Sources of Uncertainty in the Gravimetric Preparation of a Binary Gas Standard on a Twin-pan Balance

by
M J T Milton, P E Holland, A J Davenport, C Brookes, and P T Woods
Centre for Optical and Environmental Metrology

ISSN 1369-6807

National Physical Laboratory
Queens Road, Teddington, Middlesex, TW11 0LW

Approved on behalf of Managing Director, NPL
by D H Nettleton, Head of Centre for Optical and Environmental Metrology

Executive Summary

This report summarises work done at NPL to evaluate the uncertainty in the mass fraction and amount fraction of gas standards prepared gravimetrically on a two-pan balance. The influences of buoyancy of the cylinder and its expansion when containing high pressure gas are studied in detail. We show that there are two corrections for buoyancy that are applied to the masses of the major and minor components. A third correction is made for linear expansion of the cylinder and is applied as a multiplicative factor to the mass fraction. The preparation of a binary mixture of carbon monoxide in nitrogen is used as an example. In this example the correction for linear cylinder expansion is zero because the relative molecular masses of the major and minor components are equal. The largest uncertainties are associated with the determination of the mass of the minor component, and in particular, the repeatability of the balance itself.

CONTENTS

Sources of Uncertainty in the Gravimetric Preparation of a Binary Gas Standard on aTwo-pan Balance

by
M J T Milton, P E Holland, A J Davenport, C Brookes, and P T Woods
Centre for Optical and Environmental Metrology

Introduction

Primary gas standards are prepared at NPL gravimetrically using a two-pan balance. Since gravimetry has the potential to operate as a primary method, the values for the amount fraction (expressed in mol/mol) of these standards are traceable to the SI. In this report, the measurement equations governing the particular gravimetric procedure used at NPL are developed and it is shown that all of the uncertainties can be correctly expressed in terms of SI units.

A particular example of the preparation of a binary mixture of CO in nitrogen is presented.

The procedure discussed in this report is divided into the following steps:

- Determination of the (apparent) mass of gas in a cylinder by weighing it against a tare cylinder.
  Combining balance readings to determine the masses of the major and minor components
- Combining the masses of the two components to determine the mass fraction
- Calculating the amount fraction from the mass fraction using standard data for the relative molecular masses of the components.

The division of the procedure into these four steps simplifies the calculation of accurate corrections for buoyancy effects since it enables the three largest buoyancy effects that influence the final result to be distinguished. In particular, the discussion of the effect of cylinder expansion on the mass fraction is simplified because the correlation between its influence on the masses of the major and minor components is clarified.

The procedure described here does not include the incorporation of purity data or the subsequent gravimetric dilution steps. Both of these will be discussed in detail in other NPL reports.

Measurement Equation for the Mass Fraction

Measuring the mass of the minor component

The mass recorded from any weighing (r) on a two-pan balance is given by the difference between the apparent mass of the unknown and the tare. For simplicity, this can be written in terms of the volume of each cylinder and the difference between the density of each cylinder and the density of the air displaced:

$$r_i = V_i(\rho_i^C - \rho_i^O \quad - V_T(\rho_i^T - \rho_i^O) \qquad (1)$$

where
r_i = (apparent) mass recorded
V_i = volume of "unknown" cylinder
V_T= volume of tare cylinder
ρ_i^C = density of "unknown" cylinder
ρ_i^T = density of tare cylinder
ρ_i^O = density of air

The mass of the minor component (m_2) is derived from the difference between a weighing of an empty cylinder (r_1) and a weighing of the same cylinder with the minor component added (r_2):

$$r_2 - r_1 = V_2(\rho_2^C - \rho_2^O) - V_1(\rho_1^C - \rho_1^O \quad - V_T(\rho_1^O - \rho_2^O)$$

since $m_2 = V_2\rho_2^c - V_1\rho_1^c$

$$r_2 - r_1 = m_2 + V_1\rho_1^O - V_2\rho_2^O - V_T(\rho_1^O - \rho_2^O)$$

$$= m_2 + (V_1 - V_T)(\rho_1^O - \rho_2^O) - \Delta V_1\rho_2^O$$

Where the volume of the cylinder when evacuated (V_1) and the volume of the same cylinder with the minor component added (V_2) have been related through

$$V_2 = V_1 + \Delta V_1 \qquad (4)$$

When the readings are taken in terms of conventional mass, corrections should be made for the difference between the conditions prevailing during the measurement and the standard conditions used to define conventional mass (see Appendix 1). The most important of these is Δa_{12} , a correction for the difference between the true air density and the conventional value of 1.2 kg m^{-3}. After incorporating this correction, equation (3) can be re-arranged to express the mass of the minor component in terms of the readings from the balance and three corrections relating to the buoyancy:

$$m_2 = r_2 - r_1 + \Delta a_{12} - \Delta b_{12} + \Delta V_1\rho_2^o \qquad (5)$$

where

$$\Delta a_{12} = V_2^m(\rho_2^0 - 1.2) - V_1^m(\rho_1^0 - 1.2)$$

and

$$\Delta b_{12} = (V_1 - V_T)(\rho_1^o - \rho_2^o)$$

The derivation of Δa_{12} is explained in Appendix 1. The "differential buoyancy" (Δb_{12}) is caused by any difference in the volume between the unknown and the tare. The final term ($\Delta V_1 \rho_2^0$) is a correction for the buoyancy change due to the linear expansion of the cylinder.

Buoyancy change due to linear cylinder expansion

If we assume that the fractional volume change due to cylinder expansion is linearly proportional to the pressure (P) in the cylinder:

$$\frac{\Delta V}{V} = K(P - P_{ext}) \tag{8}$$

where K is a constant which depends on the material, shape and dimensions of the cylinder (see Appendix 2) and P_{ext} is the external pressure. The volume of the evacuated cylinder (V_1) and the same cylinder with the minor component added (V_2) can now be written in terms of the volume V_a of the cylinder when it contains gas at atmospheric pressure:

$$V_1 = V_a - KVP_{ext} \tag{9}$$

$$V_2 = V_a + KV(P - P_{ext}) \tag{10}$$

Hence $\Delta V_1 = V_2 - V_1 = KVP$. If P is expressed in terms of the mass (m) of gas in the cylinder using the ideal gas law, then:

$$\Delta V = K\left(\frac{ZRT}{M}\right)m$$

where M is the RMM and Z the compressibility of the gas [1]. Substituting (11) into (5):

$$r_2 - r_1 = m_2 - m_2 K\left(\frac{ZRT}{M_2}\right)\rho_2^0 - \Delta a_{12} + \Delta b_{12} \tag{12}$$

and re-arranging to give an expression for the mass of the minor component:

$$m_2 = \frac{r_2 - r_1 + \Delta a_{12} - \Delta b_{12}}{(1 - K(Z_2 RT / M_2)\rho_2^o)} \tag{13}$$

The term in the denominator allows for the increased buoyancy of the cylinder when it expands linearly because of the pressure of gas within it.

Measuring the mass of the major component

In the next step of the preparation procedure, a mass m_3 of the major component is added to the cylinder. An expression similar to (13) relates the mass of the major and minor components to the result of the third and first weighings:

$$m_2 + m_3 = \frac{r_3 - r_1 + \Delta a_{13} - \Delta b_{13}}{(1 - K(Z_3^* RT / M_3^*)\rho_3{}^o)}$$

where

$$\Delta a_{13} = V_3^m(\rho_3^0 - 1.2) - V_1^m(\rho_1^0 - 1.2)$$

and

$$\Delta b_{13} = (V_1 - V_T)(\rho_1{}^o - \rho_3{}^o)$$

M_3^* is the "effective RMM" calculated for the mixture of the minor and major components.

$$\frac{m_2 + m_3}{M_3^*} = \frac{m_2}{M_2} + \frac{m_3}{M_3}$$

Where M_3 is the RMM of the major component itself. Note that

$$\frac{1}{M_3^*} = \frac{w}{M_2} + \frac{1-w}{M_3}$$

The effective compressibility of the mixture (Z_3*) is calculated in the same way [1]. The mass fraction (w) of the gas mixture in the cylinder is given by dividing (13) by (14):

$$w = \frac{m_2}{m_2 + m_3} = \frac{r_2 - r_1 + \Delta a_{12} - \Delta b_{12}}{r_3 - r_1 + \Delta a_{13} - \Delta b_{13}} . C_l$$

where C_l is the correction for linear expansion given by:

$$C_l = \frac{1 - K(Z_3^* RT / M_3^*)\rho_3^0}{1 - K(Z_2 RT / M_2)\rho_2^0}$$

Equation (19) is the measurement equation for the mass fraction since it brings together all of the measured values and the appropriate corrections. It shows that two buoyancy corrections are applied to the apparent masses of both the major and minor components. The correction for linear cylinder expansion is applied as a multiplicative correction. In the following sections we discuss the uncertainties in each of the terms in equation (19).

Uncertainty in the mass fraction

Component uncertainties in a single weighing cycle

The largest sources of uncertainty in an individual weighing (*r*) are listed in Table 1. In this section, we provide some information about how these estimates were developed in the case of the preparation of a binary mixture of carbon monoxide in nitrogen at a nominal amount fraction of 50 mmol/mol.

Table 1 : Sources of uncertainty in a single weighing cycle (unknown versus tare)

Source	Type	$u(r)$ / mg (k=1)
Repeatability of weighing	A	5
Calibration of mass pieces	A	<0.1
Manual handling	B	3
Combined uncertainty		*6*

The repeatability of a single weighing was determined by repeating the readings r_1, r_2 and r_3 for the same cylinder. The values and the standard deviations of 10 repeat weighings are given in Table 2. The standard deviations of the three weighings are very similar, which confirms that the balance is performing satisfactorily over the range of mass applied. The standard deviation of this repeatability data leads to a type A estimate (k=1) of the uncertainty which arises from a large number of random effects. These include *inter alia*: repeatability of centring the cylinder on the balance, thermal drift in the balance structure, draughts caused by differences in temperature between the unknown and tare cylinders, operator error is estimating the "out-of-balance" swing and hysteresis in the knife-edge supports of the balance.

Table 2 : Mean and standard deviation of 10 repeated weighing cycles

Reading	Mean / g	*SD* /g
r_1	208.1171	0.0050
r_2	285.5940	0.0056
r_3	1822.8842	0.0040

The uncertainty due to the calibration of the mass pieces is obtained from the calibration certificate. For a typical selection of mass pieces, this source of uncertainty is estimated to be <0.1 mg. We therefore neglect it.

The estimated uncertainty due to "manual handling" takes account of possible changes in the mass of the cylinder that would influence the apparent mass of gas in the cylinder. These could include paint flaking off, damage to the surface during manual handling of the cylinder or damage to the connector during connection or disconnection of high-pressure pipe work during the weighing procedure. This has been estimated to be 3 mg which corresponds to the loss of a piece of aluminium with a volume of 1 mm^3 or a correspondingly smaller piece of a denser material such as brass or steel.

Uncertainty in buoyancy corrections applied to a single weighing cycle

There are two buoyancy corrections incorporated into the numerator and denominator of the mass fraction calculated in equation (19). The first of these is the conventional mass air density correction (Δa) which is discussed in Appendix 1.

The correction for differential buoyancy (Δb) is caused by any change in atmospheric density acting on the difference in volume between the two cylinders. A "worst case" value for this term can be calculated based on the assumption that ΔV could be as large as 200 ml . A "worst case" value for $\Delta\rho$ might be caused by a 1K temperature increase and a 1 mbar pressure decrease between the two readings, which would lead to a fractional change in air density of 0.995 . Hence, an estimate of the "worst case" uncertainty is 1.2 mg. Since this value is small compared with the uncertainties listed in Table 1, it is sufficient to treat it as a source of uncertainty rather than a correction. The assumptions used to estimate this value represent "worst cases" therefore, they can be considered to represent a rectangular uncertainty distribution, so we divide the value by √3 to convert it to a $k = 1$ basis.

Uncertainty in correction for linear cylinder expansion

The third correction for buoyancy in equation (19) is C_l the correction for linear cylinder expansion. In order to estimate the magnitude of C_l , we need to calculate the value of $KRT\rho^0$. The data reviewed in Appendix 2 suggest that a reasonable estimate for K corresponds to a fractional expansion of 0.2% at a pressure of 120 bar. The numerical term can be evaluated approximately:

$$KRT\rho^0 = \frac{0.002}{120} \cdot \left[bar^{-1}\right] 22.4 \times 10^{-3} \left[m^3 bar\ mol^{-1}\right] 1200 \left[g\ m^{-3}\right] = 4.4 \times 10^{-4} \left[g\ mol^{-1}\right]$$

Since $KRT\rho^0$ is small, and Z is close to unity, the expression for C_l can be approximated:

$$C_l \approx 1 - 4 \times 10^{-4} \left(\frac{Z_3^*}{M_3^*} - \frac{Z_2}{M_2} \right) = 1 - 4 \times 10^{-4}\ (1-w) \left(\frac{Z_3}{M_3} - \frac{Z_2}{} \right.$$

This expression reaches its maximum value for very dilute mixtures ($w \rightarrow 0$) and is zero for a 100% (pure) mixture ($w \rightarrow 1$). Table 3 gives values for the maximum correction for six different binary gas mixtures.

Table 3: Estimated maximum correction for linear cylinder expansion

Mixture	Compressibility of minor component	Maximum correction (for $w=0$)
	Z	C_l
SO_2/N_2	0.98	0.99999088
CO_2/N_2	0.994	0.99999414
C_3H_8/N_2	0.982	0.99999401
NO/N_2	0.999	0.99999893
CO/N_2	1	1.00000002
CH_4/N_2	0.998	1.00001196
Calculated using Z=0.999 for N_2		

Theses maximum values for C_l are very small because there is a very strong correlation between the correction for linear expansion in the measurement of the major and minor masses. In the case of the 50 mmol/mol mixture of carbon monoxide in nitrogen, the denominator of equation (5) is 0.9999840 and equation (6) is 0.9998402 . These correspond to the addition of 1.28 g to a minor component of 80g and 25.58 g to a total mass of 1600g (see Appendix 3). As expected, the quotient of these two numbers gives C_l = 1.00000002 which is very close to the maximum value given in Table 3.

There is some uncertainty in the estimates of C_l shown in Table 3 resulting from uncertainty in the value of K. We estimate that these effects might be equivalent to $u(C_l)$ being of the order of 50% of the estimated value of $1-C_l$ in Table 3.

Table 4 : Corrections for buoyancy

Correction	
Conventional air density correction (Δa)	0.3 mg
Differential buoyancy (Δb)	$1.2/\sqrt{3}$=0.7 mg
Linear cylinder expansion (C_l)	$0.5*(1-C_l)$

The three most significant buoyancy corrections are summarised in Table 4. It should be noted that there are significant correlations between these corrections. For example, the corrections in the numerator and denominator of (7) are correlated because the value for the air density appears in each of them. We neglect the influence of such correlations because the corrections themselves are very small.

Combining uncertainties in the masses of the components

The next step is to evaluate the sensitivity of the calculated mass fraction to uncertainties in the results of each of the three weighings. Since this step in the calculation is only intended to estimate the uncertainty, it can be greatly simplified by assuming that corrections Δa and Δb are small compared with the masses weighed. The mass fraction in equation (19) can then be written approximately as:

$$w = \frac{m_2}{m_2 + m_3} \cong \frac{r_2 - r_1}{r_3 - r}.C_l$$

The sensitivity coefficients [2] for w are given by:

$$\frac{dw}{dr_1} = \frac{(w-1)}{m_2 + m_3}$$

$$\frac{dw}{dr_2} = \frac{1}{m_2 + m_3}$$

$$\frac{dw}{dr_3} = \frac{(-w)}{m_2 + m_3}$$

$$\frac{dw}{dC_l} = \frac{w}{C_l}$$

where the approximation that C_l is close to unity has been made in the first three expressions. The uncertainty in w is then given by:

$$u(w)^2 = \frac{1}{(m_2+m_3)^2}\begin{bmatrix}(w-1)^2u(r_1)^2 + u(r_2)^2 + w^2u(r_3)^2 + 2\rho_{12}(w-1)u(r_1)u(r_2) \\ +2\rho_{13}(w-1)(-w)u(r_1)u(r_3) + 2\rho_{23}(-w)u(r_2)u(r_3)\end{bmatrix} + \frac{w^2}{C_l^2}u(C_l)^2 \qquad (26)$$

In the case where all of the estimated uncertainties and the correlations between the readings are the same:

$$\rho_{12} = \rho_{13} = \rho_{23} = \rho$$
$$u(r_1) = u(r_2) = u(r_3) = u(r)$$

equation (26) simplifies to

$$u(w)^2 = \frac{u(r)^2}{(m_2+m_3)^2}\left[2(1-\rho)(1-w+w^2)\right] + \frac{w^2}{C_l^2}u(C_l)^2$$

or

$$\frac{u(w)^2}{w^2} = \frac{u(r)^2}{m_2^2}\left[2(1-\rho)(1-w+w^2)\right] + \frac{u(C_l)^2}{C_l^2}$$

Uncertainty in converting mass fraction to amount fraction

The amount fraction (x) is calculated from the mass fraction (w) using [1]:

$$x = w\frac{M_3^*}{M_2}$$

The fractional uncertainty in x is given by:

$$\frac{u(x)^2}{x^2} = \left[1 + x(\frac{M_2}{M_3} - 1)\right]^2 \frac{u(w)^2}{w^2} + (1-x)^2\frac{u(M_2)^2}{M_2{}^2} + \frac{(1-w)^4}{(1-x)^2}\frac{u(M_3)^2}{M_3{}^2}$$

Uncertainty in the RMM of the components

The uncertainties in the standard values of the atomic masses of the elements [3] are too small to be of importance in this application. However, the uncertainties in the isotopic abundances may be significant [3]. For example, the four most abundant isotopes of CO are listed in Table 5. The fractional abundances of each isotope can be written in terms of f and g the relative abundance of $^{12}C/^{13}C$ and $^{16}O/^{18}O$.

Table 5: Most abundant isotopes of CO

Isotope	RMM (nominal)	Abundance
$^{12}C^{16}O$	28	f*g
$^{13}C^{16}O$	29	(1-f)*g
$^{12}C^{18}O$	30	f*(1-g)
$^{13}C^{18}O$	31	(1-f)*(1-g)

f = relative abundance of $^{12}C/(^{12}C+^{13}C)$
g = relative abundance of $^{16}O/(^{16}O+^{18}O)$

Therefore the RMM of CO is given by the formula:

$$M_{CO} = 28fg + 29(1-f)g + 30f(1-g) + 31(1-f)(1-g)$$
$$= 31 - f - 2g$$

Applying the law of propagation of uncertainty:

$$u(M_{CO})^2 = u(f)^2 + 4u(g)^2$$

Since the uncertainties in f and g are estimated to be $u(f)$=0.0003 and $u(g)$=0.00015 , the uncertainty in M_{CO} is approximately 0.0004. This corresponds to a fractional uncertainty of 0.0004/28=1.4 $*10^{-5}$. A similar calculation for the two isotopes of nitrogen gives a fractional uncertainty of 6 $*10^{-6}$.

Summary

The major contributions to the uncertainty in the mass fraction (w) of a binary mixture are: $u(r)$, Δa , Δb . The combined uncertainty from these sources is of the order 6 mg in a minor component of 200g ($3*10^{-5}$). The uncertainty in the estimated correction for linear expansion (C_l) is of the order $5*10^{-7}$ and can be neglected. Hence, the fractional uncertainty $u(w)$/w, in the mass fraction is of the order $6*10^{-5}$.

The subsequent calculation of the amount fraction (x) introduces the uncertainties in the RMM of the major and minor components which are of the order $1*10^{-5}$ to $1*10^{-6}$.

Combining each of these uncertainties (in quadrature) gives a combined uncertainty in the amount fraction (k=1) of 0.006% (relative), or an expanded uncertainty (k=2, 95% confidence interval) of 0.01% (relative).

In coming to this result, we note that, in principle, it is possible to verify these gravimetric values (and uncertainties) directly (*ie* by repeat measurements), but that very few such experiments have been reported. Comparisons between the amount fraction of primary standard mixtures can be made using analytical methods that can achieve uncertainties in the range 0.1 to 0.05% in the best cases. This is insufficient to verify the values derived during gravimetric preparation.

Appendix 1 Expressing balance readings in terms of conventional mass

The balance "reading" is determined by using standard mass pieces to achieve "balance" between the two arms of the balance. The difference between the readings r_2-r_1 is then expressed directly in terms of the mass of these mass pieces with an appropriate correction for their buoyancy:

$$r_2 - r_1 = (V_2^m - V_1^m)\rho_m - (V_2^m \rho_2^0 - V_1^m \rho_1^0)$$

where

V_1^m = volume of set of mass pieces used in weighing 1
V_2^m = volume of set of mass pieces used in weighing 2
ρ_1^0 = density of air at the time of weighing 1
ρ_2^0 = density of air at the time of weighing 2
ρ_m = density of mass pieces

Following OIML Recommendation No 33, standard mass pieces are usually calibrated in term of their "conventional mass", which is defined as "the mass of a reference weight of a density of 8000 kg/m^3 which it balances in air of a density of 1.2 kg/m^3 ". To facilitate this definition, the expression for the difference in the readings is re-expressed:

$$\begin{aligned} r_2 - r_1 &= 8000(V_2^m - V_1^m) - (V_2^m - V_1^m).1.2 \\ &+ (V_2^m - V_1^m)(\rho_m - 8000) - V_2^m(\rho_2^0 - 1.2) + V_1^m(\rho_1^0 - 1.2) \\ &= \Delta m_c + \Delta a_{ss} - \Delta a_{12} \end{aligned}$$

where

$$\Delta m_c = 8000(V_2^m - V_1^m) - (V_2^m - V_1^m).1.2$$

$$\Delta a_{ss} = (V_2^m - V_1^m)(\rho_m - 8000)$$

$$\Delta a_{12} = V_2^m(\rho_2^0 - 1.2) - V_1^m(\rho_1^0 - 1.2)$$

The first term (Δm_c) represent the apparent mass of a weight of density 8000 kg/m^3 in air of a density 1.2 kg/m^3 . This is the difference in masses expressed in terms of "conventional mass".

The second term (Δa_{ss}) is a correction for the difference between the true density of the mass pieces and the conventional value of 8000 kg/m^3 . Since the density of mass pieces only deviates by a few parts in 10^6 from the conventional value, $\Delta \alpha_{ss}$ can be ignored in this application.

The third term (Δa_{12}), is a correction for the difference between the true air density at the time of the two weighings and the conventional value of 1.2 kg/m^3 . The value of (Δa_{12}), can be estimated for a "worst case" where the first weighing is carried out at an ambient temperature 1K above and 1 mbar below RTP, and the second is carried out at 1 K below and 1 mbar above RTP. If the masses of the mass pieces in the two weighings are nominally 300 g and 100 g respectively, then (Δa_{12}) is approximately 0.3 mg.

Appendix 2 – Estimation of the extent of linear cylinder expansion

The extent to which a gas cylinder expands when filled with gas at a pressure significantly above atmospheric can be estimated from either calculations or selected measurements. In this Appendix, we summarise some results of these two different approaches for both steel and aluminium cylinders.

Formulae are available in standard texts [4] for the fractional volume change of a thick-walled tube and a sphere.

$$\frac{\Delta V_{tube}}{V_{tube}} = \Delta P \frac{s}{tE}\left(\frac{5}{2} - \frac{2}{m_p}\right)$$

$$\frac{\Delta V_{sphere}}{V_{sphere}} = \Delta P \frac{s}{tE}\frac{3}{2}\left(\quad - \frac{1}{m_p}\right)$$

where

m_p	=	Poisson's ratio
E	=	Young's modulus
t	=	wall thickness
s	=	radius
ΔP	=	$P_{internal} - P_{external}$

Values for Poisson's ratio and Young's modulus of steel and aluminium are given in Table 7. The fractional expansion has also been calculated for dimensions corresponding to typical 10 litre aluminium and 0.5 litre steel cylinders.

Table 7 : Material data for expansion calculations

Material	***E***	m_p	***Dimensions***		$\Delta V / V$ for $\Delta P = 10^7$ Pa	
	10^9 Pa		t / m	s / m	Tube	sphere
Steel	210	1/0.29	$2.4\ 10^{-3}$	$2.3\ 10^{-2}$	0.0009	0.0005
Steel	210	1/0.29	$2.4\ 10^{-4}$	$6\ 10^{-2}$		0.0125
Aluminium	71	1/0.34	$1.0\ 10^{-2}$	$7.5\ 10^{-2}$	0.002	0.001

Experimental measurements of cylinder expansion have reported a fractional expansion of 0.002 for a 5 litre aluminium cylinder at 120 bar [5]. This is in acceptable agreement with the calculated value of 0.002 for a 10 litre aluminium cylinder at 100 bar.

Appendix 3 – Alternative approach to correction for linear cylinder expansion

In this report, the correction for linear cylinder expansion has been carried out by the use of a linear factor applied to the mass fraction w. Re-writing equation (19) with the approximation that the corrections Δa and Δb are very small:

$$w = \frac{m_2}{m_2 + m_3} = \frac{r_2 - r_1}{r_3 - r_1}.C_l$$

where C_l is given by equation (20) repeated here:

$$C_l = \frac{1 - K(Z_3^* RT / M_3^*)\rho_3^0}{1 - K(Z_2 RT / M_2)\rho_2^0}$$

an alternative approach would be to make a correction to each of the measured masses in order to correct them individually for linear cylinder expansion. In this case, w would be written as:

$$w = \frac{m_2}{m_2 + m_3} = \frac{r_2 - r_1 + \Delta V_1 \rho_2^0}{r_3 - r_1 + \Delta V_2 \rho_3^0}$$

In Table 8, we show the values of the corrections in the numerator and denominator of equation X for an example where the balance readings are 80g for the major component and 1600g for the total. It is straightforward to confirm that the value of w calculated using these corrections is the same as that calculated using the factor C_l.

Table 8 Correction for linear cylinder expansion using independent corrections for the major and minor masses.

Mixture	Correction to minor component (balance reading of 80g) $\Delta V_1 \rho$ [g]	Correction to major component (balance reading of 1600g) $\Delta V_2 \rho$ [g]	Linear expansion correction C_l	Mass fraction w
SO_2/N_2	0.00055	0.02484	0.99999133	0.04999957
CO_2/N_2	0.00081	0.02511	0.99999443	0.04999972
C_3H_8/N_2	0.00080	0.02510	0.99999431	0.04999972
NO/N_2	0.00119	0.02549	0.99999899	0.04999995
CO/N_2	0.00128	0.02558	1.00000002	0.05000000
CH_4/N_2	0.00224	0.02653	1.00001136	0.05000057

References

1 *Gas analysis – quantities of composition*, ISO/CD 14912 (working draft).
2 *Guide to the Expression of Uncertainty in Measurement*, Geneva, International Organization for Standardization, 1993.
3 *Quantities, Units and Symbols in Physical Chemistry*, International Union of Pure and Applied Chemistry, Blackwell, Oxford, 1993.
4 "*Strength of Materials*", A Morley, Longmans, London, 1952 (Tenth edition)
5 Anton Alink , Nmi , private communication.

Initially stored as Uncertainties
Then as **Grav uncertainties Jan 01.doc**
Finally as COEM 60 Grav uncertainties April 01.doc