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CALIBRATION OF SECONDARY STANDARD LEAKS BY MEANS OF MASS COMPARISON

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Abstract – Gas leak detection is getting more important in the last years. Primary standards for leaks can be divided into sensitive and insensitive to gas species. The method proposed by authors is insensitive to gas species. The basic principle of the method is mass comparison and detection of the difference between standard weight and the leak to be calibrated. The authors made several measurements to prove the repeatability of the method. It can be seen that to get results with reasonable uncertainty the weekend measurement is sufficient.

Keywords: atmospheric leaks, refrigerant leaks

1. INTRODUCTION

The detection of halogenated hydrocarbons (freons) is increasing in importance in the last years due to environmental safety reasons. Initially, the chlorinated freons were abandoned due to their destructive influence on the ozone layer and replaced by the fluorinated freons. However, this replacement was unhappy as the substituents are very important greenhouse gases with global warming potential three orders higher than that of carbon-dioxide. Hence, the leak detection of these freons (mainly R134a, i.e. 1,1,1,2-tetrafuoroethane) is important task until they will be replaced.

The detectors of such leaks have in general very poor long term stability, resulting in the need of the secondary standard leaks for their frequent calibration. However, these secondary standard leaks also need regular calibrations that must be ensured by the proper primary standards. These primary standards can be divided into those being sensitive [1] and being insensitive [2-4] to gas species. The problem of the first group is that they can work with only limited number of gases, the problem of the second group is that they measure depleted volume of gas, i.e. a very small change of relatively large quantity which brings many experimental obstacles. An alternative gas insensitive method of weighing the secondary standard leak brings the same problems; hence it was mostly neglected in the metrology and used only rarely [5]. However, the authors show that these problems can be overcome and that the problems and resultant uncertainties of such measurement are not higher then by the other methods.

The method could be described as long-term comparison of weights. The difference from the daily used comparison of weights is that there is no need of a known standard and the only important information is the difference of the masses, not the mass of the measured object. Thus it is possible to minimize a few uncertainty sources such as the uncertainty of the standard weight or the air buoyancy factor.

2. PRINCIPLE OF THE METHOD

A secondary standard leak under test is put into a brass base to ensure its stability and with the help of the fractional masses adjusted as near as possible to 1 kg. A mass comparator is used to show a difference between this measured mass (consisting of the secondary standard leak, the base and the trim masses) and a precise 1 kg standard mass of class E1, see Fig. 1. This difference is obtained from three consequent weighings, the first weighing of the standard mass, the weighing of the measured mass and the second weighing of the standard mass. The time change of this difference is observed.

The value of the leak (mass flow) is given by the mass change δ_m during time interval δ_t:

$$Q_m = \frac{\delta_m}{\delta_t}. \tag{1}$$

Difference in indication of the mass comparator is:

$$\Delta I = \frac{I_1 - I_m + I_2 - I_m}{2} = \frac{I_1 + I_2}{2} - I_m, \tag{2}$$

where is

I_1 indication at the 1st weighing of the standard mass,
I_m indication at the weighing of the measured mass,
I_2 indication at the 2nd weighing of the standard mass.

This difference in indication must be transformed to the difference of vacuum masses of the standard m_e and measured leak artifact $m_m(t_m)$ (neglecting non-linearity of the comparator):

$$\Delta I = \frac{m_e}{2}\left(1 - \frac{\rho_a(P_1, T_1, RH_1)}{\rho_e(T_1)}\right) + \\ + \frac{m_e}{2}\left(1 - \frac{\rho_a(P_2, T_2, RH_2)}{\rho_e(T_2)}\right) + \\ + (-1) m_m(t_m)\left(1 - \frac{\rho_a(P_m, T_m, RH_m)}{\rho_m(T_m)}\right), \quad (3)$$

where is

ρ_e density of the standard mass,

ρ_m density of the secondary standard leak,

ρ_a pressure (P), temperature (T) and humidity (RH) dependent air density.

Because time interval between t_1 and t_m and between t_m and t_2 is always maximally 4 min and the comparator is placed in an air-conditioned room, we can consider slow and linear changes of laboratory conditions:

$$\Delta I(t_m) = m_e - m_e \frac{\rho_a(P_m, T_m, RH_m)}{\rho_e(T_m)} - m_m(t_m) + \\ + m_m(t_m)\frac{\rho_a(P_m, T_m, RH_m)}{\rho_e(T_m)}. \quad (4)$$

Because the magnitude of $m_e - m_m(t_m)$ is maximally 0,03 mg, the searched measured mass is:

$$m_m(t_m) = m_e - \Delta I(t_m) - m_e \rho_a(P_m, T_m, RH_m) \times \\ \times \left(\frac{1}{\rho_e(T_m)} - \frac{1}{\rho_m(T_m)}\right). \quad (5)$$

We do not know the value of ρ_m, hence the buoyancy correction can for $m_e \doteq 1$ kg become larger than the resolution of the comparator. Hence we cannot (not surprisingly) to know the absolute magnitude of the measured mass. But we are interested only in its change since time t_p to t_k:

$$\delta_m(t_p, t_k) = m_m(t_k) - m_m(t_p). \quad (6)$$

Hence we have:

$$\delta_m(t_p, t_k) = \Delta I(t_p) - \Delta I(t_k) + \\ + m_e\left(-\frac{1}{\rho_e(T(t_k))} + \frac{1}{\rho_m(T(t_k))}\right)\rho_a(P(t_k), T(t_k), RH(t_k)) + \quad (7) \\ + m_e\left(\frac{1}{\rho_e(T(t_p))} - \frac{1}{\rho_m(T(t_p))}\right)\rho_a(P(t_p), T(t_p), RH(t_p)).$$

We can neglect the correction terms in an air-conditioned room and write:

$$\delta_m(t_p, t_k) = \Delta I(t_p) - \Delta I(t_k). \quad (8)$$

This value enters leak calculation equation (1).

Another approach how to determine the leak is using the linear approximation with least squares method. Typical measurement record includes pairs of data, the indication of the measurement device and the time of recording of the indication. These data are not used for calculation of mass differences according to (8) but as pairs $[t_p; \Delta I(t_p)]$ for determination of the coefficients of the function

$$\Delta I(t_p) = \alpha t_p + \beta. \quad (9)$$

Coefficient α is then the mass flow.

3. UNCERTAINTY BUDGET

Considering the temperature changes up to 1 °C and the pressure changes up to 1 kPa, then the change of the air density will be up to 1,5 %, whereas the changes due to the linear thermal expansivity (α_{steel} = $12 \cdot 10^{-6}$ °C^{-1}, α_{brass} = $19 \cdot 10^{-6}$ °C^{-1}) only up to 21 ppm.

Hence we can write the error due to the neglected buoyancy correction terms as:

$$\xi = m_e\left(\frac{1}{\rho_e} - \frac{1}{\rho_m}\right) \times \\ \times \left(\rho_a(P(t_p), T(t_p), RH(t_p)) - \rho_a(P(t_k), T(t_k), RH(t_k))\right). \quad (10)$$

Considering the density of the measured mass between 7500 and 8400 kg·m^{-3}, the neglecting of the buoyancy correction terms can cause an error of maximally 0.15 mg.

Type B uncertainty of the leak is:

$$u_B(Q_m) = Q_m \sqrt{\left(\frac{u(\delta_m)}{\delta_m}\right)^2 + \left(\frac{u(\delta_t)}{\delta_t}\right)^2}. \quad (11)$$

The uncertainty $u(\delta_m)$ consists of the uncertainty due to the comparator resolution $u(\delta_r) = (0{,}01/\sqrt{3})$ mg, the uncertainty due to the comparator instability (determined by comparing the standard mass with itself) $u(\delta_s) = (0{,}03/\sqrt{3})$ mg and of the uncertainty due to neglecting buoyancy corrections $u(\delta_c) = (0{,}15/\sqrt{3})$ mg. The mass is weighted (reading integrated) during 10 s, taking into account also resolution 1 s and considering all these values correlated we get $u(\delta_t) = (22/\sqrt{3})$ s.

Entering the masses in mg, time in s and flow in mg/s, we get:

$$u_B(Q_m) = Q_m \frac{1}{\sqrt{3}} \sqrt{\left(\frac{\sqrt{0{,}01^2 + 0{,}03^2 + 0{,}15^2}}{\delta_m}\right)^2 + \left(\frac{22}{\delta_t}\right)^2}. \quad (12)$$

For the least square approach we have another model for uncertainty. Since data contain uncertainties in each point $[t_p;\Delta I(t_p)]$ in both directions, we used modification of the least squares method based on the approach described in [6]. For the calculation itself the procedures for Excel [7] were taken.

4. EXPERIMENTAL RESULTS

The standard was a Mettler mass comparator, type AT10005. Its range is 10 kg, resolution $1\cdot10^{-8}$ kg and best repeatability $3\cdot10^{-8}$ kg (typical $5\cdot10^{-8}$ kg). It has a relatively high range for this purpose, but enough space to place a leak.

During the measurement all weights and parts included in comparison were considered as E1 weights. They were handled only by tweezers or by hand in special gloves.

Fig. 1. Standard leak in brass base and 1 kg E1 weight in mass comparator Mettler Toledo AT10005.

The length of the time interval for determining this change was between 32 and 48 hours. The measurements were held during weekends when the best stability of environmental conditions was achieved.

The first measurement started on 9th July 2010. It consisted of two series of 10 ABA comparisons. Both series were repeated 15 times. The series scheme was 1 kg vs. 1 kg and 1 kg vs. leak. Temperature was 20,8 °C, pressure was 985 mbar and relative humidity was 60 %. Since the start delay was set to 6 hours results are marked as 10/07/10.

The second measurement started on 16th July 2010. It consisted of only one series 1 kg vs. leak which was repeated 20 times. Each group consisted of 20 ABA comparisons. Temperature was 20,9 °C, pressure was 980 mbar and relative humidity was 60 %. The real start of the measurement was also delayed so the results are marked as 17/07/10.

The last measurement started on 23rd July 2010 and consisted of one series 1 kg vs. leak repeated 17 times. The series consisted of 15 comparisons of ABBA type. Temperature was 20,8 °C, pressure was 976 mbar and relative humidity was 60 %. These measurements are marked as 24/07/10.

All conditions are summarized in Tab. 1.

Date	No. series	No. comp.	Type	t [°C]	p [mbar]	h [%]
10/07/10	15	10	ABA	20,8	985	60
17/07/10	20	20	ABA	20,9	980	60
24/07/10	17	15	ABBA	20,8	976	60

Tab 1: Summary of environmental conditions and type of measurement procedure.

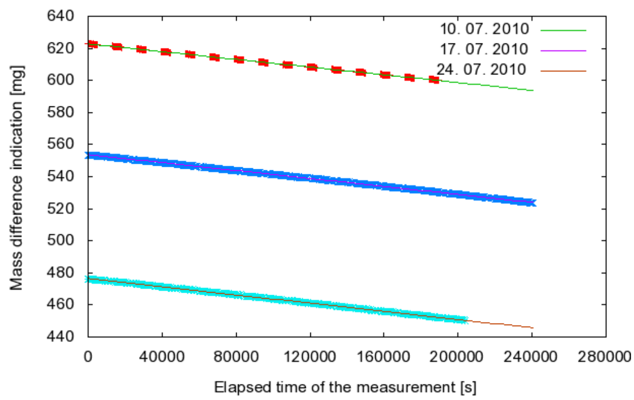

Fig. 2. The indications of the weekend measurements with fitted linear functions.

The results in Fig. 2 show that during all three weekends the conditions were sufficiently stable so that no indication shall be considered as outlier. The lines were determined by least squares method for each weekend measurement separately.

To have the leak over wider time range we put together all measured data and computed their approximation line. Since we have other approximation from each weekend we can compare them. Fig. 3 shows this comparison of results where only the first weekend fit was taken for the comparison. At the end of the time interval one can observe difference of both lines.

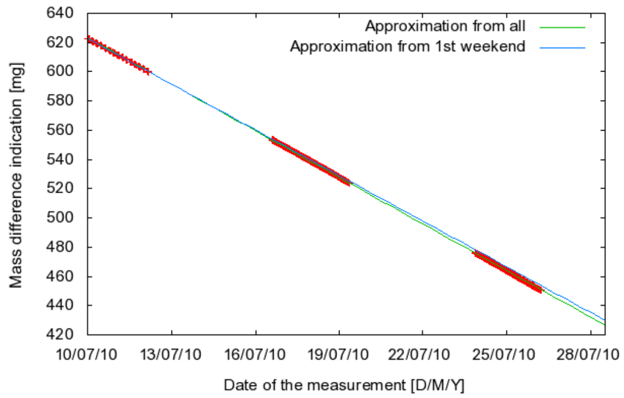

Fig. 3. All data with fitted line compared to line from first weekend.

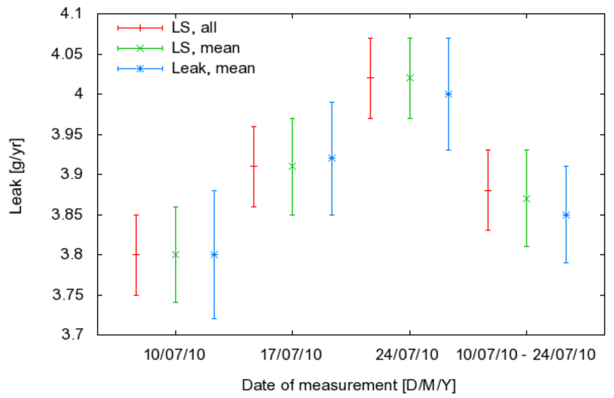

Fig. 4. Comparison of different approaches for calculation of leak. Expanded uncertainties U were used, $k = 2$.

Date	Q_{LSa} [g/yr]	$U(Q_{LSa})$ [g/yr]	Q_{LSm} [g/yr]	$U(Q_{LSm})$ [g/yr]	Q_{Lm} [g/yr]	$U(Q_{Lm})$ [g/yr]
10/07/10	3,80	0,05	3,80	0,06	3,80	0,08
17/07/10	3,91	0,05	3,91	0,06	3,92	0,07
24/07/10	4,02	0,05	4,02	0,05	4,00	0,07
All	3,88	0,05	3,87	0,06	3,85	0,06

Tab 2: Leak calculated by different methods. Due to the lack of space we used symbol yr for year.

The reason why we observed the difference in Fig. 3 is clear from Fig. 4 where we compared different approaches for mass flow determination together with their uncertainties. All results from one weekend are close to each other but are different to results from other weekend as we can also see in Tab. 2. In fact, the mass flow increases during the time.

It seems that after purchasing the leak we did not wait enough time for stabilization of the mass flow. There should be also some other leak except the main one. Another explanation of this phenomenon should be the instability of brass base due to the oxidatioon or not perfect handling.

Although there are a few problems in the results we can conclude that the mass comparison can be used for calibration of the secondary standard leaks since the uncertainty is sufficiently small especially when using the least square method.

5. CONCLUSIONS

General problems of this method are three. First, this method determines the overall leakage, i.e. if there are any leaks present in the pressure vessel they will be added to the flow through the flange. Second, this method does not allow leak measurement at a temperature different from laboratory temperature. Third, if the leak has too large dimensions it is not possible to place it on a comparator.

Other problems shall arise during the comparison such as instability of mass flow due to the shorter time for stabilization or instability of any part of the measurement system such as brass base in our case.

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