SANDIA REPORT

SAND2003--1185
Unlimited Release
Printed April 2003

Mass Spectrometric Calibration of Controlled Fluoroform Leak Rate Devices: Technique and Uncertainty Analysis

Steven D. Balsley, James F. Browning, Carol A. LaDuca

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation,
a Lockheed Martin Company, for the United States Department of
Energy under Contract DE-AC04-94AL85000.

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865)576-8401
Facsimile: (865)576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: http://www.doe.gov/bridge

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd
Springfield, VA 22161

Telephone: (800)553-6847
Facsimile: (703)605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: http://www.ntis.gov/ordering.htm

SAND2003-1185
Unlimited Release
Printed April 2003

Mass Spectrometric Calibration Of Controlled Fluoroform Leak Rate Devices: Technique And Uncertainty Analysis

Steven D. Balsley, James F. Browning, and Carol A. LaDuca
Analytical and Tritium Technologies Department
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0871

Abstract

Controlled leak rate devices of fluoroform on the order of 10^{-8} atm·cc sec^{-1} at 25°C are used to calibrate QC-1 War Reserve neutron tube exhaust stations for leak detection sensitivity. Close-out calibration of these tritium-contaminated devices is provided by the Gas Dynamics and Mass Spectrometry Laboratory, Organization 14406, which is a tritium analytical facility. The mass spectrometric technique used for the measurement is discussed, as is the first principals calculation (pressure, volume, temperature and time). The uncertainty of the measurement is largely driven by contributing factors in the determination of P, V and T. The expanded uncertainty of the leak rate measurementis shown to be 4.42%, with a coverage factor of 3 (k=3).

Contents

Figures

Tables

Introduction

The Analytical and Tritium Technologies Department, Gas Dynamics and Mass Spectrometry Laboratory (GDMSL), together with the Primary Physical Standards Laboratory (PPSL) and the Information Systems and Test Engineering Department, have established a capability for the calibration of tritium contaminated, 10^{-8} atm-cc/sec (25°C) fluoroform standard leaks. This capability serves as a secondary standards calibration for the measurement and validation of fluoroform standard leak devices. These standard leak devices are used in a QC-1 WR qualified exhaust process associated with the production of neutron tubes. Responsibilities for the administrative control and measurement of standard leak devices are delineated as follows. The GDMSL is responsible for the establishment, implementation and maintenance of the technique used for the determination/validation of controlled leak rate devices. The Information Systems and Test Engineering Department is responsible for the administrative aspects of the secondary standards laboratory status granted by the PPSL. In addition to describing the standard leak measurement, outlined below are the steps taken by the GDMSL and the PPSL to insure the validity of the technique and the traceability of the measurement, including a comprehensive uncertainty analysis.

Measurement Technique

The GDMSL uses a mass spectrometric technique for the measurement of leak rate devices and determines standard leak rates from first principals, similar to the technique described by Mehrhoff and Mason (1981). A detailed outline of the collection procedure and data reduction may be found in Section 3. A general overview of the collection technique is presented here in order to introduce the terms used for the leak rate calculation.

The controlled leak device is interfaced to an open port in the mass spectrometer inlet system (ports 1-5, Figure 1). Following evacuation and temperature equilibration, gas from the device is collected in volumes E + F of the inlet system, across which there is an approximate 25°C gradient. We refer to this volume as an *effective volume* (V_e) due to the ΔT. A thorough explanation of how V_e is determined is discussed in Section 2.1.3.

After some time interval *t,* the leak rate device is isolated from the inlet system. The gas collected in volume F is used to determine leak rate by measuring the total molar quantity of gas accumulated over *t*. The equation governing the leak rate determination is,

$$SL_R = \frac{I_c V_e}{\varepsilon t} \tag{1}$$

where,

$SL_R \equiv$ standard leak rate of the device (mTorr-cc/sec, 25°C)

$I_c \equiv$ time corrected signal (mV)

$V_e \equiv$ effective volume of the system (cc)

$\varepsilon \equiv$ sensitivity of the mass spectrometer to the gas species of interest (mV/mTorr)

$t \equiv$ collection time (sec)

Uncertainty Analysis

The uncertainty analysis used here is derived from Bevington and Robinson (2003) and Taylor (1982). The overall uncertainty in the standard leak rate value is given by,

$$\sigma_{SL_R} = \pm SL_R \left[\left(\frac{\sigma_{I_c}}{I_c} \right)^2 + \left(\frac{\sigma_{V_e}}{V_e} \right)^2 + \left(\frac{\sigma_\varepsilon}{\varepsilon} \right)^2 + \left(\frac{\sigma_t}{t} \right)^2 \right]^{\frac{1}{2}} \tag{2}$$

Inlet System Schematic

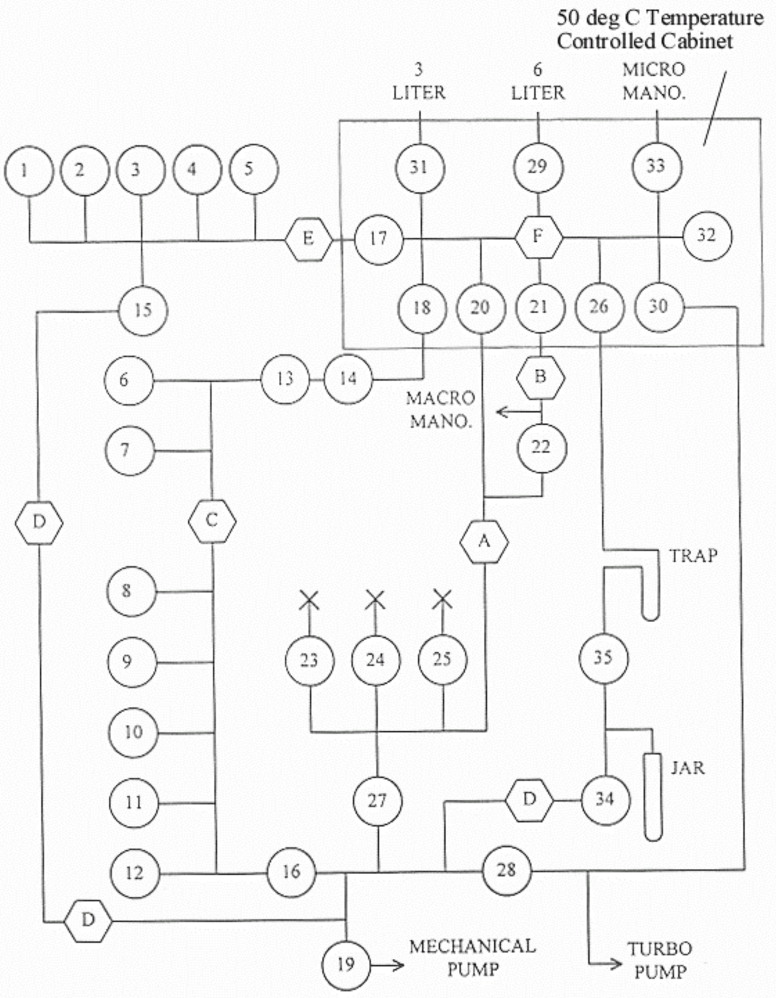


Figure 1.

Figure 1. Inlet system schematic.

Valves are depicted by circles with enclosed numbers and volumes are depicted as hexagons with enclosed letters. The molecular leak and mass spectrometer are located to the right of valve 32. Valves 1-5 are contained within a 25°C, temperature controlled cabinet.

Each term in equation 2 is defined and expanded below, and a tabulation of the contributing terms is presented in Figure 2; the complete uncertainty analysis is listed in the Appendix. The expanded uncertainty for the standard leak measurement is 4.42%, with a coverage factor of 3 (k=3).

Corrected Ion Signal

The ion signal (*I*) from the mass of interest is determined with the mass spectrometer by integration of the total charge collected on a Faraday cup detector. This signal is corrected to its time zero signal intensity level (I_c) by the following expression,

$$I_c = I \exp^{\frac{C_R t'}{V_e}} \tag{3}$$

where t' is the time (in seconds) that *I* is measured after the beginning of the mass scan.

Gas is transferred from the inlet system to the mass spectrometer via molecular flow, which is facilitated by a thin gold foil with three 0.001 inch diameter holes mounted in a 0.25 inch VCR™ connector. The conductance of the gas species of interest from V_e through the foil and into the ionization chamber of the mass spectrometer is given by,

$$C_R = \left(\frac{V_e}{t}\right) \ln\left(\frac{P_0}{P}\right) \tag{4}$$

Here, P_0 is the initial pressure and *P* represents the final pressure on the high-pressure side of the foil after some time *t*. The uncertainty in C_R is given by,

$$\sigma_{C_R} = \pm C_R \left[\left(\frac{\sigma_{V_e}}{V_e}\right)^2 + \left(\frac{\sigma_t}{t}\right)^2 + \left(\frac{\sigma_u}{u}\right)^2\right]^{\frac{1}{2}} \tag{5}$$

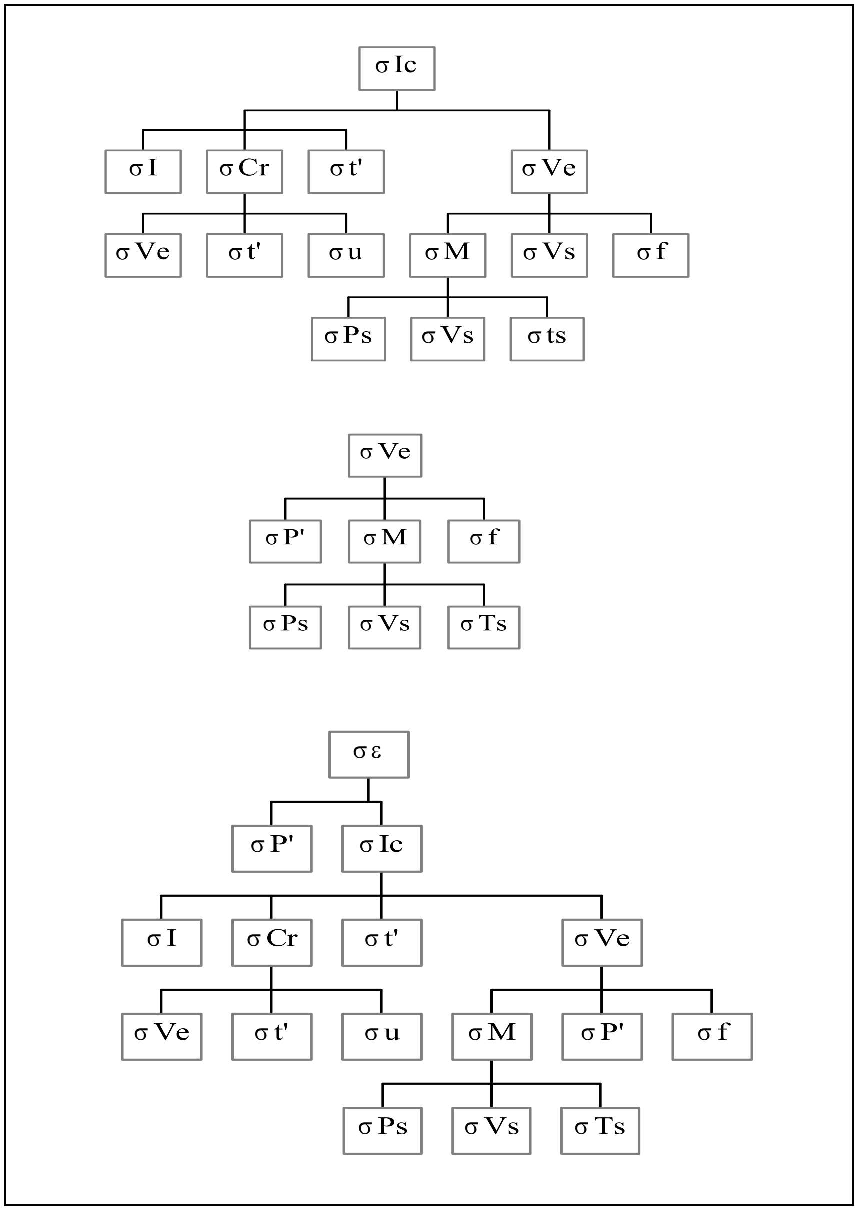


Figure 2. Uncertainty contribution terms

Contributing terms in the expanded uncertainty equation (Equation 2 in text). Note that the uncertainty in the stopwatch reading has no contributing terms and is omitted from this figure. See text for definition of terms.

where,

$$u = \left(\frac{P_0}{P} \right) \tag{6}$$

Therefore, the combined uncertainty in the corrected signal (I_c) may be expressed as follows,

$$\sigma_{I_c} = \pm I_c \left[\left(\frac{\sigma_I}{I} \right)^2 + \left(\frac{\sigma_{u'}}{u'} \right)^2 \right]^{\frac{1}{2}} \tag{7}$$

where,

$$u' = \frac{C_R t'}{V_e} \tag{8}$$

Effective Volume

In the measurement of the leak rate, we use an effective volume, V_e, due to an approximate 25°C gradient across the working volumes (E+F; see Figure 1). In order to determine the effective volume, a series of molar quantities of ultra-high purity helium are expanded into the working volumes of the inlet system. NIST-traceable pressure, volume and temperature standards (Table 1) are used to prepare molar gas quantities. A pressure response (P') to the molar quantity of helium, as measured with an in situ MKS 1-Torr capacitance micromanometer, is recorded over a pressure interval sufficient to cover the calibrated range of the micromanometer. The effective volume may then be determined from the following expressions,

$$\frac{P_s V_s}{T_s} = \frac{P' V'}{T'} \tag{9}$$

$$M \equiv \frac{P_s V_s}{T_s} \tag{10}$$

$$M = \left(\frac{V'}{T'}\right) P' \tag{11}$$

where P_s, V_s and T_s represent calibrated pressure, volume and temperature, respectively and P', V' and T' are measured quantities of the same; M is the molar quantity of gas. A plot of M versus P' across the calibrated range of the micromanometer yields a curve, the slope of which is the effective volume, V_e (Figure 3). The statistical reduction for this data is presented in Table 2.

The uncertainty in the molar quantity (M) is given by,

$$\sigma_M = \pm M\left[\left(\frac{\sigma_P}{P}\right)^2 + \left(\frac{\sigma_V}{V}\right)^2 + \left(\frac{\sigma_T}{T}\right)^2 + \left(\frac{2\sigma_{PV}}{PV}\right) - \left(\frac{2\sigma_{PT}}{PT}\right) - \left(\frac{2\sigma_{VT}}{VT}\right)\right]^{\frac{1}{2}} \tag{12}$$

Table 1. NIST traceable artifacts

Equipment	Term/ Descrip.	Serial No.	File/Work Order No.	Calibration Date	Expiration Date	Value	3σ Uncert.
Vol. Std.	V_s	102398	40418	05-02-98	05-07-00	1.212cc	0.014cc
Paroscientific 1015A-01	P_s	50808	6786	11-17-98	11-17-99	See cert.	See cert.
MKS (1 Torr) 690A01TRC	P’	00232308	42011	12-01-98	12-01-99	See cert.	See cert.
Fluke 8840A Multimeter	I	4022032	118773	12-10-98	12-10-99	200 mV range 2-1000 V	0.007% 0.005%
Omega Thermocouple	T_s	CR0754	122759	09-23-98	09-23-99	-73°C to 125°C	0.5°C
Analogic AN6520-8A-110	T_s	008-A023230	22346	04-14-99	04-14-00	-205°C to 400°C	1.0°C
Fisher Stopwatch	t’	98077134	41474	07-20-99	07-20-00	See cert.	0.25s of reading
Computer Clock	t	None	120820	04-13-99	10-06-99	See cert.	0.007%
MKS (1 Torr) 690A01TRC	V_e	00278532	42461	03-09-99	05-25-00	See cert.	See cert.
MKS (100 Torr) 690A012TRC	V_e	94133109A	11603	12-01-98	12-01-99	See cert.	See cert.

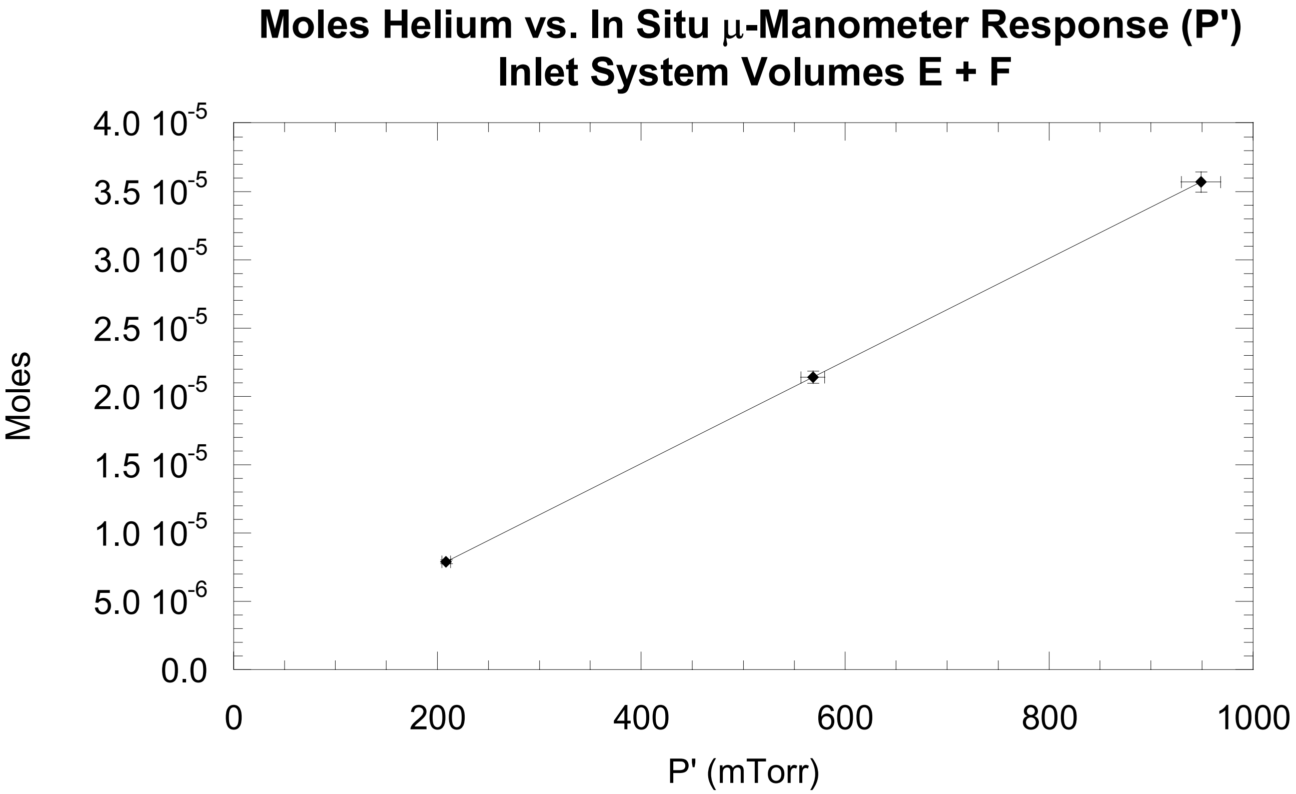


Figure 3. Moles helium vs. P'

Plot of molar quantity (M) versus *P'* for volumes E+F across the calibrated range of the 1 Torr micromanometer head, located in the 50^0C temperature controlled portion of the inlet system. The slope of M vs. *P'* yields the effective volume of E+F. Error bars are as calculated for M and *P'* in the Appendix.

Table 2. Statistical results of data from figure 3.

R=0.99999972	Rsqr=0.99999944	Adj Rsqr=0.99999887			
Analysis of Variance					
	DF	SS	MS	F	P
Regression	1	134087.3813	134087.3813	1774145.4432	0.0005
Residual	1	0.0756	0.0756		
Total	2	134087.4569	67043.7285		
Regression Diagnotstics					
Row	Predicted	Residual	Std. Res.	Stud. Res.	Stud. Del. Res.
1	639.4442	-0.1062	-0.3862	-1.000	0.000
2	366.7916	0.2244	0.8161	1.000	0.000
3	121.8352	-0.1182	-0.4299	-1.000	(+inf)
95% Confidence					
Row	Predicted	Regr. 5%	Regr. 95%	Pop. 5%	Pop. 95%
1	639.4442	636.2221	642.6663	634.6919	644.1964
2	366.7916	364.7730	368.8103	362.7572	370.8261
3	121.8352	118.6813	124.9891	117.1289	126.5415

Data Summary				
P’	M	Residual %	99% Confidence Limits	
173.36	121.717	-0.097096	106.03453	137.63583.
519.61	367.016	0.061131	356.67825	376.90503
905.02	639.339	-0.016607	623.30185	655.58651

The combined uncertainty in V_e also includes contributions from the response (P') the fit to the data set and the standard deviation of the data set. The combined uncertainty in V_e can then be written as,

$$\sigma_{V_e} = \pm V_e\left[\left(\frac{\sigma_M}{M}\right)^2+\left(\frac{\sigma_{P'}}{P'}\right)^2+\sigma_f{}^2+\sigma_{sd}{}^2\right]^{\frac{1}{2}} \tag{13}$$

A summary of final effective volume determinations and associated uncertainties for the entire inlet system may be found in Table 3.

Ion Signal Linearity

The sensitivity (ε') of the mass spectrometer to the mass/charge (m/q) of interest is defined by,

$$\varepsilon' = \frac{I_C}{P'} \tag{14}$$

Table 3. Volumes and associated uncertainties

Expansion Volume*	Calculated from Fit		Volume ID	Calculated Volume (L)	Mean Volume (L)	3σ (%)	Ttl Vol. Uncertainty 3σ (%)
	Vol (L)	3σ (%)					
BJ+Trap+F	1.4990	2.900	F	--	0.5419	0.012	1.881
BJ+Trap+F+E	1.6478	1.286	E	0.1488	0.1488	0.060	1.882
BJ+Trap+F+A	1.7373	2.654	A	0.2383	0.2397	2.491	3.122
BJ+Trap+F+3L	4.1841	0.665	3L	2.6851	2.6889	0.600	1.974
BJ+Trap+F+6L	6.9041	0.453	6L	5.4051	5.3996	0.432	1.930
E+F	0.6908	0.097					
E+F+C	0.8930	0.319	C	0.2022	--	0.478	1.941
E+F+3L	3.3835	0.449	3L	2.6927	--	--	--
E+F+D	1.0315	0.013	D	0.3407	--	0.146	1.887
E+F+A	0.9319	0.029	A	0.2411	0.2397	2.478	3.111
E+F+6L	6.0849	0.129	6L	5.3941	--	--	--
E+F+Trap	1.2822	0.407	Trap	0.5914	--	0.610	1.977
E+F+Trap+BJ	1.6678	1.073	Belljar	0.3702	--	1.609	2.475

*Volume determinations were derived by expanding a molar quantity of He from either the belljar (BJ) or "E" region of the inlet system (see Figure 1). For "Expansion Volumes" beginning with BJ, He was expanded from the BJ region, whereas those beginning with E indicate expansions from the E region.

Disregarding the goodness of fit of the data, the associated uncertainty in the sensitivity measurement is:

$$\sigma_{\varepsilon'} = \pm\varepsilon'\left[\left(\frac{\sigma_{I_C}}{I_C}\right)^2 + \left(\frac{\sigma_{P'}}{P'}\right)^2\right]^{\frac{1}{2}} \tag{15}$$

The sensitivity measurement must be corrected due to a factor of ~1000 difference between the molar quantity of a collected sample versus the point at which the sensitivity measurement is made. Nominal CHF_3 leak rates used in the neutron tube production exhaust process are of the order 10^{-8} atm-cc/s at 22°C, which equates to an approximate molar quantity of 10^{-9} mol following a collection time of one hour. Sensitivity measurements were made so that the *P′* measurement fell within a linear region of the capacitance micromanometer, equivalent to approximately 10^{-9} to 10^{-6} mol.

To demonstrate the system (inlet system + mass spectrometer) linearity over the range 10^{-9} to 10^{-6} mol, a study using high purity CHF_3 was performed. The results conclusively show that between 3×10^{-6} to 8×10^{-10} mol CHF_3, the system acts in a linear fashion (Figure 4; Table 4). The equation of fit is linear, and takes the form,

$$I_c = \frac{n}{an + b} \tag{16}$$

where n is moles of CHF_3 and *a* and *b* are the coefficients of the fit.

With this, the combined sensitivity uncertainty is determined by the addition of the fit propagated in quadrature with $\sigma_{\varepsilon'}$:

$$\sigma_{\varepsilon} = \pm\varepsilon\left[\left(\frac{\sigma_{\varepsilon'}}{\varepsilon'}\right)^2 + (\sigma_f)^2\right]^{\frac{1}{2}} \tag{17}$$

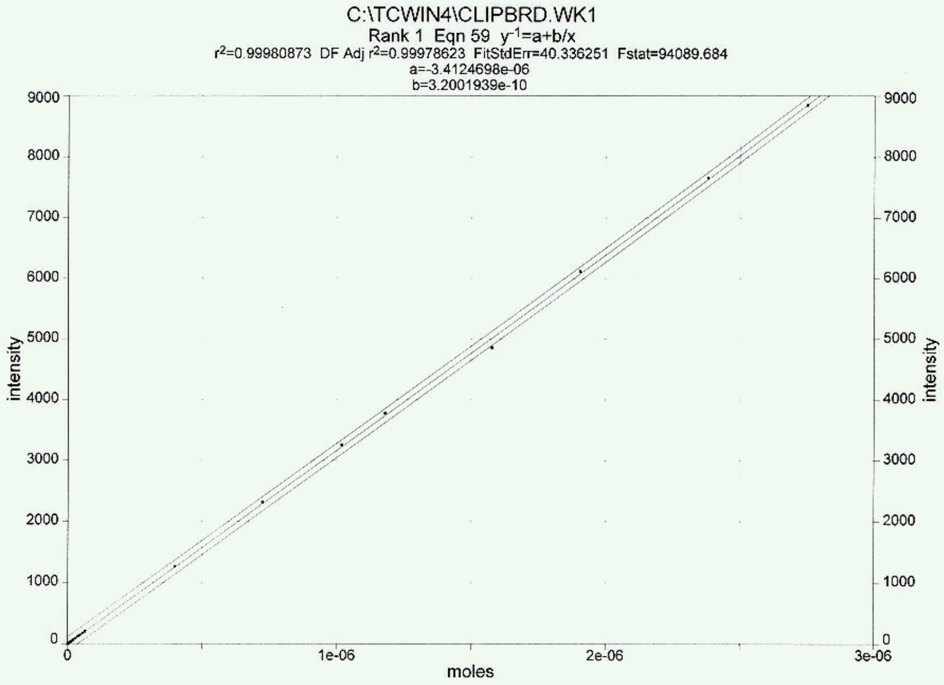


Figure 3.

Figure 4. Signal (mV) vs. moles, fluoroform

Broad range linearity of fluoroform from 7.9 x 10^{-10} moles to 2.8 x 10^{-6} moles as detected on Faraday channel 2.

Table 4. Statistical analysis of signal response
2.75 x 10^{-6} to 7.90 x 10^{-10} moles CHF_3
Fit Equation: y^{-1}=a + b/x

X value	Y value	Y Predict	Residual	Residual %	99% Confidence Limits		99% Prediction Limits	
7.896e-10	2.5815	2.4673835	0.1141165	4.4205508	2.4561281	2.4786389	-113.6381	118.57288
1.422e-9	4.5798	4.4436804	0.1361196	2.972173	4.4374324	4.4499284	-111.6618	120.54917
3.775e-9	11.839	11.795787	0.0432129	0.3650043	11.793436	11.798139	-104.3097	127.90128
1.014e-8	31.814	31.688046	0.1259544	0.3959088	31.68713	31.688919	-84.41745	147.79354
1.458e-8	45.785	45.5525	0.2324259	0.5076464	45.551968	45.55318	-70.55292	161.65807
2.096e-8	65.91	65.522137	0.3878631	0.5884739	65.521717	65.522557	-50.58336	181.62763
2.982e-8	93.6	93.226393	0.3736066	0.3991524	93.226099	93.226688	-22.8791	209.33189
3.924e-8	123.08	122.67586	0.4041374	0.3283535	122.67564	122.67609	6.5703696	238.78136
4.614e-8	145.19	144.23842	0.9515809	0.6554039	144.23823	144.23861	28.132926	260.34391
5.624e-8	176.99	175.53324	1.1567553	0.653571	175.83309	175.8334	59.727752	291.93874
6.495e-8	204.54	203.09619	1.4438148	0.7058838	203.09605	203.09632	86.990692	319.20168
6.557e-8	205.77	205.05041	0.7195947	0.3497083	205.05027	205.05054	88.944912	321.1559
3.978e-7	1262.94	1248.4547	14.485312	1.1469517	1248.4547	1248.4547	1132.3492	1364.5602
7.263e-7	2312.0	2287.3729	24.627074	1.0651849	2287.3729	2287.3729	2171.2674	2403.4784
1.019e-6	3248.5	3219.6487	28.85129	0.8881419	3219.6487	3219.6487	3103.5432	3335.7542
1.180e-6	3773.1	3734.0176	39.082423	1.0358173	3734.0176	3734.0176	3617.9121	3850.1231
1.577e-6	4857.5	5012.5134	-155.0134	-3.191217	5012.5134	5012.5134	4896.4079	5128.6189
1.906e-6	6115.1	6079.0657	36.034265	0.589267	6079.0657	6079.0657	5962.9602	6195.1712
2381e-6	7662.2	7634.9098	27.290241	0.3561672	7634.9098	7634.9098	7518.8043	7751.0153
2.751e-6	8850.0	8855.684	-5.68402	-0.064226	8855.684	8855.684	8739.5785	8971.7895

Collection Time

The collection time for the analysis (*t*) is measured with a calibrated hand held stopwatch, and is nominally one hour in duration. The associated uncertainty is determined by the PPSL, and its value is given in Table 1.

Collection Procedure

In partial fullfillment of the requirements of the PPSL for certification of the GDMSL as a secondary standards laboratory for the determination of 10^{-8} CHF_3 leak rate devices, an outline of the collection procedure and data reduction is presented below.

1. Preparation of the standard leak
    - 1.1. Mount the standard leak on a port in the temperature controlled cabinet (25°C) of the mass spectrometer inlet system. Attach a nitrogen line to operate the actuator valve on the standard leak.
    - 1.2. Using first the rough pump and then switching to the turbo pump, carefully evacuate the inlet system opening the valves to the leak and actuator.
        - 1.2.1. Pump on the leak and the collection / scan regions (E+F) of the inlet system for a period nominally overnight or of at least 2 hours. Valve 32 to the mass spectrometer should be open for at least the last 30 minutes of the pumpdown period.

2. Set-up of the mass spectrometer
    - 2.1. Load the experiment for standard leaks. The mass of interest is species CHF_2, but CF_3 and CHF_3 may be included in the scan. The detector used is FARII.
    - 2.2. Ensure that a recent mass calibration has been performed on the mass spectrometer. A center peak check on CHF_2 may be performed after a sample run on the remaining gas.
    - 2.3. Simulate a complete collection cycle in order to evaluate system "background."

3. Collection of sample
    3.1. Isolate volume regions E+F on the inlet system to begin sample collection.
    3.2. Using a calibrated stopwatch time the collection period (at least 3600 seconds).
    3.3. At the end of the collection period isolate region F.
    3.4. Record time in seconds.
    3.5. Record the temperatures of volumes E and F as indicated on the Wavetek readout.

4. Analysis of sample
    4.1. Execute the experiment on the sample gas collected in scan region F.
    4.2. Pump on the standard leak and the collection and scan regions (E+F) with valve 32 open to the mass spectrometer for at least 30 minutes prior to the next run.
    4.3. Repeat steps 3 & 4 twice more for a total of 3 runs on the sample.

5. Sensitivity and Leakrate of CHF_3 using a reference flask of CHF_3
    5.1. Following standard laboratory practice, make a sensitivity measurement of CHF_3, using the CHF_2 peak.
    5.2. Following standard laboratory practice, make a leakrate measurement of CHF_3.

6. Volume measurement of the region from valve on inlet system to standard leak (induced volume) using a flask of He-4
    6.1. Close the valve controlling the actuator of the standard leak during this measurement to prevent cross contamination of the gas.
    6.2. Following standard laboratory practice, determine the interstitial volume of the standard leak by expanding three known quantities of gas from regions E+F of the inlet system into the connecting port of the standard leak.

7. Data reduction

7.1. Record the File numbers for calibrated devices used in the measurement process to include the mass spectrometer (volume and electronic portions), capacitance manometer, stopwatch and multimeter.

7.2. Calculate the leakrate of the device using equation (1).

Measurement Bias

An approximate 10% bias was determined from early intercomparison leak rate measurements (Vaccum Technology, Inc. samples 5118 and 5020) between the Primary Standards Lab and the Gas Dynamics and Mass Spectrometry Laboratory.

The leak rate data from the intercomparison samples is presented in Table 5 (data are represented as 10^{-8} std-cc/s). Percent difference in the values is derived in the following way. The difference between the known value (PSL number) and the measured value is divided by the average of the two values, the resulting quantity is then multiplied by 100 to obtain a percent difference. The original ~10% bias observed for samples 5020 and 5118 was caused by a systematic error introduced as a result of using the in-situ manometer (the P' measurement) as a measurement of actual pressure rather than a molar response measurement. Upon substitution of molar response factors for pressure readings the apparent bias vanishes. Three additional measurements further indicate no bias to be present.

Table 5. Interlaboratory comparison results

	Sample	Date	GDMSL	PSL	% diff
	5020	11/11/98	1.47	1.476	0.41
*	5020	11/11/98	1.33	1.476	10.41
	5118	11/20/98	2.99	3.026	1.20
*	5118	11/20/98	2.75	3.026	9.56
	3815	12/15/98	2.80	2.837	1.31
	5117	12/10/98	3.12	3.186	2.09
	5080	12/16/98	5.22	5.246	0.50

*Leak rates calculated using the in-situ manometer for pressure measurement. All other leak rates calculated using the in-situ manometer as a measurement of molar response.

References

Bevington, P.R.and Robinson, D.K., “Data Reduction and Error Analysis for the Physical Sciences.” Third Edition. McGraw-Hill, NY, 2003.

Mehrhoff, T.K. and T.M. Mason, (1981). Calibration procedures for standard gas leaks. General Electric Technical Information Series, GEPP-TIS-601.

Taylor, J.R., “An Introduction to Error Analysis. The Study of Uncertainties in Physical Measurements.” Second Edition. University Science Books, Sausilto, CA, 1982.

Appendix

Error Analysis

To review, the standard leak rate equation (1) is expressed as:

$$SL_R = \frac{I_c V_e}{\varepsilon t}$$

where,

SL_R ≡ standard leak rate of the device (mTorr-cc/sec)

I_c ≡ time corrected signal (mV)

V_e ≡ effective volume of the system (cc)

ε ≡ sensitivity of the gas species of interest (mV/mTorr)

t ≡ collection time (sec)

$$\Rightarrow \sigma_{SL_R}^2 = \left[\sigma_{I_C}\left(\frac{\partial SL_R}{\partial I_C}\right) + \sigma_{V_e}\left(\frac{\partial SL_R}{\partial V_e}\right) + \sigma_{\varepsilon}\left(\frac{\partial SL_R}{\partial \varepsilon}\right) + \sigma_t\left(\frac{\partial SL_R}{\partial t}\right)\right]^2$$

Neglecting cross terms ⇒ terms uncorrelated,

$$\Rightarrow \sigma_{SL_R}^2 = \sigma_{I_C}^2\left(\frac{\partial SL_R}{\partial I_C}\right)^2 + \sigma_{V_e}^2\left(\frac{\partial SL_R}{\partial V_e}\right)^2 + \sigma_{\varepsilon}^2\left(\frac{\partial SL_R}{\partial \varepsilon}\right)^2 + \sigma_t^2\left(\frac{\partial SL_R}{\partial t}\right)^2$$

where,

$$\frac{\partial SL_R}{\partial I_C} = \frac{V_e}{\varepsilon t},$$

$$\frac{\partial SL_R}{\partial V_e} = \frac{I_C}{\varepsilon t},$$

$$\frac{\partial SL_R}{\partial \varepsilon} = -\frac{I_C V_e}{\varepsilon^2 t},$$

$$\frac{\partial SL_R}{\partial t} = -\frac{I_C V_e}{\varepsilon t^2}$$

$$\Rightarrow \left(\frac{\sigma_{SL_R}}{SL_R}\right)^2 = \frac{\varepsilon^2 t^2}{I_C^2 V_e^2}\left[\sigma_{I_C}^2\left(\frac{V_e}{\varepsilon t}\right)^2 + \sigma_{V_e}^2\left(\frac{I_C}{\varepsilon t}\right)^2 + \sigma_{\varepsilon}^2\left(-\frac{I_C V_e}{\varepsilon^2 t}\right)^2 + \sigma_{\varepsilon}^2\left(-\frac{I_C V_e}{\varepsilon t^2}\right)^2\right]$$

$$\Rightarrow \left(\frac{\sigma_{SL_R}}{SL_R}\right)^2 = \left[\left(\frac{\sigma_{I_C}}{I_C}\right)^2 + \left(\frac{\sigma_{V_e}}{V_e}\right)^2 + \left(\frac{\sigma_{\varepsilon}}{\varepsilon}\right)^2 + \left(\frac{\sigma_t}{t}\right)^2\right]$$

$$\therefore \sigma_{SL_R} = \pm SL_R\left[\left(\frac{\sigma_{I_C}}{I_C}\right)^2 + \left(\frac{\sigma_{V_e}}{V_e}\right)^2 + \left(\frac{\sigma_{\varepsilon}}{\varepsilon}\right)^2 + \left(\frac{\sigma_t}{t}\right)^2\right]^{1/2}$$

Evaluation of Contributing Terms: σ_{I_C}

σ_{I_C} ≡ Uncertainty in the corrected ion signal

I_C ≡ Corrected ion signal

I ≡ Raw ion signal

C_R ≡ Conductance of molecular species from inlet system V_e to mass spectrometer ionization chamber

V_e ≡ Effective volume of collection region

$$\Rightarrow I_C = Ie^{\frac{C_R t'}{V_e}}$$

where $t' \equiv$ time between signal acquisition and beginning of experiment.

$$\Rightarrow \text{let u} = \frac{C_R t'}{V_e} \text{ and } x = e^u$$

$$\Rightarrow I_C = Ix$$

$$\Rightarrow \sigma_{I_c}^2 = \left[\sigma_I\left(\frac{\partial I_C}{\partial I}\right) + \sigma_x\left(\frac{\partial I_C}{\partial x}\right)\right]^2$$

$$\frac{\partial I_C}{\partial I} = x,$$

$$\frac{\partial I_C}{\partial x} = I$$

$$\Rightarrow \sigma_{I_C}^2 = \left[x\sigma_I + I\sigma_x\right]^2$$

Neglecting cross terms,

$$= x^2\sigma_I^2 + I^2\sigma_x^2$$

$$\Rightarrow \left(\frac{\sigma_{I_C}}{I_C}\right)^2 = \frac{1}{(Ix)^2}\left[x^2\sigma_I^2 + I^2\sigma_x^2\right]$$

$$\sigma_{I_C} = \pm I_C\left[\left(\frac{\sigma_I}{I}\right)^2 + \left(\frac{\sigma_x}{x}\right)^2\right]^{1/2}$$

Evaluation of the $\frac{\sigma_x}{x}$ term from above:

$$x \equiv e^u \text{, where } u = \frac{C_R t}{V_e}$$

From Bevington (1969; p. 64):

$$\text{for } x = ae^{\pm bu} \Rightarrow \frac{\sigma_x}{x} = b\sigma_u,$$

$$\text{where } b = 1 \text{ for this case}$$

$$\Rightarrow \sigma_u^2 = \left[\sigma_{C_R}\left(\frac{\partial u}{\partial C_R}\right) + \sigma_{t'}\left(\frac{\partial u}{\partial t'}\right) + \sigma_{V_e}\left(\frac{\partial u}{\partial V_e}\right)\right]^2$$

where,

$$\frac{\partial u}{\partial C_R} = \frac{t'}{V_e},,$$

$$\frac{\partial u}{\partial V_e} = -\frac{C_R t'}{V_e^2},$$

$$\frac{\partial u}{\partial t'} = \frac{C_R}{V_e}$$

$$\Rightarrow \left(\frac{\sigma_u}{u}\right)^2 = \left(\frac{\sigma_{C_R}}{C_R}\right)^2 + \left(\frac{\sigma_{t'}}{t'}\right)^2 + \left(\frac{\sigma_{V_e}}{V_e}\right)^2$$

$$\sigma_u = \pm u\left[\left(\frac{\sigma_{C_R}}{C_R}\right)^2 + \left(\frac{\sigma_{t'}}{t'}\right)^2 + \left(\frac{\sigma_{V_e}}{V_e}\right)^2\right]^{1/2}$$

Further examination of the C_R term:

$$C_R = \left(\frac{V_e}{t'}\right)\ln\left(\frac{P_0}{P}\right)$$

where $P_0 \equiv$ as the initial pressure on the high pressure side of the molecular leak and $P \equiv$ as the final pressure on the high pressure side of the molecular leak. The uncertainty in C_R is determined first by direct evaluation of each term. In addition, multiple physical measurements are carried out to obtain the random contribution to the overall uncertainty.

Analyses, similar to those discussed above, are carried out on the first term, $\left(\frac{V_e}{t'}\right)$, yield the components:

$$\left(\frac{\sigma_{V_e}}{V_e}\right)^2, \left(\frac{\sigma_t}{t'}\right)^2$$

For the ln term,

$$\text{let } u' = \frac{P_0}{P}$$

Then, according to Bevington (1969), given a function of the form:

$$x = a\ln(\pm bu)$$

the uncertainty in x can be expressed as:

$$\sigma_x = a\frac{\sigma_u}{u}$$

$$\Rightarrow \sigma_{u'}^2 = \left[\sigma_{P_0} \frac{\partial u'}{\partial P_0} + \sigma_P \frac{\partial u'}{\partial P} \right]^2$$

where

$$\frac{\partial u'}{\partial P_0} = \frac{1}{P},$$

$$\frac{\partial u'}{\partial P} = -\frac{P_0}{P^2}$$

$$\Rightarrow \sigma_{u'}^2 = \left[\frac{\sigma_{P_0}}{P} + \frac{\sigma_P P_0}{P^2} \right]^2$$

$$= \left[\left(\frac{\sigma_{P_0}}{P} \right)^2 + \left(\frac{\sigma_P P_0}{P^2} \right)^2 \right]$$

$$\Rightarrow \left(\frac{\sigma_{u'}}{u'} \right)^2 = \frac{P^2}{P_0^2} \left[\left(\frac{\sigma_{P_0}}{P} \right)^2 + \left(\frac{\sigma_P P_0}{P^2} \right)^2 \right]$$

$$\left(\frac{\sigma_u}{u'} \right)^2 = \left[\frac{\sigma_{P_0}^2}{P_0^2} + \frac{\sigma_P^2}{P^2} \right]$$

$$\Rightarrow \sigma_{u'} = \pm u \left[\left(\frac{\sigma_{P_0}}{P_0} \right)^2 + \left(\frac{\sigma_P}{P} \right)^2 \right]^{1/2}$$

$$\therefore \sigma_{C_R} = \pm \text{ can be written as follows:}$$

$$\sigma_{C_R} = \pm C_R \left[\left(\frac{\sigma_{V_e}}{V_e} \right)^2 + \left(\frac{\sigma_{t'}}{t'} \right)^2 + \left(\frac{\sigma_{u'}}{u'} \right)^2 \right]^{1/2}$$

Evaluation of σ_{Ve}

Quantities associated with the determination of the effective volume of the inlet system used in the standard leakrate measurement.

1) $M \equiv \frac{P_s V_s}{T_s} \Rightarrow$ Represents the molar quantity of gas (high purity ^{4}He in this case) expanded into the working volume. P_s, V_s and T_s are standards obtained from the PSL for defining a known molar quantity.

2) P' is defined as the response of a PSL calibrated capacitance manometer, located within the inlet system, to a known molar quantity of ^{4}He delivered to the volume under calibration.

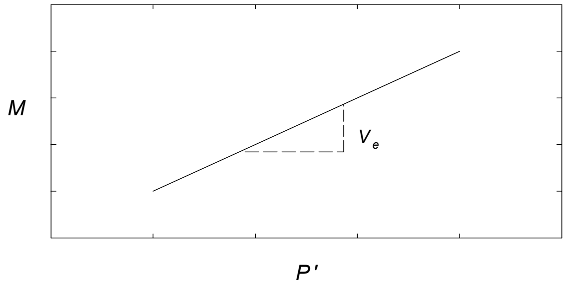
In brief, inlet system volumes are calibrated, at working temperatures, as follows. A known molar quantity of gas, from the PVT standard, is expanded into the working volume under calibration. The response of this molar quantity gas on the in situ capacitance manometer is then recorded. This process is repeated in an iterative fashion over the calibrated range of the capacitance manometer. A plot of the manometer's response verses molar input can then be made. This response should be linear. A linear fit to the data then yields the effective volume, V_e, according to the relationship;

$$M \equiv \frac{P_s V_s}{T_s} = \frac{P' V'}{T'},$$

which may be written as,

$$M = \left(\frac{V'}{T'}\right) P', \text{ let } V_e \equiv \left(\frac{V'}{T'}\right)$$

$$\Rightarrow M = V_e P'$$



Contribution to the overall uncertainty in V_e would then include,

The uncertainty in $M \Rightarrow \sigma_M$

The uncertainty in $P' \Rightarrow \sigma_{P'}$

The uncertainty associated with the fit to the data $\Rightarrow \sigma_f$

The standard deviation in the data set $\Rightarrow \sigma_{SD}$

The uncertainty in *M*

$$\sigma_M^2 = \left[\sigma_{P_S} \left(\frac{\partial M}{\partial P_S} \right) + \sigma_{V_S} \left(\frac{\partial M}{\partial V_S} \right) + \sigma_{T_S} \left(\frac{\partial M}{\partial T_S} \right) \right]^2$$

where,

$$\frac{\partial M}{\partial P_S} = \frac{V_S}{T_S}$$

$$\frac{\partial M}{\partial V_S} = \frac{P_S}{T_S}$$

$$\frac{\partial M}{\partial T_S} = -\frac{P_S V_S}{T_S^2}$$

hence,

$$\sigma_M^2 = \left[\sigma_{P_S}^2\left(\frac{V_S}{T_S}\right)^2 + \sigma_{V_S}^2\left(\frac{P_S}{T_S}\right)^2 + \sigma_{T_S}^2\left(\frac{P_S^2V_S^2}{T_S^4}\right) + 2\sigma_{P_S}\sigma_{V_S}\left(\frac{P_SV_S}{T_S^2}\right) - 2\sigma_{P_S}\sigma_{T_S}\left(\frac{P_SV_S^2}{T_S^3}\right) - 2\sigma_{V_S}\sigma_{T_S}\left(\frac{P_S^2V_S}{T_S^3}\right)\right]$$

Here, we include cross terms since the quantities P, V, & T are correlated terms.

$$\Rightarrow \left(\frac{\sigma_M}{M}\right)^2 = \frac{1}{M^2}\left[\sigma_{P_S}^2\left(\frac{V_S}{T_S}\right)^2 + \sigma_{V_S}^2\left(\frac{P_S}{T_S}\right)^2 + \sigma_{T_S}^2\left(\frac{P_S^2V_S^2}{T_S^4}\right) + 2\sigma_{P_SV_S}\left(\frac{P_SV_S}{T_S^2}\right) - 2\sigma_{P_ST_S}\left(\frac{P_SV_S^2}{T_S^3}\right) - 2\sigma_{V_ST_S}\left(\frac{P_S^2V_S}{T_S^3}\right)\right]$$

$$\Rightarrow \sigma_M = \pm M\left[\left(\frac{\sigma_{P_S}}{P_S}\right)^2 + \left(\frac{\sigma_{V_S}}{V_S}\right)^2 + \left(\frac{\sigma_{T_S}}{T_S}\right)^2 + \frac{2\sigma_{P_SV_S}}{P_SV_S} - \frac{2\sigma_{P_ST_S}}{P_ST_S} - \frac{2\sigma_{V_ST_S}}{V_ST_S}\right]^{\frac{1}{2}}$$

$$\therefore \qquad \sigma_{V_e} = \pm V_e\sqrt{\left[\left(\frac{\sigma_M}{M}\right)^2 + \left(\frac{\sigma_{P'}}{P'}\right)^2 + \sigma_f^2 + \sigma_{SD}^2\right]}$$

Evaluation of σ_ε:

We define ε as the sensitivity of the mass spectrometer to a given species. In this case, we are interested in obtaining the sensitivity of the mass spectrometer to a given amount of CHF_3. The sensitivity of CHF_3 is measured based upon the signal intensity of the mass 51 peak (CHF_2^+).

$$\varepsilon = \frac{I_C}{P'}$$

where I_C & P' are as defined previously.

$$\Rightarrow \sigma_\varepsilon^2 = \left[\sigma_{I_C}\left(\frac{\partial\varepsilon}{\partial I_C}\right) + \sigma_{P'}\left(\frac{\partial\varepsilon}{\partial P'}\right)\right]^2$$

$$\frac{\partial \varepsilon}{\partial I_C} = \frac{1}{P'}$$

$$\frac{\partial \varepsilon}{\partial P'} = -\frac{I_C}{P'^2}$$

$$\Rightarrow \sigma_\varepsilon^2 = \left[\sigma_{I_C}\left(\frac{1}{P'}\right) - \sigma_{P'}\left(\frac{I_C}{P'^2}\right)\right]^2$$

$$= \left[\left(\frac{\sigma_{I_C}}{P'}\right)^2 + \left(\frac{\sigma_{P'} I_C}{P'^2}\right)^2\right]$$

(Neglecting cross terms)

$$\Rightarrow \left(\frac{\sigma_\varepsilon}{\varepsilon}\right)^2 = \frac{1}{\varepsilon^2}\left[\left(\frac{\sigma_{I_C}}{I_C}\right)^2 + \left(\frac{\sigma_{P'} I_C}{P'^2}\right)^2\right]$$

$$= \left[\left(\frac{\sigma_{I_C}}{I_C}\right)^2 + \left(\frac{\sigma_{P'}}{P'}\right)^2\right]$$

$$\therefore \sigma_\varepsilon = \pm\varepsilon\sqrt{\left[\left(\frac{\sigma_{I_C}}{I_C}\right)^2 + \left(\frac{\sigma_{P'}}{P'}\right)^2\right]}$$

Evaluation of σ_t:

The time interval is measured using a PSL calibrated stopwatch. The uncertainty and calibration file number is stated in Table I.

Uncertainty in the Standard Leak Rate Measurement:

$$\sigma_{SL_R} = \pm SL_R \sqrt{\left(\frac{\sigma_{I_C}}{I_C}\right)^2 + \left(\frac{\sigma_{V_e}}{V_e}\right)^2 + \left(\frac{\sigma_{\varepsilon}}{\varepsilon}\right)^2 + \left(\frac{\sigma_t}{t}\right)^2}$$

$$\Rightarrow \frac{\sigma_{I_C}}{I_C} = \pm\sqrt{\left(\frac{\sigma_I}{I}\right)^2 + \left(\frac{\sigma_u}{u}\right)^2}$$

$$\Rightarrow \frac{\sigma_I}{I} = 0.00007$$

(from Table I and typical value for I)

$$\Rightarrow \frac{\sigma_u}{u} = \pm\sqrt{\left(\frac{\sigma_{C_R}}{C_R}\right)^2 + \left(\frac{\sigma_{t'}}{t'}\right)^2 + \left(\frac{\sigma_{V_e}}{V_e}\right)^2}$$

$$\Rightarrow \frac{\sigma_{C_R}}{C_R} = \pm\sqrt{\left(\frac{\sigma_{V_e}}{V_e}\right)^2 + \left(\frac{\sigma_{t'}}{t'}\right)^2 + \left(\frac{\sigma_{P'}}{P'}\right)^2}$$

$$\Rightarrow \frac{\sigma_{V_e}}{V_e} = \pm 0.0205$$

$$\Rightarrow \frac{\sigma_{t'}}{t'} = \pm 0.00866$$

$$\Rightarrow \frac{\sigma_{P'}}{P'} = \pm 0.0134$$

$$\Rightarrow \frac{\sigma_u}{u} = \pm\sqrt{(0.0205)^2 + (0.00866)^2 + (0.0134)^2} = \pm 0.0260$$

$$\therefore \qquad \frac{\sigma_{I_C}}{I_C} = \pm\sqrt{(0.00007)^2 + (0.0260)^2} = \pm 0.0260$$

$$\Rightarrow \frac{\sigma_{V_e}}{V_e} = \pm\sqrt{\left(\frac{\sigma_M}{M}\right)^2 + \left(\frac{\sigma_{P'}}{P'}\right)^2 + \sigma_f^2 + \sigma_{SD}^2}$$

$$= \pm\sqrt{(0.0132)^2 + (0.0134)^2 + (0.001)^2 + (0.0082)^2}$$

$$\therefore \qquad \frac{\sigma_{V_e}}{V_e} = \pm 0.0205$$

$$\Rightarrow \frac{\sigma_\varepsilon}{\varepsilon} = \pm\sqrt{\left(\frac{\sigma_{I_C}}{I_C}\right)^2 + \left(\frac{\sigma_{P'}}{P'}\right)}$$

$$= \pm\sqrt{(0.0260)^2 + (0.0134)^2}$$

$$\therefore \qquad \frac{\sigma_\varepsilon}{\varepsilon} = \pm 0.0292$$

$$\Rightarrow \frac{\sigma_t}{t} = \pm\frac{0.25}{3600} = \pm 6.94x10^{-5}$$

$$\Rightarrow \frac{\sigma_{SL_R}}{SL_R} = \pm\sqrt{(0.0260)^2 + (0.0205)^2 + (0.0292)^2 + \left(6.94x10^{-5}\right)^2}$$

$$\therefore \qquad \boxed{\frac{\sigma_{SL_R}}{SL_R} = \pm 0.0442}$$

DISTRIBUTION:

1 T.K. Mehrhoff
14120 82nd Ave. N
Seminole, FL 33776-3303

1	MS 0665	L.J. Azevedo, 02541
1	MS 0665	M.S. Benner, 02541
1	MS 0856	R.B. Muniz, 14408
1	MS 0856	L.A. Walla, 14408
1	MS 0868	K.G. McCaughey, 14400
1	MS 0871	R.J. Antepenko, 14406
5	MS 0871	S.D. Balsley, 14406
1	MS 0871	J.F. Browning, 14406
1	MS 0871	C.A. LaDuca, 14406
1	MS 0871	L.E. Pope, 14405
1	MS 9018	Central Technical Files, 08945-1
2	MS 0899	Technical Library, 09616
1	MS 0612	Review & Approval Desk, 09612 For DOE/OSTI