RESEARCH TRIANGLE INST

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STATUS REPORT #5
STABILITY OF ORGANIC AUDIT MATERIALS AND RESULTS OF SOURCE TEST ANALYSIS AUDITS

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SECTION 1.0
INTRODUCTION

1.1 OBJECTIVES

The need for reliable standards for source emission measurement of hydrocarbons, halocarbons and sulfur compounds is well established. The Research Triangle Institute (RTI) under contract to the U.S. Environmental Protection Agency (USEPA) has responded to this need through development of an extensive repository of gaseous compounds. The main objectives of this ongoing project are (1) to provide gas mixtures to EPA, state/local agencies, or their contractors as performance audits to assess the relative accuracy of source emission measurements in certain organic chemical manufacturing industries, (2) to corroborate the vendor's certified analysis of the gas mixtures by in-house analysis, (3) to determine the stability of the gas mixtures with time by in-house analysis, and (4) to explore the feasibility of new audit materials as requested by EPA.

This report describes the present status of this project. Included in the report are (1) a description of the experimental procedures used for initial cylinder analyses and collection of stabilty data, (2) a description of the audit procedure, (3) presently available audit results, and (4) presently available stability data. Full details of the study with additional statistical analyses for ten (10) halocarbons and eight (8) organics are presented in a journal publication (1,2). Statistical analysis for the remaining compounds will be presented in the final report.

1.2 AUDIT MATERIALS CONTAINED IN THE REPOSITORY

The RTI repository currently contains 42 different compounds for use in conducting performance audits during source testing. The compounds were selected based on the anticipated needs of the personnel of the Emissions Measurements Branch, Office of Air Quality Planning and Standards, USEPA. Table 1 lists the compounds, the concentration ranges, the number of cylinders of each compound, and the cylinder construction material. In Table 1, the audit materials fall into two concentration ranges. The low concentration range between 5 and 20 parts per million (ppm) simulates possible emission standard levels. The high concentration range between 50 and 700 ppm simulates expected source emission levels. The balance gas for all gas mixtures is nitrogen. In the case of some of the audit materials, a second compound, which serves as an internal standard, was added to the gas mixture.

TABLE 1. AUDIT MATERIALS CURRENTLY HELD IN THE REPOSITORY

Compound	Low Concentration Range			High Concentration Range		
	No. of Cylinders	Concentration Range (ppm)	Cylinder Construction*	No. of Cylinders	Concentration Range (ppm)	Cylinder Construction*
Benzene	14	8 - 13	S	17	60 - 400	Al, S
Ethylene	4	5 - 20	Al	4	300 - 700	Al
				6	3000 - 20,000	Al
Propylene	4	5 - 20	Al	4	300 - 700	Al
Methane/Ethane	-	------	-	4	1000 - 6000(M), 200 - 700(E)	Al
Propane	4	5 - 20	Al	4	300 - 700	Al
Toluene	2	5 - 20	S	2	300 - 700	S
Hydrogen Sulfide	4	5 - 20	Al	2	300 - 700	Al
Meta-Xylene	2	5 - 20	S	2	300 - 700	LS
Methyl Acetate	2	5 - 20	S	2	300 - 700	S
Chloroform	2	5 - 20	S	2	300 - 700	S
Carbonyl Sulfide	2	5 - 20	S	2	100 - 300	S
Methyl Mercaptan	4	3 - 10	Al	-	---------	-
Hexane	2	20 - 80	Al	2	1000 - 3000	LS
1,2-Dichloroethane	4	5 - 20	Al	4	100 - 600	Al
Cyclohexane	-	------	-	1	80 - 200	S
Methyl Ethyl Ketone	1	30 - 80	S	-	---------	-
Methanol	1	30 - 80	Al	-	---------	-
1,2-Dichloropropane	2	5 - 20	Al	2	300 - 700	LS
Trichloroethylene	2	5 - 20	Al	2	100 - 600	Al

*Cylinder constructions: Al = Aluminum, S = Steel, LS = Low-Pressure Steel

TABLE 1. AUDIT MATERIALS CURRENTLY HELD IN THE REPOSITORY (Continued)

Compound	Low Concentration Range			High Concentration Range		
	No. of Cylinders	Concentration Range (ppm)	Cylinder* Construction	No. of Cylinders	Concentration Range (ppm)	Cylinder* Construction
1,1-Dichloro-ethylene	2	5 - 20	Al	2	100 - 600	Al
1,2-Dibromo-ethylene	2	5 - 20	Al	2	100 - 600	Al
Perchloro-ethylene	2	5 - 20	S	2	300 - 700	LS
Vinyl Chloride	9	5 - 30	S	-	---------	--
1,3-Butadiene	1	5 - 30	S	-	---------	--
Acrylonitrile	3	5 - 20	LS, Al	3	300 - 700	LS, Al
**Aniline	1	5 - 20	Al	-	---------	--
Methyl Isobutyl Ketone	1	5 - 20	Al	1	75	Al
**Para-dichlorbenzene	2	5 - 20	S	-	---------	--
**Ethylamine	2	5 - 20	Al	-	---------	--
**Formaldehyde	-	--	-	-	---------	--
Methylene Chloride	1	5 - 20	Al	-	---------	--
Carbon Tetrachloride	1	5 - 20	Al	-	---------	--
Freon 113	1	5 - 20	Al	-	---------	--
Methyl Chloroform	1	5 - 20	Al	-	---------	--
Ethylene Oxide	1	5 - 20	Al	-	---------	--
Propylene Oxide	1	5 - 20	Al	1	75 - 200	Al
Allyl Chloride	1	5 - 20	S	1	75 - 200	S

TABLE 1. AUDIT MATERIALS CURRENTLY HELD IN THE REPOSITORY (Continued)

Compound	Low Concentration Range			High Concentration Range		
	No. of Cylinders	Concentration Range (ppm)	Cylinder* Construction	No. of Cylinders	Concentration Range (ppm)	Cylinder* Construction
Acrolein	1	5 - 20	Al	-	---------	--
Chlorobenzene	1	5 - 20	Al	-	---------	--
Carbon Disulfide	-	---	Al	1	75 - 200	Al
**Cyclohexanone	1	5 - 20	Al	-	---------	--
***EPA Method 25 Gas	3	100 - 200	Al	3	750 - 2000	Al

*Cylinder construction: Al = Aluminum, S = Steel, LS = Low Pressure Steel

**Cylinders are no longer available in the repository since the compounds are found to be unstable in the cylinders.

***The gas mixture contains an aliphatic, an aromatic and carbon dioxide in nitrogen. Concentrations shown are reported in ppmC.

SECTION 2.0
EXPERIMENTAL PROCEDURES

Analysis of the cylinder gases is required to corroborate the concentrations reported by the company which prepared the gas mixtures and also to measure concentration changes with time, that is, estimate stability of the standards.

2.1 INSTRUMENTATION

Analyses are performed with (1) a Perkin-Elmer Model 3920B Gas Chromatograph with flame ionization and flame photometric detectors, and (2) a Tracor Model 560 Gas Chromatograph with a flame photometric detector. The Tracor instrument has been used principally for measurement of the sulfur-containing species. The gaseous samples are injected onto the columns by means of gas sampling valves constructed of Hastalloy C (high nickel content and low adsorptive properties). These valves are equipped with interchangeable sample loops to allow the injection of variable but known volumes of gas. To further facilitate the injection of varying sample sizes, a sample injection system (Figure 1) is employed. The operation of the system is based upon measurement of pressure differentials. Further details on the system are published in the open literature (3).

The gas chromatographic parameters used in the measurement of individual compounds and problems that have arisen are listed in Attachment 1.

2.2 CALIBRATION

Calibration of the gas chromatographs has involved measurement of known concentrations of gases in air or nitrogen. The source or method of preparation of calibration standards varies depending on the gas involved.

National Bureau of Standards, Standard Reference Materials (NBS-SRM's) of methane and propane are used for the calibration of the GC for the measurement of methane and propane audit materials. These

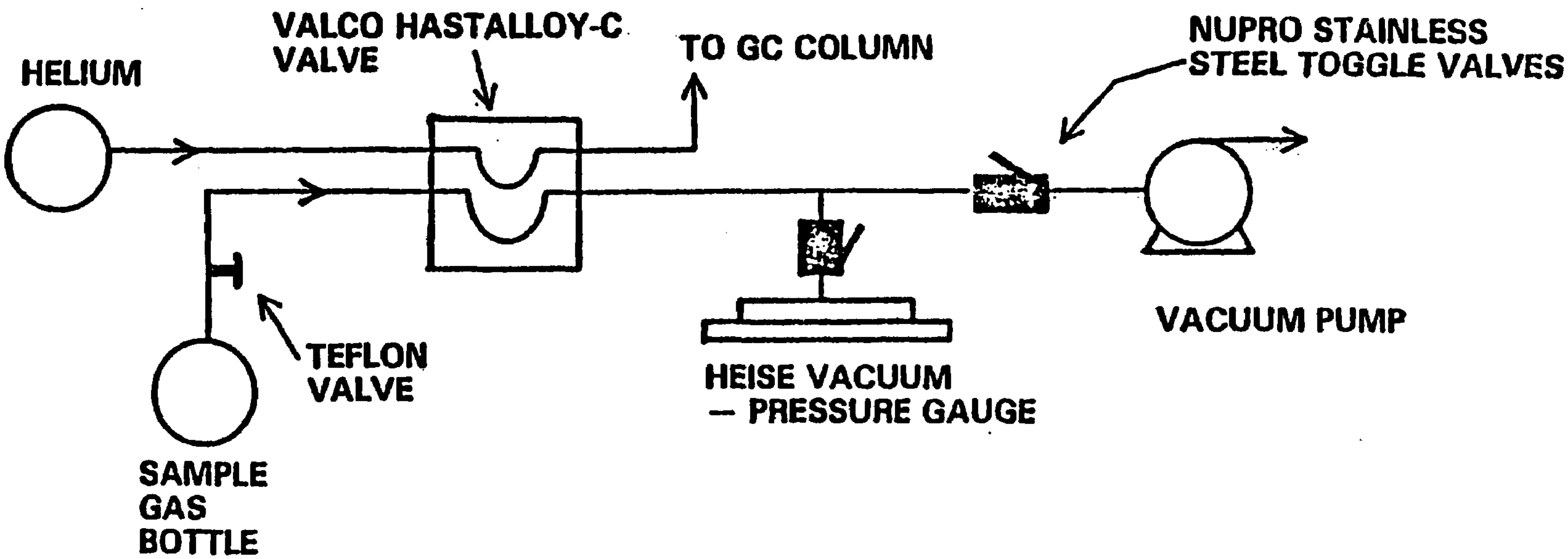

Figure 1. Sample injection system.

same gases are used to calibrate the chromatographic system for measurement of ethylene and propylene, assuming the FID response per carbon is constant from compound to compound.

A second method for the quantitation of gaseous compounds involves the use of permeation tubes. Thus, the calibration gases for vinyl chloride and ethylene oxide have been generated using permeation tubes. The tube is placed in a temperature-controlled chamber and zero air is passed over the tube at a known flow rate. The resultant gaseous mixture is further diluted if necessary with additional zero air in a glass dilution bulb. The final mixture is collected in a gas sampling bulb or a Tedlar® bag and analyzed by GC-FID. The permeation rates of the tubes are determined periodically by weight loss.

A third method for developing a standard is the "glass bulb" technique. A known volume of the compound, either gas or liquid, is injected into an evacuated glass bulb of known volume. The bulb is then returned to atmospheric pressure with a balance gas of choice. If a pure liquid is injected, total vaporization is assumed and the concentration is calculated by using the ideal gas law. Additional dilutions are also made, if necessary, by utilizing additional bulbs or by repeatedly pressurizing with a balance gas to a known pressure and then partially evacuating to a known pressure.

With each of these approaches, multipoint calibration curves are prepared each time a sample is analyzed. Certain quality control procedures are followed, for example, equilibrating the permeation system and the glass bulbs with the sample gas before taking an aliquot for GC measurement. Also, an NBS standard cylinder of methane is used to verify the constancy of the detector response. Blank measurements are taken during the process of cylinder analysis and generally, blank measurements have shown no signal above the baseline.

SECTION 3.0
PERFORMANCE AUDITS

RTI supplies repository cylinders for audits upon request from the EPA, state or local agencies or contractors. A contractor must be performing source emission tests at the request of EPA or a state or local agency in order to qualify for the performance audit. When a request is received, the contents of the cylinders are analyzed, the tank pressures are measured and the cylinders are shipped by overland carrier. Tank regulators are also provided when requested. A letter is included with the cylinders which provides general instructions for performance of the audit. The audit concentrations and cylinder pressures are provided to the requesting agency audit coordinator.

To date, 106 individual audits have been initiated, and 102 are complete. The audit results collected to date are presented in Table 2. Generally, the results of the audits show close agreement (± 10%) with the actual cylinder concentrations measured prior to shipment.

TABLE 2. SUMMARY OF PERFORMANCE AUDIT RESULTS

Audit No.	Client	Industry	Audit material	RTI audit conc. (ppm)	Client audit % bias (Avg.)	Status of audit
1	A	Ethylene oxide	Ethylene in N_2	3,239	-22.5	E
		production	Ethylene in N_2	21,226	-20.0	
2	A	Ethylene oxide	Methane/ethane in N_2	1,710Me/220Et	+9/-20	E
		production	Methane/ethane in N_2	8,130Me/597Et	+9/-1.00	
3	A	Ethylene oxide	Methane/ethane in N_2	1,021Me/315Et	+21.5/-4.50	E
		production	Methane/ethane in N_2	6,207Me/773Et	+23.5/-4.50	
4	A	Acetone	Benzene in N_2	79.0	-19.0	E
		production	Benzene in N_2	374.0	-11.0	
5	A	Maleic anhydride	Benzene in N_2	138	-9.40	E
		production	Benzene in N_2	300	+4.70	
6	A	Ethylene oxide	Ethylene in N_2	5,442	-27.0	E
		production	Ethylene in N_2	18,918	-33.0	
7	B	Maleic anhydride	Benzene in N_2	80.0	+2.30	E
		production	Benzene in N_2	355	+27.5	
8	C	Maleic anhydride	Benzene in N_2	101	+12.9	E
		production	Benzene in N_2	387	+14.5	
9	D	Ethyl benzene	Benzene in N_2	71.0	-2.80	E
		styrene	Benzene in N_2	229	-3.90	
		manufacturer				
10	E	Gasoline bulk	Benzene in N_2	62.0	+3.80	E
		terminal	Benzene in N_2	80.0	+3.40	
11	F	Gasoline transfer	Benzene in N_2	142	-3.50	E
		terminal	Benzene in N_2	294	+3.20	
12	F	Gasoline transfer	Benzene in N_2	268	-11.8	E
		terminal	Benzene in N_2	343	-1.00	

TABLE 2. SUMMARY OF PERFORMANCE AUDIT RESULTS (Continued)

Audit No.	Client	Industry	Audit material	RTI Audit conc. (ppm)	Client Audit % bias (Avg.)	Status of audit
13	F	Gasoline transfer	Benzene in N_2	129	+4.70	E
		terminal	Benzene in N_2	318	+8.70	
14	F	Gasoline transfer terminal	Benzene in N_2	10.7	+2.60	E
15	C	Nitrobenzene	Benzene in N_2	9.73	-4.60	E
		manufacturing	Benzene in N_2	269	-2.60	
16	F	Gasoline bulk	Benzene in N_2	8.20	-2.30	E
		terminal	Benzene in N_2	140	-1.80	
17a	F	Gasoline bulk	Benzene in N_2	9.50	+10.4	E
		terminal	Benzene in N_2	127	-2.80	
17b	F	Gasoline bulk	Benzene in N_2	9.50	+12.5	E
		terminal	Benzene in N_2	127	-6.30	
18	G	Coke oven	Hydrogen sulfide in N_2	7.05	-24.8	E
			Hydrogen sulfide in N_2	9.73	-22.9	
19	F	Gasoline bulk	Benzene in N_2	12.0	-0.80	E
		terminal	Benzene in N_2	218	+7.30	
20	F	Gasoline bulk	Benzene in N_2	7.65	+16.3	E
		terminal	Benzene in N_2	396	+1.50	
21	F	Linear alkyl-	Benzene in N_2	98	+5.70	E
		benzene manu-	Benzene in N_2	294	+6.80	
		facturing	Benzene in N_2	331	+4.50	
22	F	Gasoline bulk	Benzene in N_2	9.85	-4.10	E
		terminal	Benzene in N_2	81.0	-6.80	
23	F	Gasoline bulk	Benzene in N_2	10.15	+4.60	E
		terminal	Benzene in N_2	61.0	-9.50	

TABLE 2. SUMMARY OF PERFORMANCE AUDIT RESULTS (Continued)

Audit No.	Client	Industry	Audit material	RTI audit conc. (ppm)	Client audit % bias (Avg.)	Status of audit
24	H	Industrial surface coating process	Toluene in N_2	14.8	-1.90	E
			Propylene in N_2	474	+0.20	
			Propane in N_2	20.3	-2.30	
			Methane/ethane in N_2	1,640Me/195et	-13.5(as methane)	
25	C	Acrylic acid and ester Production	Propane in N_2	10.1	+8.60	E
			Propane in N_2	710	+5.60	
26	C	Acrylic acid and ester Production	Propane in N_2	5.1	+17.6	E
			Propane in N_2	607	-3.60	
27	E	Maleic anhydride	Benzene in N_2	10.2	NA	F
			Benzene in N_2	218	NA	
28A	A	Carbon adsorber	Toluene in N_2	8.55	-6.40	E
			Toluene in N_2	405	-1.00	
28B	A	Carbon adsorber	Toluene in N_2	8.55	+4.10	E
			Toluene in N_2	405	NA	
28C	A	Carbon adsorber	Toluene in N_2	8.55	-8.80	E
			Toluene in N_2	405	NA	
29	EPA, QAD	Instrument check-out	Ethylene in N_2	4.75	+4.00	E
			Ethylene in N_2	19.6	+3.10	
			Ethylene in N_2	312	-0.80	
			Ethylene in N_2	3021	+5.30	
			Ethylene in N_2	20456	-8.60	

TABLE 2. SUMMARY OF PERFORMANCE AUDIT RESULTS (Continued)

Audit No.	Client	Industry	Audit material	RTI Audit conc. (ppm)	Client Audit % bias (Avg.)	Status of audit
30	EPA, QAD	Instrument check-out	Benzene in N_2	8.20	+0.30	E
			Benzene in N_2	78.0	-0.90	
			Benzene in N_2	133	-4.00	
			Benzene in N_2	348	-0.90	
31	EPA, QAD	Instrument check-out	Toluene in N_2	405	+3.20	E
			Toluene in N_2	579	+1.00	
32	EPA, QAD	Instrument check-out	Methyl acetate in N_2	6.80	-2.60	E
			Methyl acetate in N_2	17.2	+1.70	
			Methyl acetate in N_2	326	-1.50	
			Methyl acetate in N_2	455	-1.30	
33	EPA, QAD	Instrument check-out	Propylene in N_2	4.90	-22.4	E
			Propylene in N_2	19.7	-7.80	
			Propylene in N_2	300	+1.00	
			Propylene in N_2	685	-1.80	
34	EPA, QAD	Instrument check-out	Propane in N_2	14.6	-0.70	E
			Propane in N_2	303	+7.60	
			Propane in N_2	439	+6.20	
35a	I	Vegetable oil plant	Hexane in N_2	82.2	+8.10	E
			Hexane in N_2	1982	+3.00	
35b	I	Vegetable oil plant	Hexane in N_2	82.2	-1.20	E
			Hexane in N_2	1982	-1.30	
36	A	Carbon adsorber	Toluene in N_2	8.20	-2.40	E

TABLE 2. SUMMARY OF PERFORMANCE AUDIT RESULTS (Continued)

Audit No.	Client	Industry	Audit material	RTI audit conc. (ppm)	Client audit % bias (Avg.)	Status of audit
37	B	Coke oven	Benzene in N_2	12.1	+0.80	E
			Benzene in N_2	105	+2.90	
38	D	Ethylbenzene/	Benzene in N_2	9.90	+5.70	E
		styrene	Benzene in N_2	77.9	+3.60	
			Benzene in N_2	345	+1.50	
39	B	Coke oven	Benzene in N_2	8.20	-2.60	E
		Byproduct	Benzene in N_2	85.4	-8.70	
40	D	Coke oven	Benzene in N_2	10.9	+20.0	
		Byproduct	Benzene in N_2	147	+6.80	
41	H	Paint spray	Benzene in N_2	10.8	NA	F
			m-Xylene in N_2	16.4	NA	
42	H	Tire manufacturing	Cyclohexane in N_2	93.4	-11.1	D
43	B	Coke oven	Benzene in N_2	7.54	+0.10	D
			Benzene in N_2	225	+0.40	
44	D	Ethylbenzene/	Benzene in N_2	8.20	-3.40	D
		styrene	Benzene in N_2	74.5	-0.20	
			Propane in N_2	10.6	-3.00	
45	F	Industrial	Propane in Air	316	-3.20	E
		surface coating	Propane in Air	450	-2.00	
46	EPA, QAD	Tire	Propane in Air	15	NA	F
		manufacturing	Propane in Air	316	NA	

TABLE 2. SUMMARY OF PERFORMANCE AUDIT RESULTS (Continued)

Audit No.	Client	Industry	Audit material	RTI audit conc. (ppm)	Client audit % bias (Avg.)*	Status of audit**
47	EPA, QAD	Tire manufacturing	Propane in air	20.8	-18.4	E
			Propane in air	453	+13.4	
48	D	Dimethyl terephthalate production	Meta-Xylene in air	487	-2.10	E
49	EPA, QAD	Instrument check-out	Toluene in N_2	61.5	NA	F
			Methanol in N_2	55.2	NA	
50	EPA, QAD	Tire oven manufacturing	Propane in air	4.9	-48.8	E
			Propane in air	613	+16.9	
			Propane in air	718	+16.8	
51	EPA, QAD	Instrument check-out	Propane in air	20.8	+20.0	E
			Propane in air	316	-9.20	
52	D	Styrene manufacturing	Benzene in N_2	106	-4.90	E
			Benzene in N_2	358	-3.70	
			1,3-Butadiene in N_2	20.9	+23.8	
53	I	Veg. oil manufacturing	Cyclohexane in N_2	99.0	-3.50	E
54	M	Research	Chloroform in N_2	16.51	NA	F
			Chloroform in N_2	531	NA	
55	J		Ethylene in N_2	300	+1.40	E

TABLE 2. SUMMARY OF PERFORMANCE AUDIT RESULTS (Continued)

Audit No.	Client	Industry	Audit material	RTI audit conc. (ppm)	Client audit % bias (Avg.)*	Status of audit**
56	K	Reactivity of vent activated charcoal	Chloroform in N_2	8.11	NA	F
57	EPA, QAD	Instrument check-out	Hydrogen sulfide in N_2	16.2	NA	F
58	C	Coil coating	Propane in N_2 Propane in N_2	5.20 472	NA -8.40	E
59	L		Benzene in N_2 Benzene in N_2	9.45 341	NA NA	F
60	M		Audit not initiated	--	--	--
61	EPA (State of Conn.)		Benzene in N_2	132.9	NA	F
62	O		Meta-xylene in N_2 Hexane in N_2	760 1986	NA NA	F
63	M		Methyl mercaptan in N_2	4.44	NA	F
64	P		Benzene in N_2 Methyl ethyl ketone in N_2	13.4 44.5	NA NA	F
65	E	Coke oven Byproduct Recovery	Benzene in N_2 Benzene in N_2	7.93 132	-2.90 +1.39	E

TABLE 2. SUMMARY OF PERFORMANCE AUDIT RESULTS (Continued)

Audit No.	Client	Industry	Audit material	RTI audit conc. (ppm)	Client audit % bias (Avg.)*	Status of audit**
66	D	Rubber manufacturing	Benzene in N_2	12.0	+14.2	E
			Benzene in N_2	10.2	0	
			Benzene in N_2	100.4	+6.40	
			Benzene in N_2	335	+6.00	
			Hexane in N_2	79.8	+1.80	
			Hexane in N_2	3076	-7.50	
			Propane in N_2	9.97	-3.20	
			Propane in N_2	314	-10.8	
67	E	Coke oven Byproduct Recovery	Benzene in N_2	8.29	-2.20	E
			Benzene in N_2	75.7	-2.50	
68	EPA, Region II		Vinyl chloride in N_2	5.74	NA	F
			Vinyl chloride in N_2	28.3	NA	
69	EPA, QAD	Instrument Check-out	Propylene in N_2	328	-7.00	E
			Propylene in N_2	725	-8.30	
70	EPA, Region I		Vinyl chloride in N_2	7.5	NA	F
71	E	Degreasing vent	Trichloroethylene in N_2	14.9	-0.40	E
			Trichloroethylene in N_2	566	-8.70	
72	EPA, QAD	Instrument check-out	Hexane in N_2	3076	NA	F
73	EPA, QAD	Combustion efficiency test	Hydrogen sulfide in N_2	16.2	-7.50	E
			Methyl mercaptan in N_2	8.22	-8.90	

TABLE 2. SUMMARY OF PERFORMANCE AUDIT RESULTS (Continued)

Audit No.	Client	Industry	Audit material	RTI audit conc. (ppm)	Client audit % bias (Avg.)*	Status of audit**
74	E	Vinyl chloride manufacturing	1,2-Dichloroethane in N_2	9.30	+6.00	E
			1,2-Dichloroethane in N_2	462	+3.70	
75	N	Coil coating	Propane in air	10.01	NA	F
			Propane in air	309	NA	
76	F	Coil coating	Propane in air	10.01	NA	F
			Propane in air	309	NA	
77	D	Maleic anhydride	Benzene in N_2	9.46	-6.60	E
			Benzene in N_2	66.9	-11.7	
78	EPA, Region VII	Instrument checkout	Benzene in N_2	120	NA	F
			Hexane in N_2	30.2	NA	
79	D	Maleic anhydride	Benzene in N_2	9.46	-4.60	E
			Benzene in N_2	127.60	+12.5	
80	F	Plywood/veneer drying	Propylene in N_2	14.8	-4.70	E
			Propylene in N_2	328	+4.40	
			Toluene in N_2	430	-0.80	
81	P	Plywood/veneer drying	Propylene in N_2	20.3	+18.2	E
			Propylene in N_2	479	-22.5	
			Toluene in N_2	487	+32.5	
82	J	Polypropylene manufacturing	Propylene in N_2	9.63	-0.35	E
			Propane in N_2	19.70	+0.84	
			Propane in N_2	296	+0.45	
83	I	Coke oven	Hydrogen sulfide in N_2	428	+4.90	E
			Hydrogen sulfide in N_2	647	-16.5	
			Carbonyl sulfide	101	+1.98	

TABLE 2. SUMMARY OF PERFORMANCE AUDIT RESULTS (Continued)

Audit No.	Client	Industry	Audit material	RTI audit conc. (ppm)	Client audit % bias (Avg.)*	Status of audit**
84	J	Compliance testing	Benzene in N_2	7.45		E
			Hexane in N_2	72.6	+3.70	
			Toluene in N_2	15.0		
			Methyl mercaptan in N_2	5.40		
85	I	Steel manufacturing	Hydrogen sulfide in N_2	647		E
			Carbonyl sulfide in N_2	9.08		
86	I	Oil shale	Hydrogen sulfide in N_2	437		E
			Carbonyl sulfide in N_2	117		
			Methyl mercaptan in N_2	8.42		
87	Q	Maleic Anhydride Production	Benzene in N_2	55.7	+528.4	E
			Hexane in N_2	323.7	+20.5	
88	R	Refining	Hydrogen sulfide in N_2	17.5	21.1	E
			Hydrogen sulfide in N_2	437	22.0	
89	Air Quality Bureau, New Mexico	Refining	Hydrogen sulfide in N_2	647	NA	F
90	S	Oil shale	Carbonyl sulfide in N_2	117.4	-29.1	E
			Methyl mercaptan in N_2	8.42	-14.8	
			Hydrogen sulfide in N_2	437	-3.65	
91	F	Compliance testing & demonstration	Trichlorethylene in N_2	94.6	NA	E
			Propane in N_2	10.0	NA	
			Propane in N_2	309	-54.0	
			Propane in N_2	73.8	8.7	

TABLE 2. SUMMARY OF PERFORMANCE AUDIT RESULTS (Continued)

Audit No.	Client	Industry	Audit material	RTI audit conc. (ppm)	Client audit % bias (Avg.)*	Status of audit**
92	EPA, Region I	Research Method Development	Toluene in N_2	347	NA	F
93	D	Method Validation	Hydrogen sulfide in N_2	8.32	NA	F
94	USEPA, Region I	Research-Method Development	Vinylchloride in N_2	8.39	-20.2	E
			1,1-dichlorethylene in N_2	14.2	+10.6	
			Trichloroethylene in N_2	13.46	+55.6	
			Perchloroethylene in N_2	7.94	+48.1	
95	E	Acrylonitrile Production	Acrylonitrile in N_2	413	NA	E
			Acrylonitrile in N_2	10.8	6.94	
96	USEPA, Region I	Resource Recovery Garbage Burning Emissions	Propane in N_2	10.0	-35.0	E
			Propane in N_2	296	-17.2	
97	Tewksbury State Hospital, MA	Research-Method Development	Vinyl chloride	8.39	+57	E
			1,1-dichloroethylene	14.2	-9.9	
			Trichloroethylene	13.5	-4.4	
			Tetrachloroethylene	7.94	+48.6	
98	T	Plywood Veneer	CO_2, propane, toluene	102		A
			CO_2, propane, toluene	1944		
99	U	Hazardous Materials Incineration	Trichloroethylene in N_2	8.91	NA	F
			Perchloroethylene in N_2	7.94	NA	
			Chloroform in N_2	16.5	NA	

TABLE 2. SUMMARY OF PERFORMANCE AUDIT RESULTS (Continued)

Audit No.	Client	Industry	Audit material	RTI audit conc. (ppm)	Client audit % bias (Avg.)*	Status of audit**
100	USEPA, Region I	Research Method Development	Chlorobenzene	9.20	NA	F
			Benzene	127.8	NA	
			Hexane	30.2	NA	
			M-xylene	6.82 (cold bulb)	NA	
				2.68 (warm bulb)		
101	U	Hazardous Materials Incineration	Trichloroethylene in N_2	13.46	NA	F
			Perchloroethylene in N_2	14.54	NA	
102	Allegheny County	Source Testing	Toluene	8.51		A
			MEK	38.69		
			Acrylonitrile	11.60		
			MIBK (n-pentane tracer)	9.49		
103	I	Hazardous Waste Incineration	Vinylidiene chloride in N_2	14.20		A
104	I	Hazardous Waste Incineration	Vinylidiene chloride in	9.00		A
105	USEPA, Region VI	Plastics	Vinylchloride	8.41		A
106	USEPA, Region VI	Vinyl Chloride Manufacturing	Vinylchloride	8.44		A

NA = Not analyzed

$$\text{*Client \% Bias} = 100 \times \frac{\text{Client-Measured Concentration} - \text{RTI-Measured Concentration}}{\text{RTI-Measured Concentration}}$$

**Status Codes:

A = Cylinder shipped; audit results not yet received;
B = Audit results received;
C = Audit report submitted to EPA;
D = Audit results received, audit report submitted to EPA, cylinder not yet returned by client;
E = Audit complete;
F = Audit completed without analysis of audit materials by client.

1977 - Audits 1-8
1978 - Audits 9-28
1979 - Audits 29-49
1980 - Audits 50-75
1981 - Audits 76-82
1982 - Audits 83-86
1983 - Audits 87-106

SECTION 4.0
STABILITY STUDIES

An ideal calibration standard or audit material should be stable over its total time of usage. Any change or instability should be less than the measurement error tolerated during its use. The stabilities of the compounds in the repository are being estimated through periodic analysis of the cylinder contents. Improved estimates of stabilities could be determined by increasing considerably the frequency of the analyses, however, this increase is beyond the scope and financial limits of this project. The primary objective of this project is to conduct performance audits during source testing to assess the relative accuracy of the analytical results.

In this project, the gas mixtures in the repository are initially analyzed upon receipt from the specialty gas vendor to corroborate the vendor's analysis. If the RTI analysis differs from the vendor's value by more than 10 percent, the cylinder is given to a third party for analysis. The gas mixtures are again analyzed at 1 month, at 2 months, and at one year following the initial analysis. These subsequent analyses are made to determine the stability of the gas mixtures. In some cases, analyses are not peformed on the dates specified above; however, every attempt is made to acquire the data on this schedule. Cylinder concentrations are also determined prior to each performance audit, providing additional data for use in stability studies.

The estimates of stability have been calculated in terms of percent change per month. These rates of change are calculated from a linear regression analysis of the concentration/time data. Stability estimates have been calculated only for cylinder contents analyzed three or more times. Two standard deviations of percentage change per month have been calculated only for cylinder contents analyzed four or more times. Attachment 1 shows the concentrations and time periods on which the calculations are based and the percent change per month for each cylinder. Sample calculations for a 100 ppm benzene cylinder are given in Attachment 2 (See Page 76).

As the number of analyses per cylinder increases, additional statistical analyses will be performed. These additional statistical analyses will include testing models other than the linear regression model. Such models are needed especially where the change is rapid at first but later becomes slow or nonexistent. The results will be presented in a final report. Statistical analysis for ten (10) halocarbons and eight (8) organics were recently published in the open literature (1,2).

Absolute accuracies of the cylinder analyses have not been determined due to lack of NBS-SRM's as standards for most gas mixtures. Recently NBS has issued SRM's for both benzene and for tetrachlorethylene and is in the process of preparing SRM's containing up to eight different organic components. The available NBS-SRM's will be used in the future to estimate the absolute accuracy. Absolute accuracy could also be estimated by performing the analyses using several different analytical methods or by having a relatively large number of laboratories perform analyses on the same cylinders; both of these approaches are beyond the financial limits of this project. An examination of the data in Attachment 1 shows values for individual cylinder analyses usually have varied by less than 10 percent for 4-8 analyses over 2-3 years. This variation indicates either a real change in cylinder contents (i.e., instability) and/or the precision of the measurement process. The possible sources of experimental error that could result in apparent changes in concentrations include (1) the variability of the analytical technique used for analysis, (2) stability of and/or accuracy of calibration standards, and (3) the ability to reproduce standards for which NBS-SRM's do not exist. Each of the above sources of variability impacts to some extent on the resulting data presented in Attachment 1.

In some cases, the cylinder contents were lost after only a few analyses. The possible reasons include leakage during storage or shipping, misuse, multiple use in audits or initial low pressure in the cylinder.

SECTION 5.0
SUMMARY AND CONCLUSIONS

Cylinder gases of hydrocarbons, halocarbons, and sulfur containing organic species have been used successfully as audit materials to assess the relative accuracy of gas chromatographic systems used to measure source emissions. Absolute accuracy has not been determined because of lack of standard reference materials for most gas mixtures; instead interlaboratory bias has been reported for the performance audits conducted during source testing. The interlaboratory bias determined has been generally within 10 percent for both low and high concentration gases (Table 2).

Of the 42 gaseous compounds studied or currently under study, 37 have demonstrated sufficient stability in cylinders to be used further as audit materials. Four compounds (ethylamine, paradichlorobenzene, cyclohexanone, and aniline) are not recommended as audit materials for various reasons as discussed in Attachment 1. One gaseous compound (formaldehyde) was ordered but the speciality gas manufacturer indicated that cylinder gases of this compound could not be prepared. As stated previously, the percent change per month values reported in Attachment 1 are only estimates of stability. Detailed statistical analyses which would separate statistical deviations from true concentration changes with time are in progress and will be presented in a final report.

REFERENCES

1. R. K. M. Jayanty, C. Parker, C. E. Decker, W. F. Gutknecht, J. E. Knoll and D. J. VonLehmden, "Quality Assurance for Emissions Analysis Systems," Environmental Science and Technology, 17 (6), 257-263A (1983).

2. G. B. Howe, R. K. M. Jayanty, V. J. Rao, W. F. Gutknecht, C. E. Decker and D. J. VonLehmden, "Evaluation of Selected Gaseous Halocarbons for Use in Source Test Performance Audits," Accepted for publication in J. of Air Pollution Control Association, (in print).

3. S. K. Gangwal and D. E. Wagoner, "Response Correlation of Low Molecular Weight Sulfur Compounds Using a Novel Flame Photometric Detector," J. Chrom. Sci., 17, 196-201 (1979).

ATTACHMENT 1

Stability Data
as of
June 1983

1.0 BENZENE STABILITY STUDY

2.0 ETHYLENE STABILITY STUDY

3.0 PROPYLENE STABILITY STUDY

4.0 METHANE/ETHANE STABILITY STUDY

5.0 PROPANE STABILITY STUDY

6.0 TOLUENE STABILITY STUDY

7.0 HYDROGEN SULFIDE STABILITY STUDY

8.0 META-XYLENE STABILITY STUDY

9.0 METHYL ACETATE STABILITY STUDY

10.0 CHLOROFORM STABILITY STUDY

11.0 CARBONYL SULFIDE STABILITY STUDY

12.0 METHYL MERCAPTAN STABILITY STUDY

13.0 HEXANE STABILITY STUDY

14.0 1,2-DICHLOROETHANE STABILITY STUDY

15.0 CYCLOHEXANE STABILITY STUDY

16.0 METHYL ETHYL KETONE STABILITY STUDY

17.0 METHANOL STABILITY STUDY

18.0 1,2-DICHLOROPROPANE STABILITY STUDY

19.0 TRICHLOROETHYLENE STABILITY STUDY

20.0 1,1-DICHLOROETHYLENE STABILITY STUDY

21.0 1,2-DIBROMOETHYLENE STABILITY STUDY

22.0 PERCHLOROETHYLENE STABILITY STUDY

23.0 VINYL CHLORIDE STABILITY STUDY

24.0 1,3-BUTADIENE STABILITY STUDY

25.0 ACRYLONITRILE STABILITY STUDY

26.0 ANILINE STABILITY STUDY

27.0 METHYL ISOBUTYL KETONE STABILITY STUDY

28.0 CYCLOHEXANONE STABILITY STUDY

29.0 PARADICHLOROBENZENE STABILITY STUDY

30.0 ETHYLAMINE STABILITY STUDY

31.0 FORMALDEHYDE STABILITY STUDY

32.0 METHYLENE CHLORIDE STABILITY STUDY

33.0 CARBON TETRACHLORIDE STABILITY STUDY

34.0 FREON 113 STABILITY STUDY

35.0 METHYL CHLOROFORM STABILITY STUDY

36.0 ETHYLENE OXIDE STABILITY STUDY

37.0 PROPYLENE OXIDE STABILITY STUDY

38.0 ALLYL CHLORIDE STABILITY STUDY

39.0 ACROLEIN STABILITY STUDY

40.0 CHLOROBENZENE STABILITY STUDY

41.0 CARBON DISULFIDE STABILITY STUDY

42.0 METHOD 25 GAS MIXTURE

1.0 BENZENE STABILITY STUDY

Cylinder No.		1A	1B	1C	1D	1E	1F	1G
Cylinder Construction*		Al	Al	Al	Al	S	S	S
Manufacturer Concentration	ppm	65.4	324	200	117	61.0	71.0	80.0
RTI Concentration	Date	7/27/77	7/27/77	7/27/77	7/27/77	2/10/78	2/10/78	2/10/78
	ppm	(79.0)	(374)	(241)	(138)	(62.0)	(71.0)	(80.0)
	Day	136	136	247	29	78	232	78
	ppm	(74.0)	(337)	(216)	(144)	(62.0)	(73.0)	(81.0)
	Day	156	156	252	157	216	385	216
	ppm	(78.0)	(350)	(215)	(134)	(61.0)	(75.0)	(81.0)
	Day	167	167	381	252	385	586	385
	ppm	(80.0)	(355)	(218)	(129)	(65.0)	(74.5)	(84.0)
	Day	630	402		290	722	882	504
	ppm	(77.9)	(331)		(127)	(66.9)	(75.7)	(85.4)
	Day	**	433		414	1337	1292	1292
	ppm		(343)		(127)	(55.7)	(65.7)	(74.0)
	Day		969		1247	1858		
	ppm		(358)		(132)	(58.7)		
	Day		1274					
	ppm		(348)					
			1491					
			(324)					
			2056					
			(305)					
% Change/month		-0.01	-0.16	-0.87	-0.12	-0.13	-0.14	-0.17
Two Std. Dev. of % Change/month		0.42	0.12	0.66	0.27	0.19	0.29	0.25

* Al = Aluminum; S = Steel; LS = Low-Pressure Steel.

** Cylinder empty

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 on Chramosorb W-P column at 60°.

CALIBRATION: Reagent-grade "Benzene" liquid is used as a standard. Glass-bulb dilution technique is used for making the series of standards for calibration.

Cylinder No.		1H	1I	1J	1K	1L	1M	1N
Cylinder Construction***		S	S	S	S	S	S	S
Manufacturer Concentration	ppm	100	139	232	265	296	326	344
RTI Concentration	Date	2/8/78	2/9/78	2/9/78	2/9/78	2/9/78	2/9/78	2/9/78
	ppm	(101)	(139)	(229)	(264)	(295)	(319)	(332)
	Day	65	49	233	49	49	49	49
	ppm	(102)	(139)	(237)	(261)	(292)	(316)	(327)
	Day	206	50	386	50	51	51	54
	ppm	(98.0)	(142)	(243)	(268)	(294)	(318)	(342)
	Day	237	96	557	69	93	96	69
	ppm	(101)	(139)	(225)	(254)	(298)	(323)	(335)
	Day	434	127		84	205	433	809
	ppm	(105)	(140)		(269)	(294)	(345)	(342)
	Day	773	205			237	830	**
	ppm	(106)	(138)			(302)	(335)	
	Day	831	505			809	1294	
	ppm	(100)	(147)			(295)	(320)	
	Day	1294	1293			1294		
	ppm	(92.0)	(128)			(290)		
			1338					
			(128)					
% Change/month		-0.12	-0.16	-0.02	-0.04	-0.03	0.06	0.10
Two Std. Dev. of % Change/month		0.21	0.12	0.62	2.51	0.06	0.17	0.16

***Al = Aluminum; S = Steel; LS = Low Pressure Steel.

**Empty

		1O	1P	1Q	1R	1S	1T	1U
Cylinder No.		1O	1P	1Q	1R	1S	1T	1U
Cylinder Construction***		S	S	S	S	S	S	S
Manufacturer Concentration	ppm	389	8.04	9.85	9.89	9.93	10.0	10.9
RTI Concentration	Date	2/9/78	4/21/78	4/21/78	4/21/78	4/21/78	4/21/78	4/21/78
	ppm	(387)	(8.37)	(9.99)	(10.0)	(10.0)	(10.7)	(11.5)
	Day	64	4	5	4	4	25	4
	ppm	(369)	(8.33)	(9.88)	(10.1)	(10.1)	(10.2)	(10.7)
	Day	205	25	25	13	26	146	25
	ppm	(396)	(8.20)	(10.1)	(9.73)	(9.80)	(9.20)	(10.8)
	Day	809	26	332	332	56	362	332
	ppm	(396)	(8.34)	(9.71)	(9.77)	(9.50)	(9.90)	(10.7)
	Day	1294	56		1018	146	1222	434
	ppm	(389)	(8.19)		(9.46)	(8.90)	(9.56)	(10.9)
	Day		134		1270	628	**	759
	ppm		(7.81)		(9.64)	(9.57)		(10.2)
	Day		434			738		1222
	ppm		(8.21)			(9.45)		(9.69)
	Day		766			**		
	ppm		(7.93)					
			1222					
			(7.68)					
% Change/month		0.06	-0.16	-0.25	-0.10	-0.13	-0.15	-0.29
Two Std. Dev. of % Change/month		0.16	0.10	0.26	0.08	0.33	0.35	0.15

** Cylinder empty.

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

1.0 BENZENE STABILITY STUDY (Continued)

Cylinder No. Cylinder Construction***		1V S	1W S	1X S	1Y S	1Z S	1AA S	1AB Al
Manufacturer Concentration	ppm	12.2	8.09	11.0	11.2	8.09	9.14	270
RTI Concentration	Date ppm	4/25/78 (12.7)	5/19/78 (8.10)	5/4/78 (11.2)	5/4/78 (10.9)	5/4/78 (8.20)	5/4/78 (9.10)	7/27/77 (300)
	Day ppm	1 (12.5)	105 (7.70)	132 (10.2)	132 (9.90)	132 (7.04)	132 (7.80)	29 (319)
	Day ppm	21 (12.3)	287 (8.10)	**	302 (10.7)	302 (7.70)	302 (8.50)	157 (312)
	Day ppm	109 (12.0)	488 (8.20)		393 (10.8)	473 (7.54)	1005 (8.17)	2056 (305)
	Day ppm	358 (12.1)	784 (8.30)				1209 (8.42)	
	Day ppm	755 (12.0)	1194 (7.45)					
		1218 (11.7)						
% Change/month		-0.14	-0.09	-2.04	0.11	-0.27	-0.08	-0.02
Two Std. Dev. of % Change/month		0.09	0.25	---	1.04	1.21	0.35	0.11

** Cylinder empty.

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

2.0 ETHYLENE STABILITY STUDY

Cylinder No.		2A	2B	2C	2D	2E	2F	2G
Cylinder Construction***		Al	Al	Al	Al	Al	Al	Al
Manufacturer Concentration	ppm	2920	3000	4960	4970	19900	19900	4.95
	Date	2/23/78	2/23/78	2/23/78	2/23/78	2/24/78	2/24/78	4/27/78
	ppm	(3066)	(3127)	(5214)	(5202)	(20438)	(20622)	(4.70)
RTI Concentration	Day	49	49	48	48	48	48	29
	ppm	(3115)	(3177)	(5341)	(5284)	(20780)	(20822)	(4.70)
	Day	198	198	201	201	200	200	106
	ppm	(2883)	(2942)	(4662)	(4913)	(20150)	(20320)	(4.85)
	Day	809	809	809	809	808	808	741
	ppm	(3203)	(3272)	(5383)	(5338)	(18906)	(18960)	(4.62)
	Day							1180
	ppm							(5.12)
% Change/month		0.18	0.19	0.14	0.10	-0.31	-0.32	+0.14
Two Std. Dev. % of Change/month		0.44	0.44	0.72	0.39	0.10	0.07	0.22

***Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, Durapak n-octane on Porasil C column at 30 degrees Celsius.

CALIBRATION: NBS-SRM Propane is used for standard calibration.

Cylinder No.		2H	2I	2J	2K	2L	2M	2N
Cylinder Construction***		Al	Al	Al	Al	Al	Al	Al
Manufacturer Concentration	ppm	10.0	15.0	19.9	300	448	603	701
RTI Concentration	Date	4/27/78	4/28/78	4/28/78	4/28/78	4/28/78	4/28/78	4/28/78
	ppm	(9.7)	(14.4)	(19.2)	(306)	(468)	(629)	(740)
	Day	29	28	28	33	33	34	34
	ppm	(9.6)	(14.4)	(19.3)	(319)	(493)	(646)	(749)
	Day	106	104	104	105	104	104	104
	ppm	(9.9)	(14.9)	(20.3)	(312)	(473)	(636)	(737)
	Day	740	739	739	728	740	740	740
	ppm	(8.4)	(18.0)	(27.5)	(300)	(457)	(606)	(703)
	Day	1180	1179	1179				
	ppm	(10.0)	(14.4)	(18.9)				
% Change/month		-0.07	+0.18	+0.29	-0.17	-0.19	-0.20	-0.23
Two Std. Dev. of % Change/month		0.44	0.66	1.14	0.22	0.27	0.14	0.08

***Al = Aluminum; S = Steel; LS = Low Pressure Steel.

3.0 PROPYLENE STABILITY STUDY

		3A	3B	3C	3D	3E	3F	3G	3H
Cylinder No.		3A	3B	3C	3D	3E	3F	3G	3H
Cylinder Construction***		Al	Al	Al	Al	Al	Al	Al	Al
Manufacturer Concentration	ppm	4.94	9.91	14.8	20.0	298	446	585	683
RTI Concentration	Date	4/27/78	4/27/78	4/27/78	4/27/78	4/27/78	4/27/78	4/27/78	4/27/78
	ppm	(4.86)	(9.83)	(14.6)	(19.8)	(296)	(442)	(577)	(672)
	Day	26	26	26	27	27	27	27	27
	ppm	(4.94)	(9.85)	(14.5)	(19.0)	(286)	(428)	(560)	(655)
	Day	27	104	104	104	104	105	104	105
	ppm	(4.78)	(10.3)	(14.8)	(20.0)	(317)	(474)	(629)	(729)
	Day	104	749	749	749	750	750	750	750
	ppm	(4.98)	(9.76)	(14.8)	(20.3)	(324)	(479)	(620)	(721)
	Day	749	1250			820			820
	ppm	(4.93)	(9.63)			(328)			(725)
% Change/month		0.05	-0.08	0.06	0.16	0.38	0.33	0.27	0.25
Two Std. Dev. of % Change/month		0.17	0.12	0.09	0.25	0.29	0.47	0.56	0.32

***Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, Durapak n-octane on Porasil C column at 30 degrees Celsius

CALIBRATION: NBS-SRM Propane is used for standard calibration.

4.0 METHANE/ETHANE STABILITY STUDY

Cylinder No.		4A		4B		4C		4D	
Cylinder Construction***		Al		Al		Al		Al	
Audit Material****		M	E	M	E	M	E	M	E
Manufacturer Concentration	ppm	6000	714	8130	597	1000	295	1670	202
RTI Concentration	Date	7/21/78	7/21/78	7/21/78	7/21/78	7/21/77	7/21/77	7/21/77	7/21/77
	ppm	(6207)	(773)	(8130)	(654)	(1021)	(315)	(1710)	(220)
	Day	264	163	35	35	264	163	35	29
	ppm	(5982)	(715)	(7551)	(663)	(983)	(292)	(1563)	(218)
	Day	662	264	264	163	1027	264	264	157
	ppm	(6584)	(684)	(7824)	(606)	(1289)	(283)	(1640)	(202)
	Day		662	662	264		1027	1027	258
	ppm		(703)	(8592)	(577)		(284)	(1953)	(195)
	Day				662				1027
	ppm				(598)				(206)
% Change/month		0.32	-0.34	0.43	-0.43	0.90	-0.20	0.59	-0.13
Two Std. Dev. of % Change/month		---	0.61	0.53	0.57	---	0.36	0.41	0.39

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

**** M = Methane; E = Ethane.

ANALYTICAL CONDITIONS: Flame ionization detector, Durapak n-octane on Porasil C column at 30 degrees Celsius.

CALIBRATION: NBS-SRM methane is used for standard calibration.

5.0 PROPANE STABILITY STUDY

		5A	5B	5C	5D	5E	5F	5G	5H
Cylinder No. / Cylinder Construction***		Al	Al	Al	Al	Al	Al	Al	Al
Manufacturer Concentration	ppm	5.01	10.0	14.6	20.0	303	439	604	708
RTI Concentration	Date	4/25/78	4/25/78	4/25/78	4/25/78	4/26/78	4/26/78	4/26/78	4/27/78
	ppm	(4.90)	(9.70)	(14.3)	(19.5)	(304)	(441)	(615)	(730)
	Day	24	24	25	25	24	24	27	26
	ppm	(4.90)	(9.80)	(14.5)	(19.8)	(301)	(436)	(615)	(723)
	Day	108	108	108	108	107	107	107	106
	ppm	(5.10)	(10.1)	(14.9)	(20.3)	(305)	(440)	(607)	(710)
	Day	605	513	582	582	530	530	604	603
	ppm	(4.89)	(10.6)	(15.0)	(20.8)	(316)	(450)	(613)	(718)
	Day	729	752	736	736	581	581	735	734
	ppm	(5.20)	(10.0)	(14.7)	(20.1)	(316)	(453)	(628)	(734)
	Day		914		1252	735	728		
	ppm		(10.0)		(19.7)	(313)	(472)		
	Day					752			
	ppm					(314)			
	Day					913			
	ppm					(309)			
						1251			
						(296)			
% Change/month		0.11	0.09	0.10	0.01	0.01	0.25	0.08	0.3
Two Std. Dev. of % Change/month		0.26	0.22	0.16	0.14	0.12	0.12	0.10	0.13

*** Al = Aluminum; S = Steel, LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, Durapak n-octane on Porasil C column at 30 degrees Celsius.

CALIBRATION: NBS-SRM Propane is used for standard calibration.

5.0 PROPANE STABILITY STUDY (Continued)

Cylinder No.		5I	5J	5K	5L
Cylinder Construction***		Al	Al	Al	Al
Manufacturer Concentration	ppm	1000	2000	10,000	20,000
RTI Concentration	Date	3/3/83	3/383	3/3/83	3/3/83
	ppm	1270	2100	11,760	20,073
% Change/month		----	----	----	----
Two Std. Dev. of % Change/month		----	----	----	----

***Al = Aluminum; S = Steel, LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, Durapak n-octane on Porasil C column at 30 degrees Celsius.

CALIBRATION: NBS-SRM Propane is used for standard calibration.

6.0 TOLUENE STABILITY STUDY

		6A	6B	6C	6D	6E
Cylinder No.		6A	6B	6C	6D	6E
Cylinder Construction***		LS	LS	S	S	S
Manufacturer Concentration	ppm	408	606	16.2	9.11	9.00
	Date	12/6/78	12/6/78	10/3/78	10/3/78	3/29/83
	ppm	(405)	(585)	(17.3)	(9.62)	(8.5)
RTI Concentration	Day	3	3	48	64	
	ppm	(405)	(579)	(14.9)	(8.50)	
	Day	86	86	365	66	
	ppm	(394)	(577)	(15.0)	(8.60)	
	Day	100	358	1046	160	
	ppm	(393)	(615)	(8.91)	(8.20)	
	Day	**	982		**	
	ppm		(491)			
	Day		985	1373		
	ppm		(487)	(14.8)		
% Change/month		-0.29	-0.50	-0.54	-2.67	----
Two Std. Dev. of % Change/month		0.06	0.06	0.92	1.97	----

** Cylinder empty.

*** Al = Aluminum, S = Steel, LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 Chromosorb WHP column at 60 degrees Celsius.

CALIBRATION: Reagent grade "Toluene" liquid is used as a standard. "Glass bulb" technique is utilized for generation of series of standards for calibration.

ANALTYICAL PROBLEMS: All analyses of Cylinder No. 6B before Day 982 and of Cylinder No. 6C before Day 1046 used glass calibration bulbs at room temperature rather than bulbs which were heated to above toluene's boiling point. As a result, toluene may have condensed on the walls of the room-temperature bulbs. This may explain why the earlier concentrations are greater than those of the most recent analyses. However, actual degradation may have occurred in these cylinders.

7.0 HYDROGEN SULFIDE STABILITY STUDY

		7A	7B	7C	7D	7E	7F	7G
Cylinder No.		7A	7B	7C	7D	7E	7F	7G
Cylinder Construction***		Al	Al	Al	Al	Al	Al	Al
Manufacturer Concentration	ppm	399	9.15	16.7	649	6.95	6.45	6.71
RTI Concentration	Date	10/1/78	7/7/78	10/1/78	10/1/78	10/1/78	10/1/78	3/2/83
	ppm	(371)	(9.73)	(16.1)	(641)	(7.05)	(4.94)	(628)
	Day	38	87	38	38	87	38	
	ppm	(424)	(6.72)	(16.5)	(655)	(5.75)	(5.14)	
	Day	111	124	111	111	124	111	
	ppm	(414)	(7.11)	(15.7)	(690)	(5.62)	(4.81)	
	Day	1030	197	580	1030	197	580	
	ppm	(437)	(6.36)	(16.2)	(647))	(5.23)	(4.35)	
	Day		696	1030		696	1030	
	ppm		(6.23)	(17.5)	**	(5.14)	(3.71)	
	Day		1116			1116		
	ppm		(8.32)			(5.38)		
% Change/month		+0.28	-0.05	+0.22	-0.05	-0.43	-0.75	
Two Std. Dev. of % Change/month		0.47	1.24	0.20	0.28	0.67	0.16	

* Cylinder empty.

*** Al = Aluminum, S = Steel, LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 Chromosorb WHP column at 60 degrees Celsius.

CALIBRATION: Reagent grade pure "Hydrogen sulfide" gas is used as a standard. Dilutions are made in a Tedlar bag for generation of series of standards for calibration.

ANALYTICAL PROBLEMS: Only a Teflon® column and Teflon® lines should be used. The air-to-hydrogen ratio is critical to the sensitivity of the FPD.

8.0 M-XYLENE STABILITY STUDY

Cylinder No.		8A	8B	8C	8D
Cylinder Construction***		LS	LS	S	S
Manufacturer Concentration	ppm	405	613	17.3	7.33
	Date	10/5/78	10/5/78	10/5/78	10/5/78
	ppm	(480)	(720)	(16.6)	(6.20)
	Day	63	63	63	63
	ppm	(445)	(676)	(17.2)	(6.81)
RTI	Day	158	158	166	166
Concentration	ppm	(425)	(656)	(20.8)	(6.82)
	Day	412	606	302	948
	ppm	(487)	(760)*	(16.4)	(4.36)*
	Day	606	1040	948	1036
	ppm	(507)*	(534)	(14.1)*	(5.66)
	Day	1040		1036	1596
	ppm	(364)		(19.0)	(2.68)
% Change/month		0.35**	-1.65**	+0.24	-0.95
Two Std. Dev. of % Change/month		0.74	0.77	0.84	0.52

* Questionable value. Not included in the calculation of % change/month.

** Calculated only through Day 412 because of change in analytical procedures as described under analytical problems.

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

CALIBRATION: Reagent grade "M-Xylene" liquid is used. "Glass bulb" technique is used for generation of series of standards for calibration.

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 on Chromosorb WHP column at 60, 120 or 140 degrees Celsius.

ANALYTICAL PROBLEMS: All analyses before Day 948 used glass calibration bulbs at room temperature rather than bulbs which were heated to above meta-xylene's boiling point. As a result, meta-xylene may have condensed on the walls of the room-temperature bulbs. This may explain why the RTI concentration for cylinder Nos. 8A and 8B before day 1040 are greater than those for the analysis on Day 1040.

9.0 METHYL ACETATE STABILITY STUDY

Cylinder No.		9A	9B	9C	9D
Cylinder Construction***		S	S	S	S
Manufacturer Concentration	ppm	326	455	6.84	17.2
RTI Concentration	Date	10/13/78	10/13/78	10/13/78	10/13/78
	ppm	(271)	(428)	(5.29)	(12.9)
	Day	230	230	230	230
	ppm	(340)	(437)	(4.86)	(12.5)
	Day	286	286	286	286
	ppm	(324)	(442)	(5.02)	(11.8)
	Day	629	629	630	630
	ppm	(348)	(479)	(5.88)	(12.5)
% Change/month		1.15	0.60	0.68	-0.13
Two Std. Dev. of % Change/month		1.08	0.21	1.13	0.56

***Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-275 on Chromosorb WHP column at 50 degrees Celsius.

CALIBRATION: Reagent grade "Methyl acetate" liquid is used as a standard. "Glass bulb" technique is utilized for generation of series of standards for calibration.

10.0 CHLOROFORM STABILITY STUDY

Cylinder No.		10A	10B	10C	10D
Cylinder Construction***		S	S	S	S
Manufacturer Concentration	ppm	520	348	8.70	16.9
RTI Concentration	Date	10/17/78	10/17/78	10/17/78	10/17/78
	ppm	(529)	(345)	(8.08)	(17.6)
	Day	161	161	161	161
	ppm	(515)	(351)	(7.39)	(16.5)
	Day	256	256	256	256
	ppm	(514)	(340)	(7.50)	(16.2)
	Day	553	975	553	553
	ppm	(531)	(325)	(8.11)	(16.5)
% Change/month		0.06	-0.20	0.14	-0.29
Two Std. Dev. of % Change/month		0.31	0.12	0.88	0.51

*** Al = Aluminum; S = Steel; LS = Low Pressure.

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 on Chromosorb WHP column at 50 or 100 degrees Celsius.

CALIBRATION: Reagent grade "Chloroform" liquid is used as a standard. "Glass bulb" technique is utilized for generation of series of standards for calibration .

11.0 CARBONYL SULFIDE STABILITY STUDY

Cylinder No.		11A	11B	11C	11D	11E	11F
Cylinder Construction***		S	S	S	S	AL	AL
Manufacturer Concentration	ppm	251	100	9.96	7.03	9.54	101
RTI Concentration	Date	11/3/78	11/3/78	11/3/78	11/3/78	9/18/81	9/18/81
	ppm	(276)	(109)	(9.10)	(6.81)	(12.9)	(111)
	Day	78	78	78	78		
	ppm	(281)	(111)	(8.66)	(6.48)		
	Day	185	185	185	185		
	ppm	(275)	(95)	(8.23)	(6.41)		
		*	*	*	*		
% Change/month		-0.09	-2.13	-1.55	-0.92	**	**
Two Std. Dev. of % Change/month		---	---	---	---	---	---

* Cylinder empty.

** Calculations for % change/month are only done when three or more analyses are available.

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame photometric detector, Carbopak B column at 50 degrees Celsius or Chromosil 330 column at 60 degrees Celsius.

CALIBRATION: Reagent grade pure "Carbonyl Sulfide" gas is used as a standard. Dilutions are made in Teflon® bag for generation of series of standards for calibration.

ANALYTICAL PROBLEMS: Only a Teflon column and Teflon lines should be used. The air-to-hydrogen ratio is critical to the sensitivity of the FPD.

12.0 METHYL MERCAPTAN STABILITY STUDY

Cylinder No.		12A	12B	12C	12D
Cylinder Construction***		Al	Al	Al	Al
Manufacturer Concentration	ppm	8.03	10.0	3.55	4.22
	Date	1/24/79	1/24/79	1/24/79	1/24/79
	ppm	(5.66)	(7.94)	(3.65)	(4.23)
RTI Concentration	Day	104	104	104	104
	ppm	(5.60)	(8.10)	(3.50)	(4.76)
	Day	139	139	139	139
	ppm	(5.65)	(7.90)	(3.56)	(4.54)
		985	985	985	*
		(5.40)	(8.42)	(3.64)	
% Change/month		-0.14	0.18	0.05	2.04
Two Std. Dev. of % Change/month		0.04	0.10	0.17	---

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

* Empty

ANALYTICAL CONDITIONS: Flame photometric detector, Carbopak B column at 50 degrees Celsius or Chromosil 330 column at 60 degrees Celsius.

CALIBRATION: Reagent grade pure "Methyl mercaptan" gas is used a standard. Dilutions are made in a Teflon® bag for generation of series of standards for calibration.

ANALYTICAL PROBLEMS: Only a Teflon column and Teflon lines should be used. The air-to-hydrogen ratio is a critical variable.

13.0 HEXANE STABILITY STUDY

Cylinder No. Cylinder Construction***		13A LS	13B LS	13C Al	13D Al	13E Al
Manufacturer Concentration	ppm	1975	2973	30.6	79.2	80.0
RTI Concentration	Date	2/6/79	2/6/79	2/6/79	2/6/79	3/25/83
	ppm	(2170)	(3070)	(30.8)	(82.2)	(83.2)
	Day	6	6	296	296	
	ppm	(1982)	(2855)	(30.1)	(81.0)	
	Day	337	338	337	337	
	ppm	(2069)	(2946)	(30.6)	(81.3)	
	Day	469	469	469	469	
	ppm	(1986)	(3076)	(32.0)	(79.8)	
	Day			523	835	
	ppm			(30.0)	(80.2)	
	Day			835	12.47	
	ppm			(30.2)	(82.7)	
% Change/month		-0.22	0.16	-0.05	-0.01	----
Two Std. Dev. of % Change/month		0.69	0.60	0.26	0.09	----

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 on Chromosorb WHP column at 60 or 100 degrees Celsius.

CALIBRATION: Reagent grade "Hexane" liquid is used as a standard. "Glass bulb" technique is utilized for making series of standards for calibration.

14.0 1,2 DICHLOROETHANE (ETHYLENE DICHLORIDE) STABILITY STUDY

		14A	14B	14C	14D	14E	14F	14G	14H
Cylinder No. Cylinder Construction***		Al	Al	Al	Al	Al	Al	Al	Al
Manufacturer Concentration	ppm	14.4	9.64	100	526	6.92	12.5	97.9	439
RTI Concentration	Date	1/19/79	1/19/79	1/19/79	1/19/79	4/5/79	4/5/79	4/5/79	4/5/79
	ppm	(14.1)	(9.20)	(96.2)	(498)	(10.0)	(15.2)	(102)	(463)
	Day	58	58	58	58	30	30	30	30
	ppm	(15.2)	(10.8)	(103)	(534)	(9.42)	(14.7)	(105)	(451)
	Day	155	155	155	155	69	69	69	69
	ppm	(14.9)	(10.0)	(98.2)	(524)	(9.30)	(14.3)	(99.0)	(462)
	Day	811	811	501	501	586	811	425	589
	ppm	(14.2)	(9.56)	(87.3)	(592)	(9.14)	(14.5)	(87.3)	(432)
	Day	835	835	920	920	811	835	844	697
	ppm	(13.5)	(9.19)	(102)	(502)	(9.70)	(13.8)	(101)	(451)
	Day					835			844
	ppm					(9.16)			(453)
% Change/month		-0.22	-0.23	-0.01	+0.04	-0.09	-0.16	-0.18	-0.10
Two Std. Dev. of % Change/month		0.28	0.50	0.58	0.64	0.25	0.21	0.62	0.16

***Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 on Chromosorb WHP column at 100 degrees Celsius.

CALIBRATION: Reagent grade "1,2 Dichloroethane" liquid is used as a standard. "Glass bulb" technique is utilized for making series of standards for calibration.

15.0 CYCLOHEXANE STABILITY STUDY

Cylinder No.		15A
Cylinder Construction***		Al
Manufacturer Concentration	ppm	99.1
RTI Concentration	Date	3/19/79
	ppm	(106)
	Day	147
	ppm	(93.4)
	Day	394
	ppm	(99.0)
		926
		(102)
% Change/month		0.02
Two Std. Dev. of % Change/month		0.55

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 on Chromosorb WHP column at 100 degrees Celsius.

CALIBRATION: Reagent grade "Cyclohexane" liquid is used as a standard. "Glass bulb" technique is used for making series of standards for calibration.

16.0 METHYL ETHYL KETONE STABILITY STUDY

Cylinder No.		16A
Cylinder Construction***		S
Manufacturer Concentration	ppm	43.7
RTI Concentration	Date	5/23/79
	ppm	(42.3)
	Day	28
	ppm	(40.0)
	Day	58
	ppm	(39.9)
	Day	380
	ppm	(44.5)
	Day	653
	ppm	(38.7)
% Change/month		-0.08
Two Std. Dev. of % Change/month		0.67

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, Chromosorb 101 column at 180 degrees Celsius.

CALIBRATION: Reagent grade "Methyl ethyl ketone" liquid is used as a standard. "Glass bulb" technique is utilized for making series of standards for calibration.

17.0 METHANOL STABILITY STUDY

Cylinder No.		17A
Cylinder Construction***		Al
Manufacturer Concentration	ppm	50.0
RTI Concentration	Date	5/17/79
	ppm	(58.8)
	Day	21
	ppm	(52.3)
	Day	51
	ppm	(51.1)
	Day	196
	ppm	(55.2)
% Change/month		-1.03
Two Std. Dev. of % Change/month		3.01

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, Chromosorb 101 column at 50 degrees Celsius or 0.2% Carbowax 1500 plus 0.1% SP-2100 on Carbowax C at 60 degrees Celsius.

CALIBRATION: Reagent grade "Methanol" is used as a standard. "Glass bulb" dilution technique is utilized for making series of standards for calibration.

18.0 1,2-DICHLOROPROPANE (PROPYLENE DICHLORIDE) STABILITY STUDY

Cylinder No.		18A	18B	18C	18D
Cylinder Construction***		Al	Al	Al	Al
Manufacturer Concentration	ppm	7.07	14.6	476	664
	Date	7/10/79	7/10/79	7/10/79	7/10/79
	ppm	(6.06)	(15.6)	(496)	(685)
RTI Concentration	Day	28	28	28	28
	ppm	(5.52)	(16.4)	(455)	(621)
	Day	48	48	48	48
	ppm	(5.94)	(15.0)	(480)	(675)
	Day	497	749	372	372
	ppm	(6.03)	(16.3)	(497)	(685)
	Day	749			
	ppm	(5.59)			
% Change/month		-0.09	+0.16	+0.33	+0.30
Two Std. Dev. of % Change/month		0.43	0.43	0.89	1.05

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 on Chromosorb WHP column at 100 degrees Celsius.

CALIBRATION: Reagent grade "1,2-Dichloropropane" liquid is used as a standard. "Glass bulb" dilution technique is utilized for making series of standards for calibration.

19.0 TRICHLOROETHYLENE STABILITY STUDY

Cylinder No.		19A	19B	19C	19D
Cylinder Construction***		Al	Al	Al	Al
Manufacturer Concentration	ppm	9.23	14.7	100	505
	Date	5/24/79	5/24/79	5/24/79	5/24/79
	ppm	(9.58)	(14.3)	(102)	(506)
RTI	Day	77	77	77	77
Concentration	ppm	(10.2)	(15.1)	(103)	(503)
	Day	92	92	92	92
	ppm	(9.78)	(14.9)	(100)	(499)
	Day	683	683	810	810
	ppm	(9.03)	(13.6)	(105)	(522)
		820	820	820	820
		(8.91)	(13.5)	(94.6)	(490)
% Change/month		-0.37	-0.33	-0.08	0.02
Two Std. Dev. of % Change/month		0.23	0.21	0.31	0.19

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 on Chromosorb WHP column at 100 degrees Celsius.

CALIBRATION: Reagent grade "Trichloroethylene" liquid is used as a standard. "Glass bulb" technique is used for making series of standards for calibration.

20.0 1,1-DICHLOROETHYLENE (VINYLIDENE CHLORIDE) STABILITY STUDY

Cylinder No.		20A	20B	20C	20D
Cylinder Construction***		Al	Al	Al	Al
Manufacturer Concentration	ppm	9.58	14.8	96.8	490
	Date	6/1/79	6/1/79	6/1/79	6/1/79
	ppm	(10.3)	(15.6)	(101)	(524)
RTI	Day	35	35	35	35
Concentration	ppm	(9.90)	(15.1)	(99)	(510)
	Day	62	62	62	62
	ppm	(10.1)	(15.5)	(102)	(505)
	Day	404	404	817	404
	ppm	(11.5)	(17.1)	(94)	(498)
		818	818		
		(9.0)	(14.2)		
% Change/month		-0.25	-0.17	+0.40	-0.26
Two Std. Dev. of % Change/month		0.81	0.63	0.14	0.31

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 on Chromosorb WHP column at 100 degrees Celsius or 10% SP-2100 on Supelcoport column at 100 degrees Celsius.

CALIBRATION: Reagent grade "1,1-Dichloroethylene" pure liquid is used as a standard. "Glass bulb" dilution technique is utilized for making series of standards for calibration.

21.0 1,2-DIBROMOETHYLENE (ETHYLENE DIBROMIDE) STABILITY STUDY

Cylinder No. Cylinder Construction***		21A LS	21B LS	21C LS	21D LS
Manufacturer Concentration	ppm	10.0	14.9	99.9	301
	Date	6/18/79	6/18/79	6/1/79	6/18/79
	ppm	(7.90)	(12.2)	(110)	(265)
RTI	Day	61	61	61	61
Concentration	ppm	(7.80)	(12.0)	(107)	(266)
	Day	89	89	89	89
	ppm	(7.40)	(11.6)	(105)	(257)
	Day	722	772	787	643
	ppm	(7.72)	(8.02)	(99.2)	(309)
% Change/month		-1.90*	-1.53*	-1.52*	-0.83*
Two Std. Dev. of % Change/month		0.35	0.10	0.17	0.29

* % change/month is calculated for only the first three analyses and are approximate because of change in calculation procedure as described below in the analytical problems.

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 on Chromosorb WHP column at 100 degrees Celsius.

CALIBRATION: Reagent grade "1,2-Dibromoethylene" pure liquid is used as a standard. "Glass bulb" dilution techniques is utilized for making series of standards for calibration.

ANALYTICAL PROBLEMS: The gas mixtures and the calibration standards contain substantial amounts of both the cis and the trans isomers of 1,2-Dibromoethylene. The first three sets of analyses are questionable because only one isomer was measured during the calibrations and cylinder analyses.

22.0 PERCHLOROETHYLENE STABILITY STUDY

Cylinder No. Cylinder Construction***		22A S	22B S	22C LS	22D LS
Manufacturer Concentration	ppm	7.98	13.0	487	629
RTI Concentration	Date	7/6/79	7/6/79	7/6/79	7/6/79
	ppm	(8.40)	(15.0)	(419)	(624)
	Day	35	35	35	35
	ppm	(7.97)	(14.9)	(453)	(642)
	Day	52	52	52	52
	ppm	(7.92)	(14.7)	(440)	(619)
	Day	376	376	677	677
	ppm	(7.94)	(14.5)	(361)	(542)
				713	713
				(387)	(571)
% Change/month		-0.22	-0.23	-0.63	-0.51
Two Std. Dev. of % Change/month		0.61	0.17	0.37	0.22

***Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 on Chromosorb WHP column at 50 or 100 degrees Celsius.

CALIBRATION: Reagent grade "Perchloroethylene" liquid is used as a standard. "Glass bulb" dilution technique is utilized for making series of standards for calibration.

23.0 VINYL CHLORIDE STABILITY STUDY

		23A	23B	23C	23D	23E	23F	23G	23H	23I
Cylinder No.		23A	23B	23C	23D	23E	23F	23G	23H	23I
Cylinder Construction***		S	S	S	S	S	S	S	S	S
Manufacturer Concentration	ppm	5.94	8.00	8.03	8.52	20.0	20.1	30.0	30.3	7.98
RTI Concentration	Date ppm	10/1/79 (5.87)	10/1/79 (7.71)	10/1/79 (7.82)	10/1/79 (7.85)	10/1/79 (19.7)	10/1/79 (20.1)	10/1/79 (29.6)	10/1/79 (29.8)	10/1/79 (7.31)
		18 (5.74)	18 (7.50)	18 (7.45)	18 (7.61)	18 (19.1)	18 (19.3)	18 (28.3)	18 (28.7)	18 (7.12)
		700 (6.60)		700 (8.44)	700 (8.41)	700 (20.7)	700 (20.9)	700 (20.4)	700 (29.4)	700 (8.39)
% Change/month		0.59	**	0.45	0.38	0.29	0.25	0.21	0.01	0.71

**Calculations for % change/month are only done when three or more analyses are available.

***Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 0.4% Carbowax 1500 on Carbopak C at 50 degrees Celsius.

CALIBRATION: Vinyl chloride permeation tube purchased from Metronics is used for calibration. Permeation tube is maintained at 30°C.

24.0 1,3 BUTADIENE STABILITY STUDY

Cylinder No.		24A
Cylinder Construction***		S
Manufacturer Concentration	ppm	22.6
RTI Concentration	Date	3/21/80
	ppm	(20.9)
	Date	95
	ppm	(23.1)
	Day	480
	ppm	(24.0)
% Change/month		°+0.73

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 0.1% SP-1000 on Carbopak C column at 90 degrees Celsius or 10% OV-101 on Chromosorb WHP column at 60 degrees Celsius.

CALIBRATION: Reagent grade "1,3 Butadiene" liquid is used as a standard. "Glass bulb" dilution technique is utilized for making series of standards for calibration.

25.0 ACRYLONITRILE STABILITY STUDY

Cylinder No.		25A	25B	25C	25D	25E	25F
Cylinder Construction***		LS	LS	LS	LS	AL	AL
Manufacturer Concentration	ppm	20.1	348	11.7	638	-	-
RTI Concentration	Date	7/24/79	7/24/79	7/24/79	7/24/79	11/8/82	11/18/82
	ppm	(14.6)	(411)	(6.38)	(678)	(413)	(10.8)
	Day	185	185	185	185	134	139
	ppm	(12.7)	(416)	(3.35)	(699)	(410)	(15.7)
	Day	349	349	349	349		
	ppm	(13.2)	(441)	(2.87)	(703)		
	Day	841	841	841	841		
	ppm	(9.96)	(397)	(4.05)	(667)		
% Change/month		-1.07	-0.14	-1.12	-0.10	----	----
Two Std. Dev. of % Change/month		0.46	0.47	3.49	0.26	----	----

*** Al = Aluminum; S = Steel; LS= Low Pressure Steel

ANALYTICAL CONDITIONS: Flame ionization detector, 4% Carbowax 20M on Carbopak B at 50 or 150 degrees Celsius.

CALIBRATION: Acrylonitrile permeation tube is used for GC-FID calibration. Permeation tube is maintained at 30° ± 0.1°C.

ANALYTICAL PROBLEMS: The large changes noted at the low concentration levels are, at least in part, a result of difficulty in making precise measurements at these levels.

26.0 ANILINE STABILITY STUDY

		26A	26B
Cylinder No.		26A	26B
Cylinder Construction***		Al	Al
Manufacturer	ppm	11.3	18.4
RTI Analysis		See Analytical Problems	

***Al = Aluminum; S = Steel; LS = Low Pressure Steel

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 on Chromosorb WHP column at 250 degrees Celsius.

CALIBRATION: Reagent grade "Aniline" pure liquid is used as a standard. "Glass bulb" dilution technique is utilized for making series of standards for calibration.

ANALYTICAL PROBLEMS: Because aniline has an extremely high boiling point (186°C), special handling would be required to measure this compound. A completely heated system for sampling in the vapor phase and for preparing standards would be required. Temperature-dependent condensation in the cylinder and the regulator causes the amount of aniline which is delivered by the cylinder to vary. As a result, aniline is not considered to be practical as an audit material.

27.0 METHYL ISOBUTYL KETONE STABILITY STUDY

Cylinder No.		27A	27C
Cylinder Construction***		Al	Al
Manufacturer Concentration	ppm	9.51	72.9
RTI Concentration	Date	12/18/80	7/8/81
	ppm	(10.2)	(75.4)
	Day	27	See Analytical Problems
	ppm	(10.6)	
	Day	83	
	ppm	(9.53)	
	Day	202	
	ppm	(9.49)	
% Change/month		-1.40	**
Two Std. Dev. of % Change/month		1.58	

**Calculations for % change/month are only done when three or more analyses are available.

***Al = Aluminum; S = Steel; LS = Low Pressure Steel

ANALYTICAL CONDITIONS: Flame ionization detector, 0.1% SP-1000 on Carbopak C column at 180° degrees Celsius.

CALIBRATION: Reagent grade "Methyl isobutyl ketone" liquid is used as a standard. "Glass bulb" technique is utilized for making series of standards for calibration.

ANALYTICAL PROBLEMS: Methyl isobutyl ketone at high concentrations is not practical as an audit material because pressurization of the cylinder above approximately 200 psi results in condensation of the analyte.

28.0 CYCLOHEXANONE STABILITY STUDY

		28A	28B
Cylinder No.		28A	28B
Cylinder Construction***		Al	Al
Manufacturer Concentration	ppm	10.1	19.0
RTI Analysis	Date	12/11/80	12/11/80
	ppm	(8.19)	(25.5)
	Day	85	85
	ppm	(3.26)	(17.1)
% Change/month		**	**

** Calculations for % change/month are only done when three or more analyses are available.

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel

ANALYTICAL CONDITIONS: Flame ionization detector, 10% SP-1000 on Supelcoport column at 200 degrees Celsius.

CALIBRATION: Reagent grade "Cyclohexanone" liquid is used as a standard. "Glass bulb" technique is used for making series of standards for calibration.

ANALYTICAL PROBLEMS: The analysis of cyclohexanone gas is dependent on the temperatures of the cylinder and the regulator and on the length of the sampling line between the regulator and the gas chromatograph. The concentration in the cylinder decreases with time. Therefore, cyclohexanone is not practical as an audit material.

29.0 PARADICHLOROBENZENE STABILITY STUDY

Cylinder No.		29A	29B
Cylinder Construction***		S	S
Manufacturer Concentration	ppm	15.6	38.1
RTI Analysis		See Analytical Problems	

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel

ANALYTICAL CONDITIONS: Flame ionization detector, 10% SP-1000 on Supelcoport column at 200 degrees Celsius.

CALIBRATION: Reagent grade "Paradichlorobenzene" is used as a standard. "Glass bulb" technique is used for making series of standards for calibration.

ANALYTICAL PROBLEMS: The stability study for this compound was terminated because of analytical difficulties and because the cylinder pressure was less than 200 psig. Paradichlorobenzene is a solid at room temperature with a melting point of 54°C. Condensation in the cylinder, regulator and sampling lines was extreme. Paradichlorobenzene is not practical as an audit material.

30.0 ETHYLAMINE STABILITY STUDY

Cylinder No.		30A	30B
Cylinder Construction***		S	S
Manufacturer Concentration	ppm	10	20
RTI Analysis		See Analytical Problems	

*** Al = Aluminum; S = Steel; LS = Low Pressure Steel

ANALYTICAL CONDITIONS: Flame ionization detector, 10% OV-101 Chromosorb WHP column at 250 degrees Celsius.

CALIBRATION: Reagent grade "Ethylamine" liquid is used as a standard. "Glass bulb" technique is utilized for making series of standards for calibration.

ANALYTICAL PROBLEMS: Because of vapor pressure considerations, the cylinders could not be fully pressurized. The pressure in the cylinder is less than 200 psi. A completely heated system for sampling in the vapor phase and for preparing standards would be required. Temperature-dependent condensation in the cylinder and the regulator causes the amount of ethylamine which is delivered by the cylinder to vary. As a result of these problems, ethylamine is not considered to be practical as an audit material.

31.0 FORMALDEHYDE STABILITY STUDY

RTI Requested Concentration	ppm	10	20

The speciality gas supplier indicated that they could not make gas mixtures containing formaldehyde.

32.0 METHYLENE CHLORIDE STABILITY STUDY

Cylinder No.		32A
Cylinder Construction*		Al
Manufacturer Concentration	ppm	10.2
RTI Concentration	Date	3/5/82
	ppm	(10.8)
	Day	31
	ppm	(10.8)
	Day	70
	ppm	(10.6)
	Day	96
	ppm	(11.2)
	Day	124
	ppm	(11.4)
	Day	160
	ppm	(10.9)
	Day	277
	ppm	(10.2)
	Day	278
	ppm	(10.2)
	Day	278
	ppm	(9.8)
	Day	381
	ppm	(9.7)
% Change/month		-0.94
Two Std. Dev. of % Change/Month		0.53

*Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 20 ft. x 1/8" SS column packed with 10% SP-1000 on 80/100 Supelcoport. 30 cm^3/minute He carrier gas. Column temp. = 100°C. Detector temp. = 175°C.

CALIBRATION: Reagent grade "Methylene chloride" liquid is used as a standard. "Glass bulb" technique is utilized for making series of standards for calibration.

33.0 CARBON TETRACHLORIDE STABILITY STUDY

Cylinder No.		33A
Cylinder Construction*		AL
Manufacturer Concentration	ppm	11.3
RTI Concentration	Date	3/4/82
	ppm	(12.7)
	Day	74
	ppm	(11.7)
	Day	74
	ppm	(10.2)
	Day	98
	ppm	(11.1)
	Day	124
	ppm	(10.6)
	Day	161
	ppm	(10.2)
	Day	279
	ppm	(9.3)
	Day	279
	ppm	(9.4)
	Day	382
	ppm	(10.5)
% Change/Month		-1.57
Two Std. Dev. of % Change/Month		1.21

*Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 20 ft. x 1/8" SS column packed with 10% SP-1000 on 80/1000 Supelcoport. 30 cm^3/minute He carrier gas. Column temp. = 100°C. Detector temp. = 175°C.

CALIBRATION: Reagent grade "Carbon tetrachloride" liquid is used as a standard. "Glass bulb" dilution technique is utilized for making series of standards for calibration.

34.0 FREON 113 STABILITY STUDY

Cylinder No.		34A
Cylinder Construction*		Al
Manufacturer Concentration	ppm	10.4
RTI Concentration	Date	3/3/82
	ppm	(10.8)
	Day	34
	ppm	(10.1)
	Day	70
	ppm	(10.0)
	Day	70
	ppm	(9.6)
	Day	98
	ppm	(10.0)
	Day	125
	ppm	(10.0)
	Day	162
	ppm	(10.3)
	Day	384
	ppm	(9.8)
% Change/month		-0.37
Two Std. Dev. of % Change/Month		0.66

*Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 20 ft. x 1/8" SS column packed with 10% SP-1000 on 80/100 Supelcoport. 30 cm^3/minute He carrier gas. Column temp. = 100°C. Detector temp. - 175°C.

CALIBRATION: Reagent grade "Freon 113" liquid is used as a standard. "Glass bulb" dilution technique is utilized for making series of standards for calibration.

35.0 METHYL CHLOROFORM STABILITY STUDY

Cylinder No.		35A
Cylinder Construction*		Al
Manufacturer Concentration	ppm	10.2
RTI Concentration	Date	3/2/82
	ppm	(10.3)
	Day	70
	ppm	(11.8)
	Day	99
	ppm	(10.7)
	Day	136
	ppm	(10.6)
	Day	161
	ppm	(10.0)
	Day	381
	ppm	(10.4)
% Change/Month		-0.35
Two Std. Dev. of % Change/Month		1.28

*Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 20 ft. x 1/8" SS column packed with 10% SP-1000 on 80/100 Supelcoport. 30 cm^3/minute He carrier gas. Column temp. = 100°C. Detector temp. = 175°C.

CALIBRATION: Reagent grade "Methyl chloroform" is used as a standard. "Glass bulb" dilution technique is utilized for making series of standards for calibration.

36.0 ETHYLENE OXIDE STABILITY STUDY

Cylinder No.		36A
Cylinder Construction*		Al
Manufacturer Concentration	ppm	10.0
RTI Concentration	Date	3/12/82
	ppm	(11.2)
	Day	73
	ppm	(9.60)
	Day	88
	ppm	(9.80)
	Day	157
	ppm	(9.8)
	Day	122
	ppm	(9.6)
% Change/month		-2.54
Two Std. Dev. of % Change/Month		2.24

* Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame Ionization detector, 6 ft. x 1/8" SS column packed with 80/100 mesh Porapak QS. 30 cm^3/minute Helium carrier gas. Column temp. = 150°C. Detector temp. = 175°C.

CALIBRATION: Ethylene oxide permeation tube purchased from Metronics is used for GC-FID calibration. Permeation tube is maintained at 30°C.

ANALYTICAL PROBLEMS: There appeared to be some loss of ethylene oxide when a brass regulator was used on the cylinder.

37.0 PROPYLENE OXIDE STABILITY STUDY

		37A	37B
Cylinder No.		37A	37B
Cylinder Construction*		Al	Al
Manufacturer Concentration	ppm	9.48	96.0
RTI Concentration	Date	8/4/82	8/4/82
	ppm	(12.3)	(89.5)
	Date	55	55
	ppm	(11.8)	(86.9)
	Date	76	76
	ppm	(10.6)	(83.6)
	Date		121
	ppm		(90.8)
% Change/Month		----	0.09
Two Std. Dev. of % Change/Month		----	3.06

* Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 6 ft. X 1/8" SS column packed with 80/100 mesh Porapak QS. 30 cm^3/min Helium carrier gas. Column temp. = 150°C. Detector temp. = 175°C.

CALIBRATION: Reagent grade "propylene oxide" is used as a standard. "Glass bulb" dilution technique is utilized for making series of standards for calibration.

38.0 ALLYL CHLORIDE STABILITY STUDY

Cylinder No.		38A	38B
Cylinder Construction*		S	S
Manufacturer Concentration	ppm	10.2	99.5
RTI Concentration	Date	8/13/82**	8/13/82**
	ppm	(11.6)	(124)
	Day	75	74
	ppm	(5.25)	(87.2)
	Day	110	110
	ppm	(5.08)	(87.7)
	Day	167	167
	ppm	(5.36)	(83.4)
% Change/Month		+0.92	-1.45
Two Std. Dev. of % Change/Month		3.10	1.58

* Al = Aluminum; S = Steel; LS = Low Pressure Steel.

** Initial analysis was discarded.

ANALYTICAL CONDITIONS: Flame ionization detector, 20 ft. X 1/8" SS column packed with 10 % SP-1000 Supelcoport. 30 cm^3/minute Helium carrier gas. Column temp. = 100°C. Detector temp. = 175°C,

CALIBRATION: Reagent grade "Allyl chloride" is used as a standard. "Glass bulb" dilution technique is utilized for making series of standards for calibration.

39.0 ACROLEIN STABILITY STUDY

Cylinder No.		39A	39B
Cylinder Construction*		Al	Al
Requested Concentration	ppm	10.2	107
RTI Concentration	Date	8/18/82	8/18/82
	ppm	(10.6)	(90.4)
	Day	28	28
	ppm	(11.0)	(103)
	Day	69	69
	ppm	(9.74)	(106)
% Change/Month		-3.80	6.94
Two Std. Dev. of % Change/Month		6.82	6.70

*

Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detector, 20 ft. X 1/8" SS column packed with 10 % SP-1000 on 80/100 Supelcoport. 30 cm^3/min Helium carrier gas. Column temp = 100°C. Detector temp. = 175°C.

CALIBRATION: Reagent grade "acrolein" is used as a standard. "Glass bulb" dilution technique is utilized for making series of standards for calibration.

40.0 CHLOROBENZENE STABILITY STUDY

Cylinder No.		40A
Cylinder Construction*		Al
Manufacturer Concentration	ppm	9.66
RTI	Date	8/6/82
Concentration	ppm	(9.03)
	Day	39
	ppm	(9.15)
	Day	75
	ppm	(9.20)
% Change/Month		0.76
Two Std. Dev. of % Change/Month		0.32

* Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame ionization detection, 20' X 1/8" stainless steel column packed with 10% SP-1000 on 80/100 mesh Supelcoport. 30 cc/min Helium carrier gas. Column temp. = 150°C. Detector temp = 175°C.

CALIBRATION: Reagent grade chlorobenzene was used as a standard. "Glass bulb" dilution technique is utilized for making a series of standards.

41.0 CARBON DISULFIDE STABILITY STUDY

Cylinder No.		41A
Cylinder Construction*		Al
Manufacturer Concentration	ppm	108
RTI Concentration	Date	7/14/82
	ppm	(100)
	Day	34
	ppm	(114)
	Day	72
	ppm	(116)
% Change/Month		6.42
Two Std. Dev. of % Change/Month		6.06

* Al = Aluminum; S = Steel; LS = Low Pressure Steel.

ANALYTICAL CONDITIONS: Flame photometric detector, 4.6' X 1/4" Teflon® column packed with Carbopak BHT 100. 90 cc/min Helium carrier gas. Column temp. = 75°C. Detector temp. = 175°C.

CALIBRATION: Reagent grade carbon disulfide is injected into a Teflon® bag being filled with N_2 at 5 L/min. through a mass flow controller. The injection fitting is heated slightly to ensure volatilization.

ANALYTICAL PROBLEMS: There is significant peak "tailing" unless a very high flow rate is used. "Tailing" is also caused by "bleed" from the sample loop. Sample valve should be in the inject position for exactly 5 seconds and then switched back to the sampling position to attenuate tailing.

All sample lines and regulators must be conditioned extensively.

42.0 EPA METHOD 25 GAS MIXTURE*

		42A	42B	42C	42D	42E	42F
Cylinder No.		42A	42B	42C	42D	42E	42F
Cylinder Construction**		Al	Al	Al	Al	Al	Al
Manufacturer Concentration	ppm	100	100	200	750	1000	2000
RTI	Date	3/16/83	3/16/83	3/16/83	3/16/83	3/16/83	3/16/83
Concentration	ppmC	102	107	205	775	1043	1944

* Gas Mixture contains an aliphatic, an aromatic and carbon dioxide in nitrogen.

** Al = Aluminum; S = Steel; LS = Low Pressure Steel

ATTACHMENT 2

SAMPLE CALCULATIONS OF % CHANGE/MONTH

ATTACHMENT 2

Sample Calculations of % Change/Month

Example: (Data shown for benzene cylinder.)

Data:

Date of Analysis	Concentration, ppm
2/8/78	101
4/13/78	102
9/1/78	98
10/2/78	101
4/17/79	105

1) Linear Regression, X and Y Data Points, Slope

X values correspond to the dates of analyses, with the first date being day 1 (2/8/78). The second X value is equal to the number of calendar days (i.e., 65) between the first analysis date and the second analysis date (4/13/78) and so on. The Y values are the concentrations (ppm) that were determined on the respective analysis dates.

X	Y
1	101
65	102
206	98
237	101
434	105

Perform the regression analysis and determine the slope of the line utilizing commercially-available hand calculators or by the following formula:

$$m = \frac{\Sigma(X_i-\overline{X})(Y_i-\overline{Y})}{\Sigma(X_i-\overline{X})^2} = 0.0071$$

Standard deviation of slope =

$$\left[\frac{\Sigma(Y_i-\overline{Y})^2 - \frac{\left[\Sigma(X_i-\overline{X})(Y_i-\overline{Y})\right]^2}{\Sigma(X_i-\overline{X})^2}}{(N-2)\ \Sigma\ (X_i-\overline{X})^2}\right]^{1/2} = 0.0076$$

m = slope of regression line

X_i = x-coordinate of an individual value

Y_i = y-coordinate of an individual value

$\overline{X}$ = average of all x_i

$\overline{Y}$ - average of all Y_i

N = number of analyses

2) <u>Percent change/month</u>

$$\% \text{ change/month} = \frac{m \text{ (slope)}}{b} \times 100 \times 30 \text{ days}$$

where

$$b = y \text{ intercept} = \frac{1}{n} (Y - bX) = 100.06$$

Therefore,

$$\% \text{ change/month} = \frac{0.0071}{100.06} \times 100 \times 30 = 0.21$$

3) <u>Standard deviation of percent change/month</u>

$$\text{Standard deviation in units of \% change/month} = \frac{\text{Standard deviation of slope}}{\text{Intercept}} \times 100 \times 30 = 0.2270$$

95% Confidence interval for % change/month = 0.21 $\pm$ 2 X 0.2270 = (-0.255, 0.664)