samples from various selected sites and analyzing the samples to compile a data base for the gas industry.

important techniques for qualitative identification and measurement of uncommon trace species. Laboratory preconcentration techniques are utilized, when needed, to separate interferents from the sample and to improve the detection limits for given components.

To date, we have successfully completed our survey work of the following gas producing areas:

- On-shore Texas-Louisiana Gulf Coast
- Off-shore Texas-Louisiana Gulf Coast
- Alabama coal-seam
- Abo Field - New Mexico
- Anadarko Basin
- Arkoma Basin
- Permian Basin
- Appalachian
- Appalachian shale formation
- Illinois basin
- Mid-continental
- San Juan Basin
- Wyoming gas
- Rocky Mountain
- Canadian gas

Survey results plus field operating data, sampling parameters and other pertinent information are presented later in this report.

CONCLUSION AND SUMMARY

A project, sponsored by GRI, was initiated to develop a set of sampling and analytical schemes to survey the concentration of all measurable trace constituents of natural gas that may be of operational or environmental concern.

Many sampling and analytical techniques have been developed in this program to characterize and measure natural gas trace constituents. Specific analytical methods have been developed for speciating and measuring trace components by GC-AED and GC-MS, and for determining various target compounds by other techniques. Moisture, oxygen and sulfur contents are measured on site using dedicated field instruments. Arsenic, mercury and radon are sampled by specific solid sorbents for subsequent laboratory analysis. A long list of other components of interest are measured in the cryogenic condensate and whole gas samples.

We plan to publish, in a single volume, all of the sampling and analytical methods that were developed for this project in late 1993.

A short list of target components that we are surveying at the present time are listed in Table 1.

Table 2. presents data on the concentration range of the various components we have measured in processed natural gas sampled from above 15 producing areas.

An immersion cooler (FTS Model FC-100) is used for constant temperature control of the cryogenic bath containing one part of methanol and 3 parts of isopropanol. Dry ice is used to accelerate the cooling rate and to reach the desired cryogenic temperature quickly. A Honda EM2200X electric generator is used to provide all power required for the immersion cooler and other field operations, if electric services is not available at a given sampling site.

Solid sorbent are used to collect mercury, arsenic and radon in field for subsequent analysis in the IGT laboratory. Mercury is sampled at a flow rate of 1L/min using two 6mm ID sorbent tubes packed with 2.5 cm length of 1% gilded silica beads connected in series, and measured by thermal desorption with continuous atomic spectroscopic detection. Arsenic is sampled at a flow rate of 1L/min with a 6mm tube packed with two 4 cm sections of either the HGR carbon or the FECL (25% $FeCl_3$) sorbent, and determined by X-ray fluorescence (XRF) and atomic spectroscopic techniques, respectively. Radon is collected at a flow rate of 1.2L/min with two 2"x3" carbon cartridge and measured by Gamma ray spectroscopy.

A hygrometer from Stephens Analytical is used for moisture determination in a range of 10 to 6000 ppmv. The Delta F trace oxygen analyzer is used with an Ascarite scrubbing tube to remove CO_2 interferents from the tested natural gas. This on-line instrument provides an accurate and fast measurement of oxygen with a range of 1 to 1000 ppmv. A Scintrex sulfur analyzer, Model OVD-229, from Heath Consultants, Inc. is used to monitor the concentration of odorants and H_2S in natural gas at a concentration level of 0.1-10 ppmv. An extended-frame van, a Ford Econoline 150, is fitted with racks to carry sampling devices and monitoring instruments to the field.

In the laboratory, the cryo-trap sample collected in the field is expanded twice at 0°C and 25°C. The residual condensate in the trap is rinsed and recovered with 5 ml of hexadecane. Selected samples of whole gas, pipeline condensate, expansion gas, cryo-trap condensate and washings are analyzed. The composition of these samples are screened, characterized and measured according to the following analytical procedures.

- ASTM 1945 and 1946 methods for major and minor components in gas
- Modified GPA extended hydrocarbons analysis with capillary GC column
- Target halocarbons analysis by GC-ELCD (Hall-Effect)
- Trace sulfur compounds analysis by Flame Photometric Detector (FPD) and/or Sulfur Chemiluminescence Detector (SCD)
- Target nitrogen compounds analysis by Gas Chromatograph-Atomic Emission Detector (GC-AED)
- Target oxygen containing compounds analysis by GC-AED and by a modified EPA TO-11 analytical method developed for aldehydes and ketones in air
- Elemental speciation by GC-AED
- Compound identification by GC-Mass Spectrometer (GC-MS) analysis
- PAHs analysis of condensate and washings by HPLC
- PCBs analysis of condensate and washings by GC-Electron Capture Detector (GC-ECD)
- NO/NOx analysis of whole gas samples by chemiluminescence

Gas chromatographs equipped with a variety of columns and detectors for specific analytical purposes are used for this program in IGT laboratories. Two standard GC columns, DB-5 and DB-Wax columns are employed for analysis of non-polar and polar compounds, respectively. GC-AED and GC-MS are two most

Table 1. Short List of Target Components And Their Method Detection Limits-p.2

NITROGEN-COMPOUNDS	MDL[ppm]	RP%	OXYGENATES	MDL[ppm]	RP%
Ammonia	2	15	2 Alkene Oxide	1	12
12 Alkyl amines	0.5	10	5 Aldehydes (Formaldehyde,etc.)	1(0.01)	12(10)
Acetonitrile	0.5	10	Methanol	1	12
2 N-heterocycles (pyridine & pyrrole)	0.5	10	Acetone	1(0.01)	12(10)
2 Ethanolamines	0.5	10	3 Glycols	1	12
			Maleic Anhydride	1	12
			Phenol & 3 Cresols	1	12

Note: Cryo-trap GC-AED analysis, Stabilwax-DB column for nitrogen ,and DB-Wax & DB-5 for oxygen,
( ) denotes MDL and RP% of aldehyde and ketone analysis by DNPH /HPLC .

ELEMENTAL SPECIATION	(C3-C14 only [4])	MDL		RP%
XRF/HGR ANALYSIS: [5]	(Atomic Weight >14)	100	[µg/m3]	NA
GC-AED ANALYSIS: [6]	Bromine	0.1	[ppmv]	10
	Chlorine	0.2		10
	Fluorine	1		15
	Nitrogen	0.1		10
	Oxygen	1		12
	Phosphorus	0.01		12
	Antimony [7]	0.1		ND
	Arsenic	0.002		10
	Cobalt	0.1		ND
	Copper	0.05		ND
	Germanium	0.1		10
	Iron	0.05		ND
	Lead	0.1		ND
	Mercury	0.002		10
	Nickel	0.05		ND
	Selenium	0.002		10
	Silicon	0.3		12
	Tin	0.1		10

Notes:
1. "MDL"= Method Detection Limit; It may vary as analysis and sampling parameters change.
2. "RP%"= % Relative Precision (2 S.D.)at a concentration 20 times of the MDL.
3. For C5-C14 components, expansion gas, ambient condensate and washing samples from cryogenic traps were analyzed by capillary GC and the results summed up.
4. Lower detection limits (10-1000X) are attainable, if expansion gas, ambient condensate and washing samples from cryogenic traps were analyzed and the results summed up.
5. X-Ray Fluorescence semi-quantitative analysis of trace elements collected on HGR carbon sorbent.
6. GC-AED analysis of 20 trace elements present in gas samples.
7. Only qualitative or semi-quantitative analysis can be done on those elements denoted in Italics.
8. "NA"= Not Applicable, "ND"= Not Determined

Table 1. Short List of Target Components And Their Method Detection Limits

NON-HYDROCARBONS	MDL[1]	RP%[2]
Oxygen-monitor, ppmv	1	5
Oxygen,GC, %	0.03	1
Moisture, ppmv	10	5
Helium, %	0.002	1
Hydrogen, %	0.002	1
Nitrogen, %	0.03	1
Carbon dioxide, %	0.03	1
Carbon monoxide, %	0.03	1

NON-HYDROCARBONS	MDL	RP%
Arsenic- FECL, $\mu g/m^3$	5	15
Arsenic- HGR, $\mu g/m^3$	50	10
Mercury, $\mu g/m^3$	0.01	10
NO, ppmv	0.05	10
NOx, ppmv	0.05	10
Radon, pci/L	1	15

MAJOR HYDROCARBONS	MDL [%]	RP%
Methane	0.03	2
Ethane	0.03	2
Ethene	0.03	2
Ethyne (Acetylene)	0.002	2
Propane	0.002	2
Propene	0.002	2
Propyne	0.002	2
Propadiene	0.002	2
i-Butane	0.003	2
n-Butane	0.003	2
i-Butene	0.003	2
iso-Butene	0.003	2
trans-2-Butene	0.003	2
cis-2-Butene	0.003	2
Butadiene	0.006	2
neo-Pentane	0.001	2
i-Pentane	0.001	2
n-Pentane	0.001	2
Pentenes	0.001	2
C6 Plus	0.002	5

C5 PLUS HYDROCARBONS[3]	MDL [ppmv]	RP%
Aliphatics		
Cyclopentane	1	3
Hexanes	0.2	5
Methyl cyclopentane	0.2	5
Cyclohexane	0.2	5
Heptanes	0.2	5
Methyl cyclohexane	0.2	5
Octanes	0.1	10
Nonanes	0.1	10
Decanes	0.1	10
Undecanes	0.1	10
Dodecanes	0.1	10
Tridecanes	0.1	10
Tetradecanes	0.1	10
Aromatics		
Benzene	0.2	10
Toluene	0.1	10
Xylenes	0.1	10
Ethylbenzene	0.1	10
C3-Benzenes	0.1	10
Naphthalene	0.1	10
PAHs	0.02	10

SULFUR COMPOUNDS	MDL [ppmv]	RP%
Hydrogen sulfide	1(0.1)	10(10)
Sulfur dioxide	0.02	5
5 Mercaptans	0.02(0.1)	5(10)
5 Sulfides (COS, DMS,etc.)	0.02(0.1)	5(10)
16 Disulfides (CS2,DMDS,etc.)	0.02	5
3 Trisulfides	0.02	5
8 Aromatics (Thiophene,etc.)	0.02	5
Thiophane	0.02	5

Note: GC-FPD or GC-Chemiluminescence,
( ) denotes by Scintrex OVD-229

HALOCARBONS	MDL [ppmv]	RP%
7 Freons	0.05	7
Vinyl chloride	0.05	7
27 other target compounds	0.05	7
PCBs(Arochlors)	0.01	15
PCBs(Congeners)	0.001	15

Note: Volatile halocarbons by GC-ELCD & GC-MS
PCBs by GC-ECD & GC-ELCD on condensates from cryo-trap.

Table 2. Trace Constituents in Natural Gas: Concentration Range And Median (cont.)

Sulfur Components:	Range [ppmv]	Median
Hydrogen sulfide	<0.1 - 6	0.2
Carbonyl sulfide	<0.02	<0.02
Carbon disulfide	<0.02	<0.02
Methyl mercaptan	<0.02 - 0.15	<0.02
Ethyl mercaptan	<0.02 - 0.16	0.04
i - Propyl mercaptan	<0.02 - 0.41	0.02
n - Propyl mercaptan	<0.02 - 0.02	<0.02
t - Butyl mercaptan	<0.02 - 0.08	<0.02
Dimethyl sulfide	<0.02 - 0.5	<0.02
Methyl ethyl sulfide	<0.02 - 0.06	<0.02
Diethyl sulfide	<0.02 - 0.05	<0.02
Dimethyl disulfide	<0.02 - 0.8	<0.02
Other disulfides	<0.02 - 0.48	<0.02
Trisulfides	<0.02 - 0.4	<0.02
Residual sulfides (Polysulfides)	<0.02 - 0.75	0.09

Nitrogen Compounds:	Range [ppmv]	Median
Ammonia	<2	<2
17 other target compounds	<0.5	<0.5
Other compounds	<0.5	<0.5
Oxygenates:		
Methanol	1 - 92	4
Acetone	<1 - 24	<1
15 Other target compounds	<1	<1
Other compounds (No.)	<1 - 6	<1
Halocarbons:		
35 target compounds	<0.1	<0.1
PCBs	<0.01	<0.01
Other compounds	<0.1	<0.1

Other Elements and Compounds:	Range	Median
Total Arsenic, ug/m^3	<5	<5
Total Mercury, ug/m^3	<0.2	<0.2
NOx, ppmv	<0.05 - 130	<0.05
Radon, pCi/L	<1 - >~~23~~* 1/C	<1

* Because breakthrough occurred, the radon content in one sample cannot be accurately measured, but estimated as higher than 23 pCi/L.

Table 2. Trace Constituents in Natural Gas: Concentration Range And Median

Major Components:		Range	Median
Moisture, ppmv (Lb/MMCF)		<10 - 2600	105
Oxygen, ppmv		2.9 - 42	8.1
Helium	[%]	0.002 - 0.080	0.034
Hydrogen		<0.002 - 0.120	0.006
Nitrogen		0.22 - 2.96	1.20
Carbon Dioxide		0.07 - 2.62	0.56
Methane		81.1 - 98.5	92.9
Ethane		0.09 - 11.8	3.06
Propane		0.005 - 3.95	0.46
Isobutane		<0.003 - 0.369	0.063
n - Butane		<0.003 - 0.822	0.051
Neopentane		<0.001 - 0.004	<0.001
Isopentane		<0.001 - 0.18	0.02
n - Pentane		<0.001 - 0.16	0.02
C6 & Heavier		<0.002 - 0.226	0.042
Calculated Properties:			
Relative Density		0.561 - 0.685	0.595
Compressibility		0.9969 - 0.9980	0.9978
Dry Gross Heating Value at 14.73 psia, BTU/SCF		988 - 1193	1023

C6 Plus Hydrocarbons:			Range	Median
Aliphatics:	Cyclopentane	(ppmv)	<1 - 33	7
	Hexanes		<0.2 - 1156	175
	Methyl cyclopentane		<0.2 - 115	20
	Cyclohexane		<0.2 - 109	30
	Heptanes		<0.2 - 433	90
	Methyl cyclohexane		<0.2 - 133	22
	Octanes		<0.1 - 280	46
	Nonanes		<0.1 - 280	12
	Decanes		<0.1 - 120	3.4
	Undecanes		<0.1 - 20	1.5
	Dodecanes		<0.1 - 2.1	.055
	Tridecanes		<0.1 - 0.6	<0.1
	Tetradecanes		<0.1 - 0.1	<0.1
Aromatics:	Benzene		<0.2 - 471	7
	Toluene		<0.1 - 100	7
	Ethylbenzene		<0.1 - 15	0.1
	Xylenes		<0.1 - 12	0.8
	C3 - benzenes		<0.1 - 1.5	<0.1
	Naphthalenes		<0.1	<0.1
	PAHs		<0.02	<0.02

Brooklyn Union

Laboratory Operations

ATTACHMENTS

1. Sampling Procedure/Raw Data
2. Analysis Results
3. Trace Constituents in Natural Gas - Sampling and Analysis
   Sherman Chao, Amir Attari, Institute of Gas Technology
   Presented at AGA Operations Conference, San Francisco, CA,
   May 8-11, 1994.

Brooklyn Union

Laboratory Operations

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To Marty Kapitan	From George Scherer
Co. APC	Co.
Dept.	Phone #
Fax # 610-481-5318	Fax #

ERD ref 96(b)

copy to: PJP [redacted]

TO: G.W. Scherer, Director, System Operations

FROM: R.D. Wilson, Director, Laboratory Operations

SUBJECT: Mercury Testing - APC Landfill Gas

DATE: December 4, 1995

As per your request, attached please find results of mercury testing conducted on gas received from the APC Staten Island Landfill Recovery Plant on November 16, 1995. Four samples were obtained including two samples from the APC Plant outlet and two samples from South Gate. The samples were obtained and analyzed utilizing Procedures developed by the Institute of Gas Technology (IGT), Chicago, IL (See Attached Procedure).

In summary, the samples were received by IGT under Chain-of-Custody on November 21, 1995. Analysis revealed Mercury concentrations less than the method detection limit of .02 ng Hg/Liter of Gas. The results obtained from the Land Fill Plant are consistent with those found in processed gas from various pipelines representing gas producing areas in Canada and the United States.

ROBERT D. WILSON 2508 CHMM

Robert D. Wilson, CHMM

RDW:gw
Attachments

Post-it® Fax Note 7671

Date 5/25/96	# of pages ▸ ~~8~~ 4
To SUSAN THORNELOE	From MIKE SAUERS
Co./Dept. EPA	Co. APCI - EES
Phone # 919-541-2709	Phone # 610-481-4317
Fax # -7585	Fax # 610-481-4377

Brooklyn Union

LAB # 950966

Laboratory Operations Analysis Report

CHAIN OF CUSTODY RECORD

SAMPLE ORIGINATION:	LABORATORY ACCEPTANCE:
Client Name: R. WILSON	Approved By: R. Kalberer
Area: Gas System Ops.	Date Received: 11/15/95
Location: GRNPT. LAB	Date Assigned: 11/15/95
Phone No.: (718)-963-5420	Date Completed: 11/22/95
ELAP NUMBER: 11173	Phone No.: (718)963-5420

INVOICE

Area: 926 Function: Prime: W.O. No.: 0910198500

ANALYSIS REQUEST

Matrix Identification: gas Number of Samples: 4

SAMPLE ID:	DESCRIPTION/LOCATION:	TYPE OF SERVICES:
001	APC LANDFILL PLANT GAS	Special Request
002	APC LANDFILL PLANT GAS DUP.	Special Request
003	SOUTH GATE	Special Request
004	SOUTH GATE DUP.	Special Request

Comments: SPECIAL REQUEST = MERCURY IN GAS

QUALITY ASSURANCE

Chemist:_ Laboratory Notebook:

QA Method(s): SL 6.02 Reference Page:

SAMLPES SENT TO IGT ANALYTICAL FOR ANALYSIS

Brooklyn Union

Laboratory Operations Analysis Report

APC LANDFILL & SOUTH GATE GAS

Characteristics and Amounts
BUG Quality Assurance No. 6.02

Client Name: R. WILSON	Chemist:
Area: Gas System Ops.	Date Assigned: 11/15/95
Matrix: gas	Date Completed: 11/22/95

SAMPLES:	TEST PARAMETER(S): Hg IN GAS
#1 ng Hg/L GAS	<0.02
#2 ng Hg/L GAS	<0.02
#3 ng Hg/L GAS	<0.02
#4 ng Hg/L GAS	<0.02

CERTIFIED HAZARDOUS MATERIALS MANAGER
ROBERT D. WILSON
2508
CHMM

LABORATORY DIRECTOR

IGT

SAMPLING PROCEDURE
GILDED SILICA SORBENT TUBES FOR MERCURY ANALYSIS

1) Ascertain that the sample can be obtained at a pressure not exceeding 10 psig and a flow of 1.0 liter per minute. Pressure- and flow-control devices may be required. The sampling pressure should be kept as low as possible at the specified flow rate. A total flow volume measurement device, such as a dry test meter, can be used to record the exact amounts of gas sampled for more accurate sampling.

2) Using a calibrated rotameter, determine an approximate flow control setting for a 1.0 liter per minute flow at the applied pressure. This will save time when actually setting up the first sorbent tube, and will passivate the sampling system.

3) Attach a short piece of stainless steel tubing to the inlet of the rotameter and place a short piece of white silicone tubing on the bare end of the stainless tube. Configure the sampling point with a short piece of the silicone tubing as well for attaching the sorbent tubes.

4) For each sampling, use two of the packed sorbent tubes in series. Loosen the nylon nut on the endcap on one end of each tube, slide the entire nylon endcap assembly off of each tube, and join the two tubes end-to-end with a short piece of silicone tubing. It is not necessary to take apart the endcap assemblies when removing them.

5) When you are ready to sample, connect the end of one of the sorbent tubes to the silicone tubing on the inlet of the rotameter, then connect the other end of the tubes to the sampling point. When all connections are secure, carefully open the sampling valve and quickly adjust the flow control (and pressure if necessary) to obtain the requested flowrate. Record the time and flow data (rotameter reading) at the start of sampling.

6) Flow the sample through the sorbent tube for the specified amount of time (see below) periodically checking that the flow is staying close to what it was when you started sampling and adjusting it if necessary.

7) At the end of the sampling period, record the time and flow data, disconnect both tubes, and replace all of the endcaps tightly on the tubes. It may be necessary to loosen the nylon nuts somewhat on the endcaps in order to push them tightly over the ends of the tubes. A small wrench should be used to gently snug up the nuts on all of the endcaps to prevent loosening during transit. Securely attach a label to each of the tubes, labeling the first tube as "A" and the second tube (connected to the rotameter) as "B". Securely attach a label to the tube, indicating the sample flow direction with an arrow. Also include the actual flow rate, sampling time and any other descriptive information on the label for later identification.

8) Package the tubes securely to guard against breakage in transit and return all tubes, supplied equipment, and sampling data to IGT for analysis.

TRACE CONSTITUENTS IN NATURAL GAS - SAMPLING AND ANALYSIS

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Presented at A.G.A. Operations Conference, San Francisco, CA, May 8-11, 1994

ABSTRACT

Concern over trace constituents in natural gas that may cause operational or environmental problems led the Gas Research Institute (GRI) to sponsor a program of study at IGT to develop specific sampling and analysis methods to survey the concentrations of all possible trace constituents present in natural gas.

In this paper we discuss an extensive array of sampling and analysis methods for speciation and measurement of trace constituents of natural gas. A cryogenic sampling method was developed for preservation, separation and preconcentration of trace organics heavier than butanes. Portable analyzers were selected or developed for on-line measurement. Many solid sorbents were developed and used to collect labile species such as mercury, arsenic and radon in the field. A new GC-Atomic-Emission Detector (GC-AED) technique and other chromatographic techniques with element-specific detectors were employed for a complete screening and determination of trace organic and organometallic compounds.

The sampling and analytical methods developed were fully validated and used to characterize a large number of trace constituents in processed gas from various pipelines representing important producing areas in the United States and Canada.

KEY WORDS

Gas quality, Characterization, Measurement, Sampling, Analysis, Trace constituents, Contaminants, Natural gas

BACKGROUND

Natural gas is deservedly known as the cleanest fossil fuel. It is of paramount importance to the gas industry to diligently safeguard this "clean energy" perception by making every reasonable effort to improve the methods for accurate measurement of potentially harmful trace constituents that may be present in natural gas. The availability of better sampling and analytical techniques will provide the ability to monitor the undesirable trace constituents in natural gas streams to prevent unforeseen environmental, operational and safety problems.

GRI has sponsored a program of study at IGT to develop necessary standard sampling analytical methods to survey the concentration of all measurable constituents of natural gas, specifically those trace constituents that are likely to cause operational, end use or environmental problems

The trace constituents of interest include naturally occurring species (concomitants), and trace species

continued

SAMPLING PROCEDURE
GILDED SILICA SORBENT TUBES FOR MERCURY ANALYSIS

STANDARD SAMPLING PARAMETERS:

Pressure : 10 psig max.
Flow Rate: 1.0 L/min.
Flow Time: 60 minutes (for expected levels of 0.02-2 ug Hg / m^3)
30 minutes (for expected levels of 1-4 ug Hg / m^3)
15 minutes (for expected levels of 2-10 ug Hg / m^3)

NOTES:

Any historical information regarding the sample would aid us in better analyzing your sample. This would include previous analyses or stain tube screening analyses taken on site.

Extra tubes have been included in the package. Two will serve as field blanks and are included in the analysis price. The others are spares to be used in case any break during transit. The cost of each tube is $50.00.

IGT recommends that duplicate samples be taken at each sample site. Two samplings with different durations can cover a larger mercury concentration range.

hexadecane washings, are analyzed thereafter along with whole gas samples. The acetone washing is analyzed only when the results from other tests show the possible presence of polar compounds. The detection limits of trace components heavier than butanes can be lowered by several orders of magnitude and the accuracy of determination can be improved accordingly while the cryogenic technique is applied.

The following is a partial list of the target trace components that were being measured for the GRI program. Any other component found in the initial screening analysis was characterized and its concentration determined. In selecting these components, EPA list of air toxic substances was used as a guide.

- Non-hydrocarbons: Oxygen, Arsenic, Mercury
- Hydrocarbons: Heavy paraffins, BTEX, PAHs
- Oxygenated Compounds: Acetone, Methanol, Glycols, Aldehydes, Phenols, Cresols
- Nitrogen Compounds: NH_3, NO/NO_x, Amines, N-heterocycles, etc.
- Halocarbons: C_1-C_3, cyclic, PCBs
- Sulfur Compounds: H_2S, SO_2, COS, CS_2 and organic sulfur compounds
- Organometallics: Volatile compounds of As,Co,Cu,Fe,Ge,Hg,Ni,P,Pb,Sb,Se,Si,Sn,etc.
- NORM: Radon, etc.

To facilitate the discussion, the measurement of each trace species or each types of compounds are outlined separately in the following.

ARSENIC

Arsenic compounds have been found in only two natural gas fields in the US. A new technique using a recently-developed Gas Chromatograph with Atomic Emission Detector (GC-AED)[3,4] was used very effectively for the speciation of organoarsines at very low concentrations. The results from the recent sampling and analysis of a raw natural gas sample from Abo field, located near Roswell, NM, indicated a total arsenic concentration of 1420 $\mu g/m^3$. Speciation by GC-AED analysis indicates the sample contains trimethyl arsine (970 $\mu g\ As/m^3$), dimethylethyl arsine (370 $\mu g\ As/m^3$) and a very small amount of other organoarsines, probably propyldimethyl arsine and methyldiethyl arsine.

Normally, natural gas is best stored in a 316 SS cylinder. However, it was observed that the arsenic concentrations measured in natural gas samples stored in the cylinder rapidly diminished and approached below our detectable limits. It is believed that nickel-arsine complexes, such as $Ni(AsR_3)_4$ analogues, are possibly formed upon standing[5-9]. Therefore, it is recommended that no nickel-containing vessels be used for storage, transportation and analysis of gaseous arsenic compounds. The 304 SS cylinder, having less nickel than the 316 SS, seemed to be better than the latter in sample preservation. The best containers, however, are SS cylinders that are internally coated with inert polymeric resin or coated wtih proprietary Ultraline process.

Arsenic compounds can be extracted from natural gas by oxidative liquids, and chemical impregnated solid sorbents for total arsenic determination. Saturated peroxydisulfate solution, Calgon HGR carbon and an IGT-developed FECL sorbent[3-6] were used to extract arsenic from natural gas. Once arsenic is in solution it is analyzed by a hydride AA method. The arsenic absorbed on HGR sorbent is analyzed with x-ray fluorescence (XRF) technique for As concentrations in natural gas ranging from 0.05 to 2 mg/m^3. The FECL, a patented sorbent with 10-25 wt% $FeCl_3$ on Chromosorb P, is extracted with diluted nitric acid to recover the arsenic and the extract analyzed for total arsenic by spectrochemical method. This FECL technique gives a lower detection limit of about 2 $\mu g/m^3$ and a 100 times wider dynamic range of arsenic detection than the HGR/XRF method.

(contaminants) in processed natural gas which are inadvertently added by gas processing operations or gas compression. The former include paraffinic and aromatic hydrocarbons, H_2S, organic sulfur compounds (the natural odorants), arsenic, mercury, radon and its derivatives, and oxygen. Examples of the latter are various amines, ammonia, NO_x, formaldehyde, glycols, halocarbons, mercury (from mercury spills), etc.

DISCUSSION

Direct and accurate measurement of all trace constituents at natural gas sampling sites is not only very difficult and time-consuming, but also impractical. Except for O_2, moisture and sulfur compounds, for others samples are best collected using different sampling techniques to preserve, separate and/or preconcentrate the components of interest for later analysis in the laboratory. Labile species in the sample which can react and fade on storage, however, may be measured at the site using portable instruments when they could not be properly preserved.

Gas samples either for on-line or later analysis must be representative of the actual natural gas at the collection point[1,2]. Automatic insertion probes[1] must be used for sampling. The tip of the probe is always placed at the center third of the pipeline to conform to ASTM standard practice that assures representative sampling.

For most gas components, proportional sampler was routinely used to sample pipeline gas over a long period to collect a representative sample. A sample cylinder with two valves and Swage Lock connectors on both ends was used to collect the sample. The selection of an appropriate type of cylinder is of paramount importance for storage. Normally, gas samples should be collected in a durable and inert container in such a way that the content will not be altered either qualitatively or quantitatively. Gas cylinders made of 316 SS or internally coated with phenolic resin were normally selected for gas sample collection, insuring the integrity of the sample. The phenolic resin coating has demonstrated its inertness to many reactive gaseous species. We routinely clean all sample cylinders by first washing with high purity (chromatography grade) methylene chloride and rinsing with high purity n-hexane, followed by baking at 70°C with a pure nitrogen purge for at least 2 hours.

In the absence of a well documented set of analytical procedures, IGT took steps to provide such a document. Some methods developed at IGT were modifications of air sampling and analytical methods that are in common use for the air toxic substances. These air monitoring methods, when applied to natural gas, however, present special challenges, because the latter has a much more complex matrix than the air. They may require additional refinements to prevent interfering compounds from adversely affecting the analytical results. The interfering species may include major components such as methane or trace and minor components such as moisture, heavy hydrocarbons and hydrogen sulfide.

For trace organic constituents, a cryogenic system which operates at -70°C (-94°F) and at line pressures up to 12.5×10^6 Pa (1800 psig) has been developed and tested for effective and contamination-free preservation and preconcentration by separating them from major components such as methane and ethane. This cryogenic sampler uses a heat exchange coil made of approximately 10 feet of 1/4 inch O.D. 316 SS tubing wound in a helical form, which is attached to a single ended 150ml 316 SS sample cylinder through a "tee" connector. The gas flows downward through the coil, transferring the resulting condensates to the cylinder, and exits through the annular space around the inlet to the condensate collector. Two valves are installed on the other end of each tubing above the level of chilling fluid.

The cryo-trap samples collected at -70°C in the field is expanded at 0°C and then at 25°C (room temperature) in the laboratory. After the expansions, the condensate is collected from the trap at room temperature. The trap is then washed five times with 1.0-ml aliquots of hexadecane followed by 5 ml of acetone. All four separate fractions, namely expansion #1 gas, expansion #2 gas, condensates and to 100 minutes.

NORM

NORM can be expected at nearly every petroleum facility[14]. They include Radium isotopes and their daughter radionuclei, such as Rn-222, Pb-210, etc. Although, the presence of NORM in oil and gas production facilities, gas processing plants and pipelines do not, in general, have a serious impact on environmental safety, their survey was conducted to prevent the unforeseen problems. Gamma-ray spectroscopic methods have been used for detection of other NORMs on pipeline solids and HGR sorbents. The spectrometer equipped with a NaI scintillator, although may not be sensitive enough, was used for the detection of low levels of radioactivity at 200 pCi from 0.01 to 2.48 Mev. This method cannot give a complete screening of all NORMs because some of the NORMs are not strong Gamma emitters.

SULFUR COMPOUNDS

Hydrogen sulfide and organic sulfur compounds in natural gas are labile species. If possible, they are best analyzed on location. Tedlar-lined sampling bags, aluminum and 316 SS sample cylinders with or without interior coatings are often utilized to collect samples for later laboratory measurement of sulfur species including odorants. However, loss of original sulfur species and formation of other sulfur derivatives can readily occur and provide low results and may not represent the actual concentration of sulfur species originally present in natural gas. For the GRI program, a Scintrex sulfur analyzer, Model OVD-229 from Heath Consultants, Inc., was used to monitor the concentration of all sulfur components in natural gas on site. This instrument is equipped with a GC and an electrochemical detector offering an analytical working range of 0.1-10 ppmv for each of eight sulfur components, including H_2S, mercaptans, alkyl sulfides and thiophane.

HEAVY HYDROCARBONS

GC with a Flame Ionization Detector (GC-FID) was used for extended hydrocarbons analysis using a capillary column (Petrocol DH) for more detailed hydrocarbons breakdown up to at least C_{14}. This GC column provides a clean separation of benzene and cyclohexane, improving the accuracy of benzene analysis while reporting the contents of cyclopentane, methylcyclopentane, cyclohexane and methylcyclohexane as well. This technique enables detection of each hydrocarbon species down to 1 ppmv. The cryogenic sampling and on-line cryofocussing techniques have been employed for detection of hydrocarbons heavier than pentane as low as 0.001-0.1 ppmv concentrations depending on concentration factors.

AROMATICS (BTEX & PAHs)

Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) are among the components listed as hazardous air pollutants in the 1990 Clean Air Act Amendment[15]. They are also classified as toxic substance under the OSHA and NIOSH rules, having a benzene exposure limit of 1 ppmv. Their determination can be accomplished easily with the GC-FID technique described above. However, for a more sensitive detection a Photo Ionization Detector (PID) can be employed for more specific GC analysis. A recently-developed micro GC technique by Microsensor Technology Inc. has made possible a quick measurement of BTEX using a TCEP column.

Polynuclear Aromatic Hydrocarbons (PAHs) are also classified as hazardous substances by USEPA. For this program we determined PAHs in natural gas by analyzing the cryo-condensate fraction of natural

A prototype organoarsine monitoring instrument[3,4] has been developed. The instrument is a compact GC with a low surface area (LSA) gold electrode detector operating at a voltage bias of +300 mv. Trimethylarsine (TMA) has an elution time of five minutes with a detection limit of about 0.1 ppmv (335-μg As/m^3). With a PHOS25 preconcentrator (another IGT-developed sorbent) the measurement of arsenic at a few μg/m^3 concentration level is possible. However, more work must be carried out to optimize this analyzer for better sensitivity, reproducibility and ruggedness.

MERCURY

Mercury and its alkyl compounds that are coproduced with natural gas, adversely affect materials, field operations and consumer safety[7,8]. The most common techniques used to extract mercury from natural gas for measurement are scrubbing the gas through acidic permanganate solution or recovering the mercury on activated charcoal, with or without a sulfur coating. Both of these sampling methods are prone to contamination and generally not suitable for natural gas analysis.

The preferred sampling method for mercury collection is on supported gold sorbent[9,10] with subsequent thermal desorption for mercury determination. This sampling method collects and concentrates Hg compounds while preventing interferences from species such as sulfurs. A column packed with 30-60 mesh fused silica coated with 1% Au was used at IGT. Two 6 mm Vycor tubes containing 2.5 cm length of gilded silica beads are placed in series for mercury sampling. For quantitative recovery of Hg the maximum capacity of the gilded silica beads in each sorbent tube is about 8 μg, representing an upper collection limit of 500 μg/m^3 with 15 minutes sampling at a flow rate of 1 L/min. For field applications we normally sample for 15 and 120 minutes, representing a convenient measurement range of 0.02 to 500 μg/m^3. A cold-vapor AA (CVAA) technique is currently employed in the laboratory to measure mercury thermally-desorbed at temperatures from 450 to 600°C with a heating rate of 100°C/min.

A portable Jerome 431 Hg analyzer[11] was tested unsuccessfully for direct natural gas analysis, because of interferents. However, a limited number of experiments conducted at IGT only demonstrated the feasibility of fabricating a portable Hg analyzing system consisting of the gilded silica sampling tube, a *portable heater*, a valving system and a portable Hg detector, such as gold thin-film detector or CVAA analyzer.

RADON

Radon-222, a Naturally Occurring Radioactive Materials (NORM), has been recognized as a health hazard for many years and has recently been the subject of much study and debate concerning its health effects on the general population. The USEPA, which in 1973 surveyed the concentration of Radon in natural gas, has in recent years recommended a remediation level if radon exceeds 4 pCi/L in air. Radon with a half life of 3.8 days can eventually decay and produce lead-210 with a half life of 20 years, thus becoming a more persistent safety hazard[12]. Because of solubility of radon in contact solutions, either coproduced liquids or scrubbing liquids, it is the resulting lead-210 accumulation in these solutions that concern the gas producer/processors.

For analysis, radon can be collected on two 2"x3" flow-through carbon cartridges[5]. The gamma radiation of its daughters (Pb-214 and Bi-214) on the charcoal canister is measured using a standard technique[13] (EPA 520/5/87-005). This technique allows the sampling and the measurement of radon to be conducted in the field and the laboratory, respectively. A detection limit of 1 pCi/L Rn can be easily achieved provided that a large volume of gas is sampled and the subsequent laboratory analysis performed very shortly after sampling. The working analytical range is 1 to 1000 pCi/L with a sampling interval up microwave induced helium plasma operating at about 5000°C and a diode array spectrometer (40 nm detection range). Standard compounds containing O, N, As, Hg and others were selected and used to calibrate the instrument.

The GC-AED method offers a sensitive and reliable means to screen elements that make-up the trace compounds recovered from natural gas. It is particularly useful for screening those trace elements which cannot be easily detected by any other method. Two standard GC columns, DB-5 and DB-WAX, are normally used for determination of nonpolar and polar compounds, respectively[5]. This technique can be employed for quantitation of compounds containing those specific elements, especially nitrogen- and oxygen-containing species and organometallics. On-line cryofocussing techniques can enhance the instrument sensitivity.

To supplement the qualitative elemental determination by GC-AED method, the HGR sorbent used to collect arsenic species was analyzed by XRF for several elements with atomic weights larger than 12[5]. This HGR-XRF technique was evaluated with an IGT-prepared multi-element gas standard, and was found to be capable of efficiently collecting the compounds of As, Se, Sn, and Ge.

CONCLUSIONS

A project, sponsored by GRI, was initiated to develop a set of sampling and analytical schemes to survey the concentration of all measurable trace constituents (<0.01 mole %) of natural gas that may be of operational or environmental concern.

IGT has developed many sampling and analysis techniques for determination of these trace constituents in processed gas. These methods include a new GC-Atomic Emission Detector (GC-AED) technique for a complete screening of all elements present in trace components and other chromatography techniques with specific detectors for identification of trace organic compounds containing sulfur, nitrogen, phosphorus, halogen and organic functional groups. A sampling method using cryogenic trapping at -70°C (-94°F) and at line pressures up to 12.5×10^6 Pa (1800 psig) was developed for preservation, separation and preconcentration of hydrocarbons heavier than butanes for later analysis in the laboratory. Many solid sorbents were developed and used to collect labile species such as mercury, arsenic and radon in field for subsequent analysis in IGT laboratories. The development of new monitors for arsenic and mercury in natural gas has also begun not long ago.

Extensive sampling and analysis methods have been developed and successfully employed. They are:

- Speciation of organoarsines by GC-AED
- Total arsenic by peroxydisulfate, HGR and FECL methods
- Mercury by gilded sand sorption and CVAA measurement.
- Radon by carbon adsorption and gamma ray spectroscopy
- Target halocarbons analysis by GC-ECLD
- Trace sulfur compounds analysis by Flame Photometric Detector (FPD) and/or Sulfur Chemiluminescence Detector (SCD)
- Target nitrogen compounds analysis by GC-AED
- Target oxygen containing compounds analysis by GC-AED and by a modified EPA TO-11 method
- Other organics containing specific metals by GC-AED
- PAHs analysis of condensate and washings by HPLC
- PCBs analysis of condensate and washings by GC-Electron Capture Detector (GC-ECD)

gas using the modified EPA 8310 Method[16]. Sixteen PAHs were monitored at IGT for this program by High Performance Liquid Chromatograph (HPLC) with both the fluorescence and UV detectors.

OXYGEN-CONTAINING COMPOUNDS

Fifteen oxygenates were usually determined by GC-AED at 777 nm. However, the modified EPA TO-11 analytical method[17] for aldehydes and ketones in air, which uses DNPH (Dinitrophenyl hydrozine) derivatization followed with HPLC analysis, was also successfully employed for natural gas analysis. By this method one can determine additional oxygenates in natural gas, such as acrolein and benzaldehyde. IGT-prepared DNPH sample cartridges were used to sample a large quantity of natural gas for the targeted detection limit of about 0.01 ppmv. Test results compare well with oxygenate analysis by GC-AED.

HALOCARBONS AND PCBS

Both the GC-ECD and GC-ELCD techniques are capable of detecting chlorine-containing compounds. The former GC detector is much more sensitive than the latter. With a 5-ml glass sampling loop, a VTAT[18] and an ECD, 50 ppbv of vinyl chloride can be easily determined. However, sulfur-containing organics and aromatics also respond to the ECD, reducing its selectivity for halocarbons. The latter technique is more selective, making positive identification of halocarbons much easier. At present, IGT monitors 35 halocarbon compounds in natural gas.

PCBs as six Arochlors and 15 individual congeners are examined by GC-ECD and GC-ELCD, respectively. Only cryogenic condensate and washing samples were analyzed because it is safe to assume PCBs, just like PAHs having very low vapor pressures, can be easily collected in the cryogenic sampler if indeed they are present in the gas phase in NG.

NITROGEN-CONTAINING COMPOUNDS

GC-AED was used successfully for determination of target eighteen nitrogen compounds including ammonia with a DB-Wax column. Ammonia is the only component difficult to measure because it elutes very near methane, making its detection difficult. A Photo Ionization Detector (PID) with a photo lamp (>10.15 eV) may be used for gas chromatographic measurement of low ppmv ammonia in natural gas because it is more specific to ammonia. Methane, which closely elutes with ammonia and must be vented during the GC-AED analysis, does not likely interfere with the detection of ammonia.

NO/NOX

The chemiluminescence technique originally developed for air monitoring of NO/NO_x was modified for natural gas analysis. A Columbia Model 1600 NO_x analyzer was used. A standard addition method was employed to compensate for the matrix effect and to allow interference-free measurement of the NO content in natural gas. Total nitrogen oxides (NO_x) was determined by an IGT method. This technique uses a gas glass cylinder to collect the gas and an aliquot of acidic peroxide solution to extract NO_x forming nitrate, which is subsequently determined by Ion Chromatography (IC). The concentration of NO_2 is determined by the difference of NO_x and NO. NO_2 cannot be determined directly by the chemiluminescence technique since some components in natural gas may react with NO_2 or even NO in the catalytic reaction chamber operating at about 450°C for NO_2 mode.

OTHER ELEMENTS

AED[19] offers simultaneous detection of elemental contents of every GC-eluted compounds by a

Table 1. Trace Constituents in Natural Gas: Concentration Range And Median

Components:	# of Samples	Range [ppmv]	Median
Aliphatics: Cyclopentane	17	<1 - 50	9
Hexanes	19	<0.2 - 1156	170
Methyl cyclopentane	17	<0.2 - 164	22
Cyclohexane	17	<0.2 - 146	24
Heptanes	19	<0.2 - 433	80
Methyl cyclohexane	17	<0.2 - 175	24
Octanes	19	<0.1 - 280	30
Nonanes	19	<0.1 - 280	11
Decanes	19	<0.1 - 120	6
Undecanes	19	<0.1 - 20	1
Dodecanes	19	<0.1 - 2.6	0.4
Aromatics: Benzene	17	<0.2 - 471	7
Toluene	17	<0.1 - 100	6
Ethylbenzene	17	<0.1 - 15	0.3
Xylenes	17	<0.1 - 33	1
PAHs	19	<0.02	<0.02
Other Elements and Compounds:			
Total Arsenic, ug/m^3	10	<5	<5
	7	<2-4	<2
Total Mercury, ug/m^3	19	<0.02-0.02	<0.02

Compounds:	# of Samples	Range [ppmv]	Median
Sulfurs			
Hydrogen sulfide	19	<0.1 - 6	0.2
Ethyl mercaptan	19	<0.02 - 0.16	0.04
i - Propyl mercaptan	19	<0.02 - 0.41	0.02
Nitrogen Compounds			
Ammonia	17	<4	<4
17 other target compounds	17	<0.5	<0.5
Oxygenates:			
Methanol	19	<1 - 92	8
Acetone	19	<1 - 24	<1
Halocarbons:			
35 target compounds	17	<0.1	<0.1
PCBs	17	<0.01	<0.01
NOx, ppmv	19	<0.05 - 130	<0.05
Radon, pCi/L	18	<1 - 110	3

RANGBAOA.DOC, May 4 1994

- NO/NOx analysis of whole gas samples by chemiluminescence and ion chromatography

During the on-going trace constituent survey work, multiple sets of samples were obtained and analyzed from 19 sampling sites. The concentration range and median of some trace contaminants examined in this program are summarized in Table 1.

Based on the data assembled thus far, it can be concluded that natural gas is no doubt the cleanest conventional energy source among other fossil fuels. Heavier hydrocarbons and BTEX were present in most samples analyzed. However, very little heavier hydrocarbons and BTEX were found in processed natural gas after cleanup or extraction facilities. No measurable quantities of PAHs were found in natural gas.

No target halocarbons, PCBs and amines were found at the corresponding detection limits we have set for this survey. Methanol was detected in all samples analyzed. However, higher concentrations were only found in northern climate areas, where methanol is routinely used as an antifreeze.

Two natural gas samples contained 1.2 and 130 ppmv NOx. It is suspected that the NOx contamination is the result of gas sweetening processes that use KNO_2 solution to oxidize and remove low levels of H_2S from NG.

Except for two small producing areas, where higher radon concentrations were observed, all other areas surveyed contained radon at levels below 4 pCi/l that EPA has established for air.

Finally, a wealth of experience and equipment have been gained by IGT in the performance of this work for which we gratefully acknowledge the support of GRI.

the condensate. Please refer to the copy of our condensate analysis that Mr. Yue On Chiu had at the meeting for typical mercury concentrations in the condensate.

Also as you requested, we have contacted several colleagues in the landfill gas industry (Waste Management, BFI and BKK) to determine if anyone had any data on mercury concentrations in landfill gas. None of these contacts had any data on mercury levels in landfill gas, nor were they aware of anyone who did. As we mentioned during our meeting, we measured mercury in the landfill sales gas at a facility that we operate in the Los Angeles area. That result was extremely low, 0.000003 mg/dscf. One of the stack testing firms that we have talked with reported measuring 4.7 x 10^{-7} lbs/hr of mercury from a flare stack at a landfill in Connecticut; the inlet flow of landfill gas to the flare was 1200-1600 cfm.

I hope this information is helpful to you. We look forward to further cooperation with office in this matter. As I mentioned to Mr. Chiu in a recent telephone conversation, we have obtained three quotations from testing firms to perform mercury analysis of the landfill gas that we are processing at the Fresh Kills landfill gas recovery plant.

Please contact me directly at (610) 481-4317 if you would like to discuss further actions.

Very truly yours,

Michael J. Sauers/kam

Michael J. Sauers

c: Mr. Cas Czarkowski, NY DEC
Mr. Ted Nabavi, NY DOS

gsf

bc:
M. Kapitan
P. J. Persico
G. P. Thompson
R. Wood
↳ copy Tim Holt
Fax → Cecil Bonnel

via fax

4 December 1995

GSF Energy
7201 Hamilton Boulevard
Allentown, PA 18195-1501
Telephone (610) 481-4911

ERD ref. 96ⓒ

Mr. Kenneth Eng
US EPA Region 2
290 Broadway, 21st floor
New York, NY 10007-1866

Dear Mr. Eng,

Thank you for inviting us to your office on 9 November 1995 to discuss the work that EPA has done to determine the landfill gas composition being processed at the Fresh Kills landfill gas recovery plant. The following paragraphs summarize several items that you asked us to follow up on.

Regarding the measurement of mercury in landfill gas with a Jerome meter, we offer the following. Although this instrument is a very good screening device for measuring mercury it may have some serious limitations in a landfill gas application. A representative of the manufacturer, Arizona Instruments, reported that chlorine, hydrogen sulfide and water vapor are known to be positive interferences in this instrument. All of these substances may be present in some form in the landfill gas. Although there is a filter within the instrument to remove the impurities, the Arizona Instrument representative said that there is no way to determine when the filter is depleted. We understand that the contractor, Radian, did scrub the gas to remove the hydrogen sulfide during their sampling; however, the landfill gas is saturated with water vapor and also contains chlorinated compounds. Measurements made by Radian with the Jerome meter may have been of water.

Based upon the nature of our process, our observations and measurements, we find it very difficult to believe what you reported to us regarding Radian's measurements and calculations of mercury in the landfill gas being processed through our plant. Our process involves chilling the landfill gas down to roughly zero degrees Celsius, which corresponds to a very low vapor pressure of mercury of 0.000185 mm of Hg. We would expect therefore that any mercury contained in the landfill gas to condense out during this chilling step. Moreover, if the amount of mercury that Radian calculated to be entering our plant were correct, we would expect to observe part per million levels of mercury in the condensate that we collect. Our measurements have shown trace or part per billion levels of mercury in

A Subsidiary of Air Products and Chemicals, Inc.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 2
290 BROADWAY
NEW YORK, NY 10007-1866

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DEC 15 1995
FS ENVIRONMENTAL SERVIC

ERD ref 96CD

DEC 07 1995

Mr. Michael J. Sauers
GSF Energy
7201 Hamilton Boulevard
Allentown, PA 18195-1501

Re: Testing for Mercury at the Fresh Kills landfill

Dear Mr. Sauers:

Thank you for your letter of December 4, 1995 confirming your company's commitment to test for mercury in the gas that your company processes at the Fresh Kills landfill. As mentioned in your letter, you have already obtained three quotations from testing firms to conduct the test. We are anxiously awaiting your selection of a testing firm. Once you inform us of your selection, we will proceed immediately to work with the firm to develop a test protocol and to perform the necessary tests. As you may recall in our November 9, 1995 meeting, we have tentatively agreed to try to have all the work done within a two-month period.

As a reminder, please note that the minimum level of testing to address the areas of concern with this mercury issue would include quantification and identification of mercury (both inorganic and organic forms) in the gases received and processed by the GSF plant.

Please inform us of your testing firm selection within the next week. We look forward to working with you soon. If you have any questions or would like to discuss this matter further, please contact me at (212) 637-4080.

Sincerely,

Kenneth Eng, Chief
Air Compliance Branch

cc: Michael Kormanik, NYSDEC Region 2
Cas Czarkowski, NYSDEC Region 2
Ted Nabavi, NYCDOS

file FK : Mercury

United States
Environmental Protection Agency
Region 2: NJ, NY, PR, VI
290 Broadway
New York, New York 10007-1866

NEWS

95123 Rich Cahill (212) 264-2515

MARTHA 2690288

FOR RELEASE: Friday, November 3, 1995

EPA COMPLETES AUDIT OF GAS EMISSIONS FROM THE FRESH KILLS LANDFILL ON STATEN ISLAND

NEW YORK, N.Y. -- The U.S. Environmental Protection Agency (EPA) recently completed a field audit and study of gas emissions from the Fresh Kills Landfill on Staten Island. This audit was the final phase of an effort by EPA to determine if the landfill was operating in compliance with federal guidelines for municipal solid waste landfills. The study of gas emissions is one of the most comprehensive evaluations of landfill gases ever undertaken in the United States.

Over the past several years, EPA has been working in cooperation with state and local agencies to characterize any potential health risks posed by the landfill and other sources of toxic pollutants. In its latest effort EPA found that Fresh Kills emits essentially the same types of pollutants as industrial and combustion facilities, such as an oil refinery.

EPA, state, local agencies and several academic institutions began monitoring the concentrations of a large number of hazardous pollutants in Staten Island neighborhoods in 1987 as part of the Staten Island/New Jersey Urban Air Toxics Assessment Project

- more -

ERD ref 96 (E)

N.Y.C. Department of Sanitation

Facsimile Transmission

To: Mr. Mike Sowers Fax No: 610-481-4377

From: **Mr. Ted R Nabavi , CHMM** Fax No: **212-785-3952**
Bureau of Solid Waste Management & Engineering

Re: EPA Report

Date: 12/14/95

Number of Pages Including Cover 6

Fax Only ✓

FYI

cc: P. Persico
G. P. Thompson
R. Wood
M. Kapitan
C. Bonnell
J. Desmone
T. Holt

FYI, Incredible!
Mike

If thre are any problems with this transmission, Please call (212) - 837 - 8458 determine if the Fresh Kills landfill is in compliance with federal regulations for landfills and to audit and test the air, soil, ground water and surface water at the landfill.

EPA chose to conduct the study in three phases. The first phase of the study, completed in September 1994, found that there was not sufficient information to make an assessment of the landfill's health risks. The second phase of the study, also completed in September 1994, determined that the landfill was in overall compliance with applicable federal regulations. The third and final phase of the study, completed last month, provided a comprehensive characterization of the composition and the emission rate of gases coming from the landfill.

The final report for this third and final phase of the federal study is in two volumes entitled, "Determination of Landfill Gas Composition and Pollutant Emission Rates at Fresh Kills Landfill," dated November 10, 1995.

###

(SI/NJ UATAP). The New York State Department of Environmental Conservation continues to monitor for these pollutants. This monitoring directly measures the exposure of people in Staten Island to air quality resulting from emissions of all types of sources, including the landfill. The results from the SI/NJ UATAP showed that the risks attributable to toxic pollutants in Staten Island's air were similar to other urban areas where monitoring has been carried out. The most significant contributor to the risk is benzene which is primarily emitted by automobiles and facilities which handle gasoline.

The measurements indicate that the landfill emissions may be a significant contributor to mercury in the area. EPA has recently issued a report to Congress that indicates that sources of mercury are ubiquitous. In the northeast, incinerators and coal-fired power plants appear to be the most significant sources. With the renewed interest in mercury pollution, EPA will ensure that more thorough and precise tests are conducted to verify the presence and quantity of mercury and evaluate the significance of emissions from Fresh Kills. The tests are expected to be completed before the end of this winter.

EPA received a total of $1,250,000 from Congress, funds that Congresswoman Susan Molinari was instrumental in obtaining, to

- more -

Mike
610
481-4377

file
FK:
Mercury

Staten Island Advance

SINCE 1886 SATURDAY, DECEMBER 9, 1995 50 CENTS

Audit suggests Fresh Kills may be releasing large quantities of the pollutant

EPA probes mercury level at landfill

Regional office plans to conduct more thorough and precise tests to determine if the emissions pose a health risk

By TERENCE J. KIVLAN
ADVANCE WASHINGTON BUREAU

WASHINGTON — A federal field audit of the emissions from the Fresh Kills landfill has suggested that it may be releasing large quantities of mercury — a kind of toxic pollution normally associated with heavy-duty industrial facilities.

In a statement issued yesterday, the U.S. Environmental Protection Agency (EPA) regional office in Manhattan said its investigation indicated that "landfill emissions may be a significant contributor to mercury" in the area around Fresh Kills.

The statement noted that a recent study prepared for Congress by EPA analysts here reported that they had found "ubiquitous" sources of mercury emissions in the U.S.

"In the Northeast, incinerators and coal-fired power plants seemed to be the most significant sources," the New York EPA officials said in the statement.

The officials said the regional office intended to conduct "more thorough and precise" tests over the next several months to "verify the presence and quantity of mercury and evaluate the significance of emissions at Fresh Kills."

Rich Cahill, an EPA spokesman in New York, said agency investigators detected mercury emissions at two locations in the landfill. He said although the discovery "raised questions," it didn't necessarily confirm suspicions that the landfill posed a health threat.

"It may mean nothing, but we want to check it out," Cahill said. "At this point we don't have enough evidence to draw any conclusions."

Island environmental activists and elected officials have long argued that emissions from the landfill cause what they say is the unusually high rate of respiratory disease and cancer in the surrounding area.

"There are certainly some red flags up as a result of this study," said Republican Rep. Susan Molinari, adding: "It confirms what we all have known — that Fresh Kills is a major source of air pollution."

"The next question is what long-term effect is the landfill having on the population," she said. "We still don't have the answer."

The congresswoman said it could start to unfold next year when, as they pledged several months ago, officials at the federal Centers for Disease Control in Atlanta analyze the results of all federal and state studies on Fresh Kills now under way.

The landfill is also being investigated by city and state health officials and the state

PLEASE SEE LANDFILL, PAGE A4

---

ic air pollution has mounted in
ent years. In a 1994 computer

their claims that Fresh Kills did
not represent a health risk.

Landfill

FROM PAGE A 1

Department of Conservation (DEC).

Meanwhile, the question of how a large quantity of mercury could have found its way into the landfill also remained unanswered yesterday.

"We do not accept mercury or anything containing mercury into Fresh Kills," said Kathy Dawkins, a spokeswoman for the city Department of Sanitation, which operates the facility.

But she added that "people do throw away thermometers and batteries."

Gary Scheffer, a spokesman in Albany for the DEC, said agency officials were aware that "ambient levels of mercury" existed in the neighborhoods around Fresh Kills, but they had "no information to date that it was at levels to be alarmed about."

"(Mercury) comes off most landfills, but to date not at sufficient levels to be alarmed about," Scheffer explained.

He said his agency was working with EPA to determine the quantities of mercury being released at Fresh Kills.

Evidence indicating that Fresh Kills and other large, heavily packed landfills across the coun- ry have become major sources of oxic air pollution has mounted in ecent years. In a 1994 computer [illegible] study of Fresh Kills, for instance, a Boston-based environmental consulting firm estimated that the 2,000-acre landfill, the nation's largest, was emitting 680 tons of toxic gases a year.

The study was based on a mathematical profile developed by EPA for investigating conditions at a typical U.S. landfill.

The firm warned that the concentration of decaying refuse at Fresh Kills was so monumental — 90 million tons — that the landfill would continue to exude vast quantities of toxic emissions long after it was closed and sealed.

In response to this and other revelations about the possible landfill threat, EPA officials have drafted regulations under which garbage dumps could be subject to the same stringent clean-up requirements as "smoke stack" air-pollution sources.

The EPA emissions audit was the final part of a three-phase study of Fresh Kills paid for by $1.25 million in congressional funding secured through Ms. Molinari. In the first two phases, the federal agency concluded that the landfill was being operated in accordance with federal standards but that the state and city lacked sufficient information to back up their claims that Fresh Kills did not represent a health risk.

Jerome Arizona Instrume

ERD Ref 96 (E)

Interferences

The chart below shows the results of a comparison between a Jerome 431-X Gold Film Mercury Vapor Analyzer and a UV mercury vapor detector, as performed by an independent company.

Non Mercury Vapor	Gold Film	UV
cigarette smoke	no response	full scale pegged
hexane	no response	minimal to full scale
benzene	no response	about 0.6 mg/m3 reading
dust, gravel	0.002 mg/m3*	about 0.07 mg/m3 reading

*This caused the intake filter disc to get quite dirty. After quickly and easily replacing the filter disc, the instrument reading returned to zero.

The following is taken from "Mercury Analysis in Ambient Air by Means of Thin Gold Film Resistors". This table shows the lack of interferences from a variety of organic solvents.

Influence Of Organic Vapors Of Solvents

Organic Solvent	Response
benzene	0
toulene	0
acetone	0
methylisobutylketone	0
chloroform	0
carbon disulfide	minimal
carbon tetrachloride	minimal

**"Mercury Analysis in Ambient Air by Means of This Gold Film Resistors," Ohkawa, Uenoyama, & Kondo; Rigaku Corporation & Faculty of Pharmaceutical Science, Osaka, Japan; Eisei Kagaku, Vol. 22, No. 1, pg. 11 - 18; 1976.

Note: The Jerome 431-X's internal acid gas filter quantitatively removes gases and vapors, such as chlorine, H2S and iodine, which are known to cause a resistive effect on the gold film sensor. Replacement of the filter according to a simple maintenance schedule will ensure the integrity and proper response of the sensor to mercury.

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Date 12-14-95	# of pages ▸ 1
To TED NABAV	From MIKE SAUERS
Co./Dept.	Co.
Phone #	Phone #

TECHNICAL SPECIFICATIONS

Range ——— 0.000 to 0.999 mg/m^3 Hg

Resolution ——— .001 mg/m3 Hg

Sensitivity ——— 0.003 mg/m^3 Hg

Precision ——— 5% Relative Standard Deviation
@ .100 mg/m^3 Hg

Accuracy ——— +/-5% @ 0.100 mg/m^3 Hg

Response Time
Sample Mode ——— 12 seconds
Survey Mode ——— 3 seconds

Flow Rate ——— 750cc/min
0.75 liters/min = 750cc/min

Power Requirements ——— 100-130 VAC (or 200-260 VAC), 60 cycle
115 watts maximum

Batteries ——— Rechargeable Nickel Cadmium

Construction ——— Aluminum Alloy

Dimensions ——— 6" W X 13" L X 4" H

Weight ——— 7 pounds

Digital Meter ——— Liquid Crystal Display

Operating Environmental
Range ——— 0 - 40°C, non-condensing,
non-explosive

OPTIONAL "COMMUNICATIONS" VERSION (see Appendix C)

Alarm Output ——— 30V DC, 100ma

Dosimeter Power Output ——— for Dosimeter analysis

Data Output ——— 1) Digital, Serial, RS232, Baud Rate 1200
——— (Data Logger, Base Station, JCI program
——— software
2) Digital, Serial, RS232 Data Format, but with driver for 20 ma capability and 0 & 20 ma Logic Levels; Baud Rate 1200 (industrial special applications)

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 2
290 BROADWAY
NEW YORK, NY 10007-1866

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JAN 29 1996
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ERD ref 96 (G)

JAN 24 1996

Mr. Michael J. Sauers
GSF Energy
7201 Hamilton Boulevard
Allentown, PA 18195-1501

Re: The Air Products/GSF Plant at the Fresh Kills Landfill

Dear Mr. Sauers:

This is to confirm the conversation that you had with Yue On Chiu of my staff on January 12, 1996. In the conversation, you informed Mr. Chiu that Air Products/GSF has already performed a test on the input and the output (to Brooklyn Union Gas) gas stream at its Fresh Kills Landfill plant. You stated that the test was conducted in late November by a contractor (TRC Environmental), and preliminary results show very low mercury concentrations in the two gas streams. You also said that no test protocol or notification of the test was given to EPA or the NYSDEC prior to the test. Mr. Chiu requested that copies of the test protocol and results be submitted to EPA for review. You told Mr. Chiu that you will have a copy mailed to EPA by the week of January 15, 1996.

Please note that Air Products/GSF has deviated from the agreements that were reached in our November 9, 1995 meeting -- by testing without first having given the test protocol to EPA and the NYSDEC for review. Because an approved protocol was not obtained, the test points/locations not defined, and no EPA/NYSDEC witnesses were present during the test, it is possible that additional testing maybe required of Air Products/GSF if your test results do not conform to our requirements. Nevertheless, we are awaiting receipt of your test results and associated test protocol so that we can review them.

Additionally, we are asking you to perform an emission mass-balance of the Fresh Kills plant from all the information that you have obtained thus far regarding the plant's emissions. The purpose of this request is to determine the concentrations of mercury entering/leaving the plant and to ensure that they are accounted for and permitted properly. Also, we would like to obtain copies of any emissions data (hard-copies of actual test reports, etc.) that you have available on any landfill gas processing plant. This data could aid us considerably in our study of emissions from this industry.

If you have any questions or concerns, please contact me at (212) 637-4080.

Sincerely,

Kenneth Eng, Chief
Air Compliance Branch

cc: Mr. Mike Kormanik, NYSDEC - Region 2
Mr. Cas Czarkowski, NYSDEC - Region 2
Mr. Ted Nabavi, NYCDOS

bcc: C. Simon, 2AWM-AC
K. Mangels, 2AWM-AC
R. Kapichak, 2AWM-AP
A. Tietz, 2ESD-MM
Y. Chiu, 2AWM-AC

EFD Pg 96 (A)

gsf

GSF Energy
7201 Hamilton Boulevard
Allentown, PA 18195-1501
Telephone (610) 481-4911

via overnight mail

January 25, 1996

Mr. Kenneth Eng, Chief
Air Compliance Branch
United States Environmental Protection Agency
Region 2
290 Broadway
New York, NY 10007-1866

Dear Mr. Eng:

5

This letter is in further follow-up to our meeting on 8 November 1995 and to your letter of 7 December 1995 regarding mercury testing at our landfill gas recovery facility located at the Fresh Kills landfill. In conjunction with testing we had performed at our facility for Nox RACT purposes during the week of 16 November 199~~6~~, our testing consultant, TRC, was able to also test our inlet raw landfill gas and the sales landfill gas for mercury content. The attached TRC report summarizes this work.

The results of this testing confirmed our belief that the screening level mercury measurements that were conducted by EPA/Radian must have been flawed. Using EPA Method 101A, TRC measured only part per trillion levels of mercury in both the raw landfill gas entering our plant and the sales gas leaving it. On a mass basis these levels equate to less than 14 grams of mercury passing through our plant in a year, vs. 1,975 lbs/yr calculated from EPA/Radian's screening level measurements. As we stated in our meeting and subsequent letter to you, we believe that measurements made by EPA/Radian with the Jerome meter were probably flawed due to presence of water vapor.

We hope this information is helpful to you. Based upon these results we will not be performing any further testing for mercury. We will however continue to cooperate with EPA and its contractors with any further sample collection at our facility. If you have any questions, please don't hesitate to call me at (610) 481-4317.

Very truly yours,

Michael J. Sauers

Michael J. Sauers

attachment

c: Mr. Cas Czarkowski, NY DEC
Mr. Ted Nabavi, NY DOS
Mr. Bert Breitburg, NY DEC

bc:
T. J. Holt
M. Kapitan
P. J. Persico
G. P. Thompson
R. Wood

TRC Environmental Corporation

5 Waterside Crossing
Windsor, Connecticut 06095
Telephone 860-289-8631
Facsimile 860-298-6399

January 19, 1996

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JAN 22 1996
FFS ENVIRONMENTAL SERVIC

Mr. Michael Sauers
Air Products and Chemicals, Inc
Mail Stop W2405
7201 Hamilton Boulevard
Allentown, PA 18195

Re: Report "GSF Energy, Inc. Fresh Kills Landfill Gas Recovery Facility Landfill Gas Mercury Test"

TRC Project No. 18866

Dear Mr. Sauers:

Enclosed please find four final copies of the report entitled "GSF Energy, Inc. Fresh Kills Landfill Gas Recovery Facility Landfill Gas Mercury Test" which include the revisions you requested.

If you have any questions, please do not hesitate to contact me at (203) 298-6304.

Very truly yours,
TRC ENVIRONMENTAL CORPORATION

James Canora

James E. Canora
Manager, Emissions Measurements Group

Offices located in
major industrial centers

TRC Environmental Corporation

GSF ENERGY, INC
FRESH KILLS LANDFILL GAS RECOVERY FACILITY
LANDFILL GAS MERCURY TEST

Presented to

GSF ENERGY, INC., a subsidiary of
Air Products and Chemicals, Inc.
Allentown, Pennsylvania

Prepared by

TRC Environmental Corporation
Windsor, Connecticut

James Canora
Manager, Emissions Measurement Group

TRC Project No. 18866
January, 1996

TRC Environmental Corporation
5 Waterside Crossing
Windsor, Connecticut 06095
Telephone 203-289-8631
Facsimile 203-298-6399

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1.0 INTRODUCTION

TRC Environmental Corporation (TRC) was retained by GSF Energy, Inc. (GSF) to perform a concentration measurement program at the GSF Fresh Kills Landfill Gas Recovery Facility in Staten Island, New York. The program objective was to measure mercury concentrations in the gas treatment plant (GTP) inlet and outlet gas streams to develop accurate and defensible data. This testing was conducted in response to recent EPA tests which have shown high concentrations of mercury in landfill gas. Air Products contracted with TRC to perform an independent analysis using a U.S. Environmental Protection Agency (EPA) Reference Method. Testing was performed in accordance with EPA Method 101A.

The test program was conducted on November 16, 1995 by Mr. Raymond Potter, of TRC. Mr. George Beris of Air Products and Chemicals, Inc. provided process and logistical support during the field effort.

Section 2.0 of this report presents a summary and discussion of results. Section 3.0 provides a brief process description. Section 4.0 presents the test methods utilized during the program, and section 5.0 presents TRC's quality control plan for the program.

2.0 SUMMARY AND DISCUSSION OF RESULTS

Duplicate 120-minute mercury samples were collected from the inlet and outlet of the GTP in accordance with EPA Method 101A which was modified for high pressure gas sampling. All samples were analyzed by cold vapor graphite furnace atomic absorption (CVGFAA) emission spectrometry according to SW-846 Method 7471.

The average mercury mass rate, based on two GTP inlet samples and two GTP outlet samples, was 2.4 x 10^{-6} pounds per hour. The difference between the inlet and the outlet mass rates was not significant (the difference from the mean was 21% – the average inlet mass rate was 1.9 x 10^{-6} pounds per hour and the average outlet mass rate was 2.8 x 10^{-6} pounds per hour). The concentration averaged 0.083 ug/m^3 in the GTP inlet landfill gas and 0.245 ug/m^3 in the outlet sales gas. A summary of the inlet and outlet mercury measurements is presented in **Tables 2-1 and 2-2.**

The program quality assurance data supported the validity of the measurements. The total mercury collected in both the inlet and the outlet samples was low, but was detected at levels consistently higher than in the field blank. The inlet samples contained approximately three times more total mercury than the blank and the outlet samples contained more than seven times the amount of mercury in the blank. There was no indication of the potassium permanganate absorbing solution being depleted by excessive amounts of oxidizing material (depletion of the absorbing solution can bias Method 101A low); the solution retained a purple color throughout the test.

Table 2-1

INLET LANDFILL GAS
Modified EPA Method 101A

Air Products and Chemicals, Inc.
Fresh Kills Landfill
Staten Island, New York
November 16, 1995

Test Number **Time** **Location**	**Inlet Landfill Gas -1** **10:50:12:50** **Inlet**	**Inlet Landfill Gas - 2** **08:05-10:05** **Inlet**	**Average**
Flow Conditions			
Volumetric Flowrate, Dry Std.(dscfm) [1]	6140	6140	6140
Sample Conditions			
Catch (ug) [2]	0.21	0.29	0.25
Sample Volume Dry (dscf)	105.42	106.85	106.14
Mercury Measurements			
Concentration (ug/dscf)	0.0020	0.0027	0.0024
Concentration (ug/m^3)	0.071	0.096	0.083
Mass Rate (lb/hr)	1.6E-06	2.2E-06	1.9E-06

1 - dscfm standard conditions at 68°F and 29.92 in. Hg - supplied by Air Products
2 - Blank corrected total mercury catch in micrograms

Table 2-2

OUTLET SALES GAS
Modified EPA Method 101A

Air Products and Chemicals, Inc.
Fresh Kills Landfill
Staten Island, New York
November 16, 1995

Test Number **Time** **Location**	**Outlet Sales Gas -1** **10:53-12:53** **Outlet**	**Outlet Sales Gas - 2** **08:10-10:10** **Outlet**	**Average**
Flow Conditions			
Volumetric Flowrate, Dry Std.(dscfm) [1]	3050	3050	3050
Sample Conditions			
Catch (ug) [2]	0.50	0.62	0.56
Sample Volume Dry (dscf)	81.32	81.10	81.21
Mercury Measurements			
Concentration (ug/dscf)	0.0062	0.0077	0.0069
Concentration (ug/m^3)	0.22	0.27	0.25
Mass Rate (lb/hr)	2.5E-06	3.1E-06	2.8E-06

1 - dscfm standard conditions at 68°F and 29.92 in. Hg - supplied by Air Products

2 - Blank corrected total mercury catch in micrograms

3.0 PROCESS DESCRIPTION

Air Products operates a gas treatment plant at the GSF Fresh Kills Landfill Gas Recovery Facility in Staten Island, New York. The purpose of the facility is to recover landfill gas and purify it for sale. Landfill gas is collected from a series of wells located across the landfill. The raw landfill gas consists of approximately 50% methane, 50% CO_2, and trace contaminants. The treatment plant removes CO_2 and trace contaminants to produce "pipeline quality" methane for sale to Air Products customers.

4.0 SAMPLING AND ANALYTICAL METHODOLOGY

Measurements were conducted at the inlet and outlet of the GTP at the GSF Fresh Kills Landfill Gas Recovery Facility. Duplicate 120-minute tests were conducted at each location to measure concentrations of mercury in accordance with EPA Method 101A. The following section describes this method in detail.

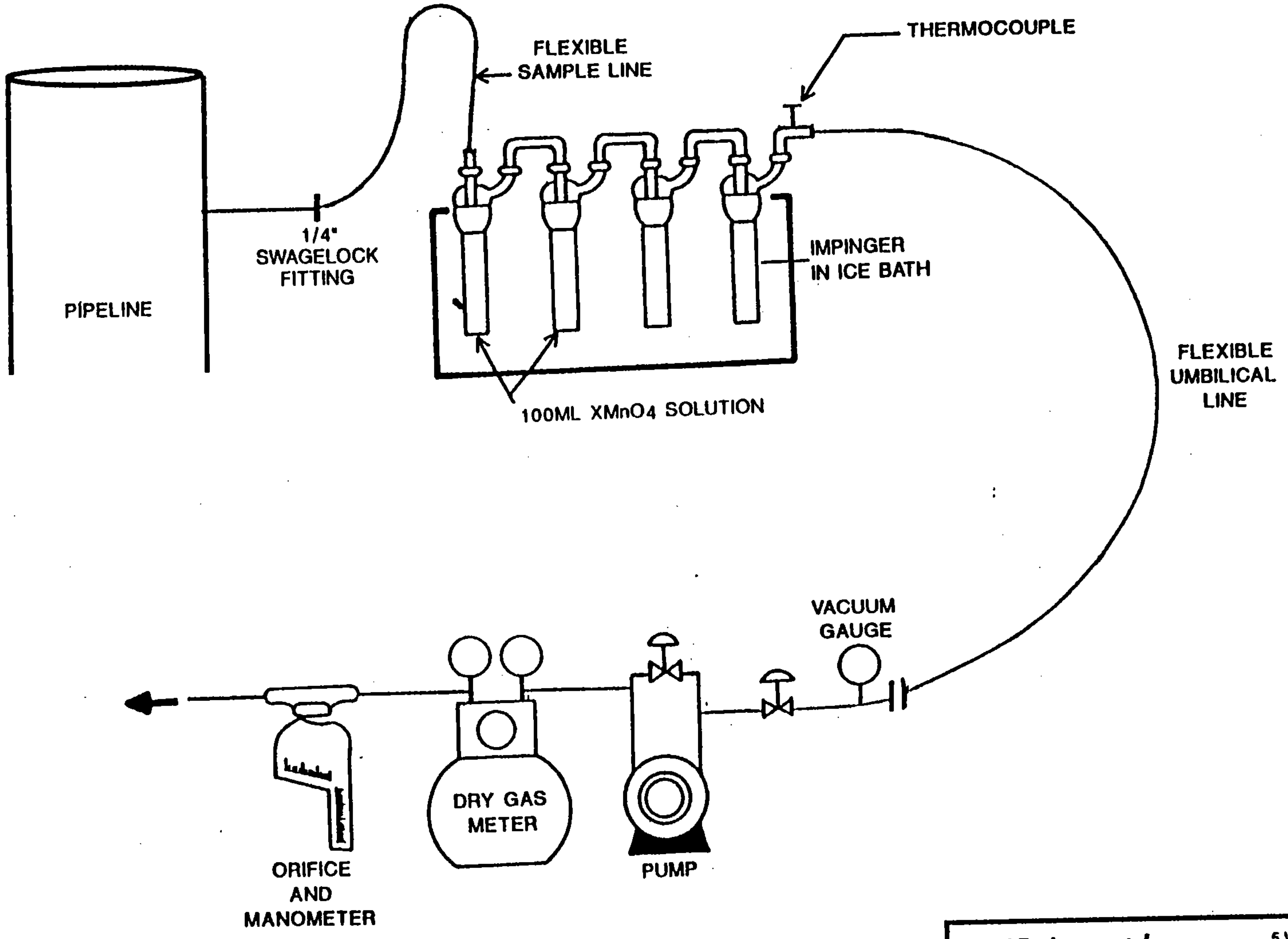
4.1 Mercury Measurements - EPA Method 101A

Duplicate 120-minute tests were conducted at each location for a total of four tests. Sampling was conducted in accordance with a modified EPA Method 101A "Determination of Particulate and Gaseous Mercury Emissions from Sewage Sludge Incinerators."

4.1.2 Sample Collection

The modified sampling train, depicted in **Figure 4-1**, consisted of a Teflon line, four impingers, dry gas meter, calibrated orifice, and an inclined manometer. An ice bath containing the four impingers was attached to the back end of the probe. The first two impingers were filled with 100 ml of 4% acidified potassium permanganate solution, the third impinger was empty, and the fourth impinger contained silica gel to remove any remaining moisture.

Both the inlet and outlet locations were pressurized. A Teflon line was attached using a swagelock fitting. Pressure from the system was used to push sample gas through the sampling train which alleviated the need for a sample pump. Sampling was conducted at approximately 0.75 cubic feet per minute. Sample flow was regulated by a needle valve placed between the first impinger and the ¼" sample tap. Before and after each run, the sampling train was leak-checked to ensure that the leak rate was less than 0.02 cfm. Pertinent test data was recorded on field data sheets.



TRC Environmental Corporation

5 Waterside Crossing
Windsor, CT 06095
(203) 289-8631

GSF ENERGY, INC
FRESH KILLS LANDFILL GAS RECOVERY FACILITY

FIGURE 4-1
MODIFIED EPA METHOD 101A
SAMPLING TRAIN

4.1.2 Sample Recovery and Analysis

After each test the samples were placed in appropriate containers as follows:

Container No. 1:	The volume of each impinger was measured to the nearest 0.1 milliliter for determination of stack moisture. Each impinger was rinsed three times with 0.1 normal nitric acid. The impinger contents and rinses were then deposited into a clean sample jar.
Container No. 2:	The silica gel was replaced in its original container and labeled.

All samples were placed in shock-proof containers for transport to the analytical laboratory for analysis. Samples were analyzed for mercury by cold vapor graphite furnace atomic absorption (CVGFAA) emission spectrometry.

4.2 Sampling Locations

Sampling was conducted at the inlet and outlet of the GTP using ¼" taps at each location. Typical 3" ports could not be used because the GTP is pressurized. TRC used ¼" Swagelok fittings and Teflon line to attach the mercury sampling trains to the taps at each location. The flow to each sampling train was regulated using a needle valve.

5.0 QUALITY ASSURANCE

The TRC quality assurance (QA) program is designed to ensure that emission measurement work is performed by qualified people using proper equipment following written procedures in order to provide accurate, defensible data. This program is based upon the EPA *Quality Assurance Handbook for Air Pollution Measurement Systems*, Volume III (EPA-600/4-77-027b).

At the beginning of each test day, a meeting was held to orient personnel to the activities scheduled for that day, to discuss results from the previous day, and to determine if any special considerations would be appropriate for the day's work.

5.1 Sampling

Prior to the field test program, full cleanup (background) evaluations of all sampling equipment were performed at the TRC laboratories to ensure the accuracy of the chosen equipment and procedures.

5.2 Analysis

All sample preparation and sample analyses were performed at or under the direction of the TRC's laboratories. Standards of QA set forth in the *Quality Assurance Handbook for Air Pollution Measurement*, Volume III (EPA-600/4-77-27b) and the *Handbook for Analytical Quality Control in Water and Wastewater Laboratories* (EPA-600/4-79-019, March 1979) were strictly followed.

5.2.1 Blanks

One field blank was collected and analyzed for mercury. The field blanks were clean demonstrating that field procedures were conducted properly. The blank results are summarized in **Appendix A.**

Appendix A
Field and Analytical Data

Isokinetic Flue Gas Sampling Data Sheet

Page 1 of 2

Project No. 188666
Client Air Products
Facility Fresh Kills
Source Gas Plant
Sample Location Outlet
Stack Diameter N/A
Date 11-16-95
Run No. O-2
Operator R Potter
Meter Box No. 80819
Meter Δ H@ 1.95
Y Factor 0.99

Very Important - Fill in All Blanks

Read and Record at the Start of Each Test Point

Sketch

Sheet 1 of 2
Train Prepared By R Potter
Pitot Number and Side N/A
Pitot Tube CP N/A
Filter No. / Thimble No. N/A
Ambient Temp. °F 40
Bar. Pressure, In. Hg 30.10
Assumed Moisture, % N/A
Heater Box Setting, °F N/A
Nozzle # / Dia., In. N/A
Probe Length / Material N/A
Probe Heater Setting N/A

Point	Clock Time		Dry Gas Meter, (ft^3)	Pitot In. H_2O Δ P	Orifice Δ H In. H_2O		Dry Gas Temp. °F		Pump Vacuum In. Hg Gauge	Temperatures °F °C					
	24 - hr	min			Desired	Actual	Inlet	Outlet		Stack	Filter Box	Imp Temp	XAD Cond	Probe	Filter Outlet
	1053	0	433.100	N/A		1.5	40	38	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		10	440			1.5	40	39							
		20	448447			1.55	40	40							
		30				—	—	—							
		40	459			1.50	40	40							
		50	465			1.5	40	39							
		60	472			1.5	40	40							
		70	478			1.5	41	40							
		80	485			1.5	41	41							

Train Leak Check:
Before Test: ______ CF ______ SEC ______ In. Hg
After Test: ______ CF ______ SEC ______ In. Hg

	I	F		Static Pressure		
Pitot Tube Leak Check			Port			
ORSAT Train Leak Check			In. H_2O			
			In. Hg			

Comments:

impingers -6
SG +4
-2

Isokinetic Fi Sampling Data Sheet

Page 2 of 2

Project No. 18866
Client Air Products
Facility Freshkills
Source Gas Plant

Date 11-16-95
Run No. O-2
Sample Location Outlet

Sheet 2 of 2
Operator RPotter

Point	Clock Time 24-hr	Clock Time min	Dry Gas Meter, (ft3)	Pitot in. H_2O ΔP	Orifice ΔH In. H_2O Desired	Orifice ΔH In. H_2O Actual	Dry Gas Temp. °F Inlet	Dry Gas Temp. °F Outlet	Pump Vacuum In. Hg Gauge	Temperatures °F °C Stack	Filter Box	Imp Temp	XAD Cond	Probe	Filter Outlet
		90	492	N/A		1.5	41	41	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		100	498	|		1.5	40	41	|	|	|	|	|	|	|
		110	503			1.5	40	40							
	1253	120	510.135												
			77.04			1.5	40								
		Total													

Comments:

Meter Leak Check During Test:

			Meter Reading Stop	Meter Reading Start
____ CF	____ SEC	____ In. Hg	____	____
____ CF	____ SEC	____ In. Hg	____	____

Static Pressure

Port	____	____	____
In. H_2O	____	____	____
In. Hg	____	____	____

AF 060

TRC

Isokinetic Flux Sampling Data Sheet

Page 2 of 2

Project No. 18866
Client Air Products
Facility Fresh Kills
Source Gas Plant

Date 11-16-95
Run No. O-1
Sample Location Outlet

Sheet 2 of 2
Operator R Potter

Point	Clock Time		Dry Gas Meter, (ft³)	Pitot in. H_2O ΔP	Orifice ΔH In. H_2O		Dry Gas Temp. °F		Pump Vacuum In. Hg Gauge	Temperatures °F °C					
	24 - hr	min			Desired	Actual	Inlet	Outlet		Stack	Filter Box	Imp Temp	XAD Cond	Probe	Filter Outlet
		96	414			1.5	35	35							
		100	420			1.5	35	35							
		110	426			1.5	35	35							
	1010	120	[illegible]												
			433.025												
			76.06			1.5	35								
		Total													

Meter Leak Check During Test:

_____ CF _____ SEC _____ In. Hg
_____ CF _____ SEC _____ In. Hg

Meter Reading Stop	Meter Reading Start

Static Pressure

Port			
In. H_2O			
In. Hg			

Comments:

AF-050

Isokinetic Flue Gas ... pling Data Sheet

Page 1 of 2

Project No. 18866
Client Air Products
Facility Fresh Kills
Source Gas Plant
Sample Location Inlet
Stack Diameter N/A
Date 11-16-95
Run No. I-2
Operator RPotter
Meter Box No. M3
Meter Δ H@ 185
Y Factor 1.01

Very Important - Fill in All Blanks

Read and Record at the Start of Each Test Point

Sketch

Sheet 1 of 2
Train Prepared By RPotter
Pitot Number and Side N/A
Pitot Tube CP N/A
Filter No. / Thimble No. N/A
Ambient Temp.°F 40
Bar. Pressure., In. Hg 30.10
Assumed Moisture, % N/A
Heater Box Setting, °F N/A
Nozzle # / Dia., In. N/A
Probe Length / Material N/A
Probe Heater Setting N/A

Point	Clock Time		Dry Gas Meter, (ft3)	Pitot In. H_2O Δ P	Orifice Δ H In. H_2O		Dry Gas Temp. °F		Pump Vacuum In. Hg Gauge	Temperatures °F °C					
	24 - hr	min			Desired	Actual	Inlet	Outlet		Stack	Filter Box	Imp Temp	XAD Cond	Probe	Filter Outlet
	1050	0	719.00	N/A		1.5	41	40	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		10	726			1.5	41	41							
		20	734			1.5	41	41							
		30	—			—	—	—							
		40	751			1.5	41	40							
		50	759			1.5	41	41							
		60	767			1.5	41	41							
		70	776			1.5	41	41							
		80	784			1.5	40	41							

Train Leak Check:
Before Test: ______ CF ______ SEC ______ In. Hg
After Test: ______ CF ______ SEC ______ In. Hg

	I	F	Static Pressure			
Pitot Tube Leak Check			Port			
ORSAT Train Leak Check			In. H_2O			
			In. Hg			

Comments:

impingers −10
56 +8
−2

Isokinetic Flue Gas Sampling Data Sheet

Page 2 of 2

Project No. 18866

Client Air Products

Facility Freshkills

Source Inlet / Gas Plant

Date 11-16-95

Run No. I-2

Sample Location

Sheet 2 of 2

Operator R Potter

Point	Clock Time 24 - hr	Clock Time min	Dry Gas Meter, (ft^3)	Pitot in. H_2O Δ P	Orifice Δ H In. H_2O Desired	Orifice Δ H In. H_2O Actual	Dry Gas Temp. °F Inlet	Dry Gas Temp. °F Outlet	Pump Vacuum In. Hg Gauge	Temperatures °F °C Stack	Filter Box	Imp Temp	XAD Cond	Probe	Filter Outlet
		90	793	N/A		1.5	42	41	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		100	801			1.5	42	42							
		110	809			1.3	42	42							
	1250	120	817.690												
			98.09			1.5	41								
		Total													

Meter Leak Check During Test:

				Meter Reading Stop	Meter Reading Start
____ CF	____ SEC	____ In. Hg		____	____
____ CF	____ SEC	____ In. Hg		____	____

Static Pressure

Port	____	____	____
In. H_2O	____	____	____
In. Hg	____	____	____

Comments:

AF-050

Isokinetic Flue Gas ...pling Data Sheet

Page 1 of 2

Project No. 18866
Client Air Products
Facility Freshkills
Source Gas Plant Inlet *
Sample Location * Inlet
Stack Diameter N/A
Date 11-16-95
Run No. I-1
Operator RPotter
Meter Box No. ~~88819~~ M3 RP
Meter Δ H@ ~~1.95~~ 1.85 RP
Y Factor ~~0.99~~ 1.01 RP

Very Important - Fill in All Blanks

Read and Record at the Start of Each Test Point

Sketch

Sheet 1 of 2
Train Prepared By RPotter
Pitot Number and Side N/A
Pitot Tube CP N/A
Filter No. / Thimble No. N/A
Ambient Temp. °F 35
Bar. Pressure., In. Hg 30.10
Assumed Moisture, % N/A
Heater Box Setting, °F N/A
Nozzle # / Dia., In. N/A
Probe Length / Material N/A
Probe Heater Setting N/A

620.460 RP

Point	Clock Time 24 - hr	Clock Time min	Dry Gas Meter, (ft³)	Pitot In. H₂O ΔP	Orifice ΔH In. H₂O Desired	Orifice ΔH In. H₂O Actual	Dry Gas Temp. °F Inlet	Dry Gas Temp. °F Outlet	Pump Vacuum In. Hg Gauge	Temperatures °F °C Stack	Filter Box	Imp Temp	XAD Cond	Probe	Filter Outlet
1	0	0805	~~356.970~~	N/A		1.5	35	35	N/A	N/A	N/A		N/A	N/A	N/A
	10		627.9			1.5	35	35				35			
	20		636			1.5	35	35							
	30		644			1.5	35	35							
	40		652			1.5	35	35							
	50		661			1.5	35	35							
	60		669			1.5	35	35							
	70		677			1.5	35	35							
	80		685			1.5	35	35							

Train Leak Check:
Before Test: ______ CF ______ SEC ______ In. Hg
After Test: ______ CF ______ SEC ______ In. Hg

	I	F		Static Pressure		
Pitot Tube Leak Check			Port			
ORSAT Train Leak Check			In. H₂O			
			In. Hg			

Comments:
*sample location is
- connected to sample location w/ 1/4" fittings - no probe/filter
start vol ~~356.970~~ RP 620.460

F-061

Isokinetic Flu [illegible] Sampling Data Sheet

Page 2 of 2

Project No. 18866
Client Air products
Facility Freshkills
Source Gas Plant Inlet

Date 11-16-95
Run No. I -1
Sample Location

Sheet 2 of 2
Operator R Potter

Point	Clock Time 24 - hr	min	Dry Gas Meter, (ft³)	Pitot in. H_2O ΔP	Orifice ΔH In. H_2O Desired	Orifice ΔH In. H_2O Actual	Dry Gas Temp. °F Inlet	Dry Gas Temp. °F Outlet	Pump Vacuum In. Hg Gauge	Temperatures °F °C Stack	Filter Box	Imp Temp	XAD Cond	Probe	Filter Outlet
	90		693		3	1.5	35	35							
	100		702			1.5	35	35							
	110		710			1.5	35	35							
	120	1005	718.690												
			98.7			1.5	35								
		Total													

Meter Leak Check During Test:

	Meter Reading Stop	Start
____ CF ____ SEC ____ In. Hg		
____ CF ____ SEC ____ In. Hg		

Static Pressure			
Port			
In. H_2O			
In. Hg			

AF-050

Comments:
moisture impingers -8
5G +9
+1

TRC

CHESTER LabNet
Portland
12242 S.W. Garden Place
Tigard, OR 97223
☎ (503)624-2183
Fax (503)624-2653

Case Narrative

Date: December 5, 1995

General Information

Client: TRC - Windsor

Sample Description: Source sample impinger solutions

Sample Numbers: 95M679 - 95M683

Job Number: T009-002

Report Number: 95-195

Analysis

Analytes: Hg

Analytical Protocols: CVAA: EPA Method 101A

Analytical Notes: Analysis was performed with no problems encountered.

QA/QC Review: All of the data have been reviewed by the analysts performing the analyses and the quality assurance officer. All of the quality control and sample-specific information in this package is complete and meets or exceeds the minimum requirements for acceptability.

Comments: If you have any questions or concerns regarding this analysis, please feel free to contact the project manager.

12/5/95
QA Officer Date
Charles Lytle

Paul D 12/5/95
Project Manager Date
Paul Duda

Client Name: TRC - Windsor
Project Number: T009-002

Lab ID: 95-M679
Client ID: Blank
Sample Date: 11/20/95
Sample Volume: 216.0 ml

Analyte	Results		
CVAA			
Hg	0.39 µg/L	0.084	µg

Lab ID: 95-M680
Client ID: I-1
Sample Date: 11/16/95
Comments: Inlet Test 1
Sample Volume: 434.0 ml

Analyte	Results		
CVAA			
Hg	0.68 µg/L	0.295	µg

Lab ID: 95-M681
Client ID: I-2
Sample Date: 11/16/95
Comments: Inlet Test 2
Sample Volume: 450.0 ml

Analyte	Results		
CVAA			
Hg	0.83 µg/L	0.374	µg

From J. Cervora @ TRC 1/3/97

Test Dates 7/15-19TH.

2 Readers -

Hg = North 7.22; 9.25; 12.86 South 30.77; 29.83; 33.24

As =

avg. = 20.5.

Method 29.

$$\frac{20.5\ \mu g}{m^3} \cdot 1.198\times10^{-4} = 2.46\times10^{-3}\ \text{ppmV.}$$

```
Client Name:    TRC - Windsor
Project Number: T009-002
====================================================

Lab ID:         95-M682
Client ID:      O-1
Sample Date:    11/16/95
Comments:       Outlet Test 1
Sample Volume:  350.0 ml

Analyte                      Results
-------             --------------------------

CVAA
  Hg               1.68 µg/L           0.588    µg

----------------------------------------------------

Lab ID:         95-M683
Client ID:      O-2
Sample Date:    11/16/95
Comments:       Outlet Test 2
Sample Volume:  288.0 ml

Analyte                      Results
-------             --------------------------

CVAA
  Hg               2.46 µg/L           0.708    µg

----------------------------------------------------
```

TRC En[illegible]ental Consultants, Inc

CHAIN OF CUSTODY RECORD

ROJECT NO. 88666

PROJECT NAME AIR PRODUCTS

SAMPLERS: (Signature)

(Printed) JEFF MICHAUD

FIELD SAMPLE NUMBER	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS	PARAMETERS: Hg per EPA 101.1							REMARKS
BLANK	11/20				95-M679	1	✓							
I-1	11/16				95-M680	1	✓							inlet-test 1
I-2	11/16				95-M681	1	✓							inlet-test 2
O-1	11/16				95-M682	1	✓							outlet-test 1
O-2	11/16				95-M683	1	✓							outlet-test 2

Relinquished by: (Signature) (Printed) Jeff michaud	Date / Time 11/20	Received by: (Signature) (Printed)	Relinquished by: (Signature) (Printed)	Date / Time	Received by: (Signature) (Printed)
Relinquished by: (Signature) (Printed)	Date / Time	Received for Laboratory by: (Signature) Paul D (Printed)	Date / Time 11/22/95 9:30	Remarks Bill TO MLA # 25928MLA5C003 Project # 18866-0000-00000	

hite and yellow); Copy to Coordinator Field Files (pink).

Method: X EPA 7470 (liquid) __ EPA 7471 (solid)

MERCURY (CVAA)
EPA METHOD 7470, 7471

Name: RB /SH
Date: 12/4/95

Job #:
Client Name: CHESTER/TRC

sample ID	Bottle number	Sample amount (mls or g)	~~Dilution~~ Sx Vol ml	µg Hg from meter	ppm Hg (mg/L or mg/Kg)
ICV -0.5	94	100 mL	N/A	0.52	0.498 µg
ICB	221	↓	↓	0.042	<0.02 µg
1 95w343	84			0.040	<0.2 µg/L
2 95w344	74			0.039	<0.2 ppb
3 95w345	135			0.036	<0.2 ppb
4 95w346	163			0.041	<0.2 ppb
5 95w347	236			0.038	<0.2 ppb
6 95m679	234		216	0.062	0.39 µg/L
7 95m680	46		434	0.091	0.68 µg/L
8 95m681	80		450	0.106	0.83 µg/L
9 95m682	227		350	1.68	16.59 µg/L
10 95m683	147		288	2.46	24.40 µg/L
MD 95m680	226		434	0.109	0.86 µg/L
MS 95m680	232	100ml + 0.5µg Hg	434	0.55	5.28 µg/L
CCV -0.5	149	100 ml	N/A	0.51	0.488
CCB	146	↓	N/A	0.040	<0.02 µg
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
MD					
MS					
CCV - 0.5	220	N/A			N/A
CCB	219				

Curve:

standard	bottle #	µg reading
blank	230	0.035
0.1	225	0.116
0.2	217	0.232
0.5	235	0.52
1.0	148	1.00
m =1.001		r =0.9994
1.5	150	1.56
2.0	228	1.96
2.5		2.55

Standard **Prep:**

QA/QC:	% recovery	RPD
ICV	99.5	
MD	23.4 * NOTE ~~Sx~~ <5x MDL	
MS	~~88.4~~ 92% REC SH 12/4/95	
CCV	97.5	
MD		
MS		
CCV		

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 2
290 BROADWAY
NEW YORK, NY 10007-1866

RECEIVED
FEB 1 1996
FFS ENVIRONMENTAL SERVI

FEB 06 1996

ERD ref. 96 I

Mr. Michael J. Sauers
GSF Energy
7201 Hamilton Boulevard
Allentown, PA 18195-1501

Re: The Air Products/GSF Plant at the Fresh Kills Landfill

Dear Mr. Sauers:

We have received a copy of the mercury test results that your contractor (TRC) prepared from their November 16, 1996 test at the Fresh Kills Air Products/GSF plant. We have completed our review of that test report (dated January 25, 1996). Unfortunately, several deficiencies, errors or deviations in the test prevent us from accepting the conclusions reached by Air Products/GSF (See Attachment).

We are proposing a procedure involving the simultaneous use of Reference Method 102 (Method 101 A with safety provisions for flammable/explosive gases) and the Radian screening test (using the Jerome Model 431 Mercury Analyzer) to test for mercury at your plant. We believe that this procedure will offer us a way to compare the two tests and provide acceptable test results. For this reason, we would like to schedule a meeting with you and your contractor to discuss this further.

We look forward to meeting and working with you. If you have any questions or concerns, please contact me, at (212) 637-4081.

Sincerely,

Kenneth Eng, Chief
Air Compliance Branch

Attachment

cc: Mr. Mike Kormanik, NYSDEC Region 2
Mr. Ted Nabavi, NYCDOS

ATTACHMENT

Deficiencies Found in the January 25, 1996 TRC Test Report:

1. Only two runs were done for each test point. EPA requires three runs per test as the minimum required by a reference method.

2. Nitric acid was used for the probe and impinger washings when Method 101A paragraph 7.2.1 requires fresh 4% $KMnO_4$ solution followed by 8 N hydrochloric acid.

3. The analysis was done with SW-846 Method 7471 when the analysis procedures in Method 101A should have been followed.

4. The wrong impinger solution volumes were used. TRC used 100 ml of the permanganate solution in each of the first two impingers. Method 101A requires 50 ml in the first and 100 ml of permanganate solution in each of the second and third impingers.

5. Stack sampling metering system calibrations were not provided.

6. Calibrations were not provided for the inlet landfill gas and the outlet sales gas volumetric flow measurements.

7. Sampling was not done isokinetically.

8. No EPA or NYSDEC representatives were present to witness the test.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY - REGION II
290 BROADWAY
NEW YORK, NEW YORK 10007-1866

ERD ref 96 J

MAY 15 1996

Mr. Mike Sauers
Environmental Manager
GSF Energy
7201 Hamilton Boulevard
Allentown, PA 18195-1501

Re: Permission to Test at Fresh Kills

Dear Mr. Sauers:

This is a follow-up to our May 7, 1996 teleconference with you, Morry Kapitan, and Ted Nabavi of the New York City Department of Sanitation (NYCDOS), about securing permission from Air Products Corporation and the NYCDOS to test for mercury at the Air Products/GSF Fresh Kills gas recovery facility. As we informed you during the teleconference, EPA Region II is currently securing funds to test and verify the mercury readings recorded by Radian Corporation during their screening tests at the Air Products facility last July. You have indicated that Air Products will cooperate with EPA to get the tests done.

We have obtained the necessary funds and a contractor work assignment has been approved for Radian Corp. to conduct additional tests. We will begin test protocol development shortly. We expect to include Air Products, the NYCDOS, and the New York State Department of Environmental Conservation (NYSDEC) in the review processes for our tests. However, please note that due to the urgent nature of these tests, the review of the documents from the testing project will require prompt attention from all reviewers involved.

Currently, EPA's testing experts have already formulated a test strategy for this project. They believe that the following tests are needed to ensure that a comprehensive set of data will be collected to address the public's concerns. The tests are:

1) EPA Method 29 for the raw landfill gas inlets, product outlet, and incinerator exhaust at the facility.

2) Jerome analyzer tests will also be conducted concurrently with Method 29 tests for the raw landfill gas inlets and product outlet of the facility. This will allow us to collect data to assess the accuracy of the Jerome analyzer data collected by Radian last year.

3) Water sampling of various process liquids within the

X

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facility.

These test are prescribe so that we can determine the fate of the mercury in the landfill gas if mercury is present in high concentrations. The Method 29 and water samples will also be analyzed for other metals to address the possible presence of these metals.

We look forward to working with you and getting this matter resolved. If you have any additional questions or concerns, please contact me at (212) 637-4080.

Sincerely,

Kenneth Eng, Chief
Air Compliance Branch

cc: Mr. Ted Nabavi
Senior Environmental Manager
New York City Department of Sanitation
44 Beaver Street, 9th floor
New York, NY 10004

Mr. Michael Kormanik
Regional Air Pollution Control Engineer
NYSDEC, Region 2

ERD ref. 96 (K)

via fax, original sent regular mail

GSF Energy
7201 Hamilton Boulevard
Allentown, PA 18195-1501
Telephone (610) 481-4911

16 May 1996

Mr. Kenneth Eng, Chief
Air Compliance Branch
United States Environmental Protection Agency
Region 2
290 Broadway
New York, NY 10007-1866

Dear Mr. Eng:

Per our phone conversation on 7 May and your follow-up letter of 15 May, I am sending you a copy of the attached 11 April 1996 letter from TRC, our mercury testing consultant, to me. Mr. James Canora of TRC prepared this letter at my request in order to address some of the concerns that you raised in your 6 February letter regarding the mercury testing that they performed for us at the GSF Energy Inc. Fresh Kills landfill gas recovery facility. While we have carefully considered your concerns about the testing that was done, we feel comfortable with Mr. Canora's assessment that "none of the deficiencies [raised in your letter] could have significantly biased the results." If mercury was really present at the levels reported by Radian using their screening meter, TRC should have observed them since the modified EPA reference method 101A is far more rigorous of a test method than the screening method used by Radian.

Moreover, the results of independent testing of our sales gas by Brooklyn Union Gas using another more rigorous test method (guilded silica sorbent tubes) than the Radian screening method, showed less than the detection limit of 0.02 ng Hg/liter.

Based upon the attached letter from TRC and the Brooklyn Union Gas results, we find it unnecessary to perform further testing. We request that EPA thoughtfully review this information, and carefully evaluate whether further testing is truly warranted.

I was surprised to read in your 15 May letter, that you plan to analyze for "other metals" beside mercury. We didn't discuss this last week. We would like to understand the nature, scope and intent of this effort before proceeding.

I hope the attached information is helpful. If you have any questions please call (610) 481-4317.

Very truly yours,

Michael J. Sauers

Michael J. Sauers

attachment

c: Mr. James Canora, TRC
Mr. Michael Kormanik, NYDEC, Region 2
Mr. Ted Nabavi, NYC DOS
Mr. Bert Breitburg, NYDEC

RECEIVED

APR 12 1996

FES ENVIRONMENTAL SERVIC

TRC Environmental Corporation

5 Waterside Crossing
Windsor, Connecticut 06095
Telephone 860-289-8631
Facsimile 860-298-6399

April 11, 1996

Mr. Michael Sauers
Air Products and Chemicals, Inc.
Mail Stop W2405
7201 Hamilton Boulevard
Allentown, PA 18195

RE: Evaluation of TRC and Radian Corporation Measurements Conducted for Mercury Vapor at the Freshkills Landfill
TRC Project No. 18866

Dear Mike:

As we discussed, there is a controversy involving a large discrepancy in mercury vapor measured in the landfill gas at the Freshkills site. TRC conducted measurements using a modification of EPA Reference Method 101A which uses a solution of acidified potassium permanganate to absorb mercury vapor and atomic absorption laboratory analysis to measure mercury absorbed in the solution. EPA's contractor, Radian Corporation, conducted mercury vapor measurements using a portable gold film analyzer and their results were approximately 10,000 times higher than TRC results. TRC measured 0.08 micrograms per cubic meter ($\mu g/m^3$) and Radian measured 8,000 $\mu g/m^3$. The two sets of measurements were taken at different dates and at different locations in the landfill gas collection system (Radian collected gas samples from the main header and TRC collected samples after the first stage of compression). However, the large margin of variation between the two measurements indicates measurement bias. Either the reference method conducted by TRC was biased low or the portable gold film analyzer used by Radian biased the results high.

EPA reviewed the test report prepared by TRC and identified eight deficiencies; however, none of these deficiencies could have significantly biased the results. The only EPA noted deficiency (Item #2), which could have biased the results at all, was that TRC used nitric acid to rinse the absorbing solution impingers rather than fresh potassium permanganate solution as specified in EPA Method 101A. This oversight may have resulted in less than 100% recovery of the solutions in the absorbing impingers. However, the impinger rinse is a small fraction of the total sample (estimated to be less than 1%) and even if the rinse efficiency was less than optimal, the overall affect would be minimal. In addition, the purpose of rinsing the impingers with fresh potassium permanganate is to refresh the absorbing solution when the existing solution has been chemically reduced by high organic content of the sample gas. There was no indication of reduced absorbing reagent on this program (indicated by precipitation of a brown solid) further minimizing the importance of a permanganate rinse. In summary, the use of nitric acid would not bias the results lower than several percent even during worst-case conditions when the absorbing solution has been reduced.

Offices located in
major industrial centers
throughout the U.S.

Although the deficiencies identified by EPA would not significantly bias the reference method data, there is a remote possibility that other chemical or physical factors may have biased Method 101A; the method was not designed for landfill gas. However, factors which could have reduced the efficiency by a factor of 10 are not likely, never mind the factor of 10,000 which is indicated by comparison to the gold film analyzer data. TRC also spoke with a chemist at EPA's technical branch in North Carolina. The EPA technical branch chemist concluded that the reference method theoretically should work on a landfill gas source.

The gold film analyzer used by Radian Corporation has one obvious deficiency for measuring mercury in landfill gas; the analyzer detector responds equally to hydrogen sulfide (H_2S) and mercury, and the Freshkills landfill gas has approximately 100,000 $\mu g/m^3$ of H_2S. The gold film analyzer uses an H_2S scrubber to remove H_2S prior to the detector when operated in a mercury test mode. Mercury vapor concentration measurements with a gold film analyzer at these high H_2S concentrations would require an extremely efficient H_2S scrubber.

If we look at the data provided by Radian, the potential interference from H_2S is developed further. Radian reported 8,000 $\mu g/m^3$ of mercury in landfill gas containing 100,000 $\mu g/m^3$ of H_2S. If the gold film analyzer used under field conditions had a 92% efficient H_2S scrubber, the analyzer would have indicated 8,000 $\mu g/m^3$ mercury vapor from the H_2S escaping from the analyzer scrubber. Radian conducted an H_2S interference check using three levels of calibration gases containing known concentrations of H_2S. (When, where, environmental conditions, the age of the gold film analyzer H_2S scrubber, whether the tests were conducted on the same analyzer and other interference test data are unknown.) The results of the gold film analyzer interference check conducted by Radian are summarized below. The first column lists the concentration of H_2S used to challenge the analyzer and the second column contains the indicated concentration of mercury vapor caused by H_2S which escaped the scrubber.

Analyzer Input: H_2S Concentration Before Scrubbing ($\mu g/m^3$)	Analyzer Response: Mercury Concentration Caused by H_2S Escaping Scrubber ($\mu g/m^3$)
38,000	420
70,000	620
141,000	1,900

These data indicate that the gold film analyzer is subject to H_2S interference at levels within the same order of magnitude (thousands of $\mu g/m^3$) of mercury vapor concentrations reported by Radian at Freshkills. It is conceivable that the H_2S scrubber on the gold film analyzer used in the field was less efficient than the analyzer used to conduct the laboratory interference check and that the 8,000 $\mu g/m^3$ of mercury vapor reported by Radian at Freshkills was actually only H_2S which passed through the analyzer scrubber . If further testing is conducted with the gold film analyzer, it is imperative to conduct H_2S interference checks before and after each landfill gas sample analysis. Without the field interference check, the H_2S contribution to the gold film analyzer mercury response is unknown, and the data is essentially meaningless.

In summary, large mercury vapor concentration measurements discrepancy was likely caused by H_2S interference to the gold film analyzer. The modified reference method measurements are unlikely to be significantly biased and the reference method deficiencies noted by EPA could bias the results low by only several percent in the worst-case scenario.

If you have any questions, please do not hesitate to contact me at (860) 298-6304.

Very truly yours,

TRC ENVIRONMENTAL CORPORATION

James Canora
Manager, Measurements Section

JC/sak

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James Canora

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Phone #	Phone # 610-481-4317	
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DATE: 5/21/96

TO: Mike Sauers

SUBJECT: Fresh kills.

OFFICE: Air Products & Chemicals

PHONE: 610-481-4317

FAX: 610-481-4377

FROM: YUE ON CHIU

OFFICE: Air & Waste Management, Air Compliance Branch

PHONE: 212 637-4065

FAX: **FTS -** **Commercial:**

Number of Pages (including cover sheet): 2

Message:

Mike:

I sent Jim Canora a copy of the agenda.

Agenda
Fresh Kills Test Protocol Development Teleconference
Thursday, May 23, 1996 - 1 to 3 PM

Participants:

EPA: Ken Eng, Karl Mangels, Yue On Chiu, Don Wright, Aarti Reddy
Radian/ERG: Clint Burklin, Jim Mcgaud
Air Product: Mike Sauers, Morry Kapitan, Paul Pursico
TRC: Jim Canora
NYSDEC: Mike Kormanik
NYCDOS: Ted Nabavi

Issues:

1) Tests to be performed

2) QA/QC
    a) Concentration to test for and test detection limits
    b) Potential interferences (H2S, organics, etc.)
    c) Types and number of samples to be taken (blanks, spiked, and split samples)
    d) Split sample analysis
    e) Sample storage and transportation

3) Witnesses
    a) for stack tests
    b) for sample analysis

4) Sampling locations

5) Safety considerations

6) Test scheduling and access to the facility.

EPA will initiate the teleconference by calling all the participants. We have a limit of six phone lines (including our own line). Please group yourselves together for the call. Thanks you.

TOTAL P.02