Calibration of reference leaks in a wide pressure range

Ana L. Fonseca, A. Marta Barreto, A. Sofia Matos, A.M.C.Moutinho and Orlando M.N.D.Teodoro
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Motivation: reference leaks for sniffers

- Inside-out He leak detection technique (sniffer)
  - He reference leaks in the range $10^{-6}$ to $10^{-5}$ mbar.L/s

- 842/2006 regulation and subsequent statements
  - R134a reference leaks of 5 g/year

of 17 May 2006
on certain fluorinated greenhouse gases

COMMISSION REGULATION (EC) No 1516/2007
of 19 December 2007
establishing, pursuant to Regulation (EC) No 842/2006 of the European Parliament and of the Council, standard leakage checking requirements for stationary refrigeration, air conditioning and heat pump equipment containing certain fluorinated greenhouse gases

2. Gas detection devices referred to in paragraph 1(a) shall be checked every 12 months to ensure their proper functioning. The sensitivity of portable gas detection devices shall be at least five grams per year.
Motivation

- Calibration by comparison using a MS leak detector is not suitable
  - Calibration pressure should be atmosphere, not vacuum

- EN 13192 method C: calibration of leaks from overpressure to atmosphere
  - Capillary with a moving slug
  - Although very simple, is of limited application (slug friction, pressure control, etc.)

- However, $p\Delta V$ method is well suited
Calibration method: $p\Delta V$

- The leak is connected to a closed volume
- A piston is actuated every time a pressure increase is detected to keep the pressure constant
- Volume \( \approx 1 \text{ mL} \), step \( < 1 \mu\text{L} \) (resolution)

3. F. Boineau, “Characterization of the LNE constant pressure flowmeter for the leak flow rates measurements with reference to vacuum and atmospheric pressure,” *PTB-Mitteilungen*, 121 (2011) 313
Calibration set-up

- Computer & Labview software
- Thermocouples
- Stepper motor (syringe pump)
- Bath, temperature control and pump
- Double wall box (water inside)
- Venting valve
- Absolute pressure gauge
- Leak under calibration
Calibration set-up

- **Piston:** 1 mL SGE gas tight syringe with PTFE plunger tip

- **Piston actuator:** syringe pump NE-500
  - 800 steps/revolution; 1 step ≈ 1.7 µm

- **Gauge:** Druck DPI 142 precision Barometer
  - Resolution ≈ 3×10⁻³ mbar; piezo sensor

- **Software:** Labview platform

- **Tubing:** 1/8” swagelok fittings and valves

- **Stainless steel double wall box with 2 computer fans inside to increase temperature homogeneity**

- **Water circulator** Julabo F25-ED
User interface

Flow rate (integrated measurement), converges with time

Pressure (≈10⁻² mbar maximum variation)

Temperature drift (3 thermocouples), critical to achieve low uncertainty

Actual measurement
Before calibration

- $\Delta pV$ method, for preliminary evaluation
- temperature stability confirmation
Syringe characterization

- Gravimetric volume calibration
  - Step volume $V_s = 28.0 \pm 0.22$ nL

- Syringe expansion without leak
  - Boyle-Mariotte relation
  - Full volume range $\approx 32,000$ steps

- Step volume $V_s$ and dead volume $V_0$ can be calculated by fitting these parameters in the experimental data

$$p = \frac{p_0 V_0}{n V_s + V_0}$$

Fitting parameters

$$V_s = \frac{V_0}{n} \left( \frac{p_0}{p} - 1 \right)$$

Step volume as function of position

Best fit:
$$V_s = 28.18\text{ nL}$$
$$V_0 = 3.862\text{ mL}$$

Dark line, average of 2000 steps

most used position = larger diameter
Measuring range, time needed for calibration

- 2000 steps averages thread defects

<table>
<thead>
<tr>
<th>total steps</th>
<th>Q</th>
<th>time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>s</td>
</tr>
<tr>
<td>2000</td>
<td>$10^{-4}$ mbar.L/s</td>
<td>560</td>
</tr>
<tr>
<td></td>
<td>$10^{-5}$ mbar.L/s</td>
<td>5600</td>
</tr>
<tr>
<td></td>
<td>$10^{-6}$ mbar.L/s</td>
<td>56000</td>
</tr>
<tr>
<td></td>
<td>5 g/year R134 a</td>
<td>1474</td>
</tr>
</tbody>
</table>
Repeatability

- Effect of the position of the syringe plunger tip (piston)

He leak, nominal leak rate = \(2.60 \times 10^{-5}\) mbar.L/s calibrated to vacuum
Repeatability

- 4 different leaks were measured 4 times each

- Repeatability depends on:
  1. Number of steps (acquisition time)
  2. Temperature drift has a major impact
  3. Leak stability

- On the graph 1000 to 10000 steps were used.
## Typical uncertainty

- **R134a leak, Q=3.48 g/year**

<table>
<thead>
<tr>
<th>Quantity, $x_i$</th>
<th>Estimate</th>
<th>$u(x_i)$</th>
<th>$c_i u(x_i)/d$ (g/year)</th>
<th>relative contribution %</th>
</tr>
</thead>
<tbody>
<tr>
<td>pressure</td>
<td>1000 mbar</td>
<td>0.015 mbar</td>
<td>1.54E-05</td>
<td>0.027</td>
</tr>
<tr>
<td>volume</td>
<td>22 µL</td>
<td>0.17 µL</td>
<td>7.79E-03</td>
<td>13.7</td>
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<tr>
<td>temperature</td>
<td>296.9 K</td>
<td>0.06 K</td>
<td>5.38E-04</td>
<td>0.4</td>
</tr>
<tr>
<td>time</td>
<td>827 s</td>
<td>9.6 x 10^{-3} s</td>
<td>1.16E-05</td>
<td>0.02</td>
</tr>
<tr>
<td>repeatability (ΔT≈0.1K)</td>
<td>0.17 g/year</td>
<td>0.049</td>
<td>85.9</td>
<td></td>
</tr>
<tr>
<td><strong>Total (k=2)</strong></td>
<td></td>
<td></td>
<td><strong>0.098</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

$Q = 3.48 \pm 0.10 \text{ g/year}$
Temperature effects

- The use of an absolute gauge turns this calibration set-up more sensitive to temperature drifts
  - A drift in the temperature is equivalent to a temporary virtual leak (positive or negative)
  - This effect is slightly cancelled by tubing dilatation

Gay-Lussac law

\[ Q_{eq} = \frac{p_0 V_0}{t} \left( \frac{T_0 + \Delta T}{T_0} - 1 \right) \]
Temperature effects

- Total temperature drift is more important than temperature uniformity.
  - If temperature changes slowly, what matters is the difference between the starting temperature and the final temperature.

- Experiment: induced temperature step
  - Temperature effects may be cancelled by positive and negative drifts.

Temperature step in the PID controller:
- \( t = 550 \text{ s}, \Delta T = -0.5 \text{ K} \)
- \( t = 2200 \text{ s}, \Delta T = +0.5 \text{ K} \)

Nominal leak rate
Method validation

- A series of R134a leaks were built with leak rates ranging 4 to 24 g/year
Method validation

-Leaks were weighted over several days (U=± 15%) and leak rate calculated.

-Then, all leaks were calibrated in the $p\Delta V$ set-up and compared.
R134a reference leaks

- Dependence on the delivering pressure
  - 2000 steps measurements ≈ 25 min

![Graph showing the relationship between leak rate and delivering pressure. The graph indicates a linear decrease with a slope of -0.033%/mbar at 23°C.]
R134a reference leaks

- Dependence on the temperature

\[ \alpha = 2.8\% / \text{K} \]

\[ \alpha = 3.1\% / \text{K} \]
He reference leaks (permeation)

- Dependence on the delivering pressure
  - 2000 steps measurements ≈ 35 min

-0.027%/mbar@23°C
Conclusions

- $p\Delta V$ calibration method was assembled with a syringe pump and is properly working at Metrovac laboratory in Lisbon.

- One absolute pressure gauge is used
  - This gauge is suitable to measure both the calibration pressure and the pressure change

- Temperature stability is critical to achieve good uncertainty

- Uncertainties $\approx 3\%$ are easily achieved for the range of $10^{-5}$ mbar.L/s or 5g/year

- R134a reference leaks were developed and fully characterized.
  - This leaks were used to validate the method
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Thanks for your attention

odt@fct.unl.pt