Measurement of Helium micro flowrates with high accuracy for gas chromatography

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Abstract: More and more chemical analysis laboratories using gas chromatographs need to measure the different flowrates involved during the analysis process (split ratio, column flow). The measurement of the column flow is certainly the most difficult because the flowrate of carrier gas is generally very small. For example, the flowrate of helium which is the most often used carrier gas is typically less than 15 µg/s (5 cm^3/min). To calibrate helium flowmeters, the "traced gas method" developed at LNE for nitrogen has been optimized for helium microflow measurements in the range of 0.75 µg/s to 30 µg/s. The traced gas method, the uncertainty estimation of the calibration bench and the calibration results of a laminar flow element type Molbloc and an industrial mass flowmeter are presented in this paper.

Keywords: Micro flowrate, Gas chromatography, Molbloc^{TM}

1. Introduction

Among a lot of applications in gas chromatography, the analysis of VOCs in air using thermal desorption systems associated with gas chromatographs (ATD/GC) requires to know helium flowrates with high accuracy in order to calculate the amount of compounds injected in front of column.

The dynamic gravimetric method commonly used is unsuitable to calibrate flowmeters for such helium micro flowrates with an accuracy of 0.5 % because it needs a lot of time up to 20 hours for one measurement at 6 µg/s (2 cm^3/min). On the other hand, the reference method developed in recent years at LNE for nitrogen and called "traced gas method" is a better alternative with not so much time and also with a traceability to primary quantities (mass, time and mole).

This is the reason why the LNE has decided to optimize this reference method for helium microflow measurements in the range of 0.75 µg/s to 30 µg/s (0.25 cm^3/min to 10 cm^3/min).

In what follows, the traced gas method, the uncertainty estimation of the calibration bench and the calibration results of a standard laminar flow element type Molbloc are presented. The calibration of an industrial laminar flow element used for the ATD/GC application is also described for helium flowrates between 1.5 µg/s and 7.5 µg/s (0.5 cm^3/min to 2.5 cm^3/min).

2. Helium micro flowrates measurement techniques

2.1 Measurement principle

A very low mass flow of helium called "traced gas" is introduced in a mixing chamber in which a main constituent of nitrogen called "dilution gas" circulates with a known flow.

An analytical comparison is then performed between the mass fraction of the traced gas in the dynamic mixture thus created and that of a reference gravimetric gas mixture by using a gas chromatograph.

The flow of the traced gas is then calculated from the mass fraction of the dynamic mixture and the dilution gas flow calibrated by the dynamic gravimetric method [1].

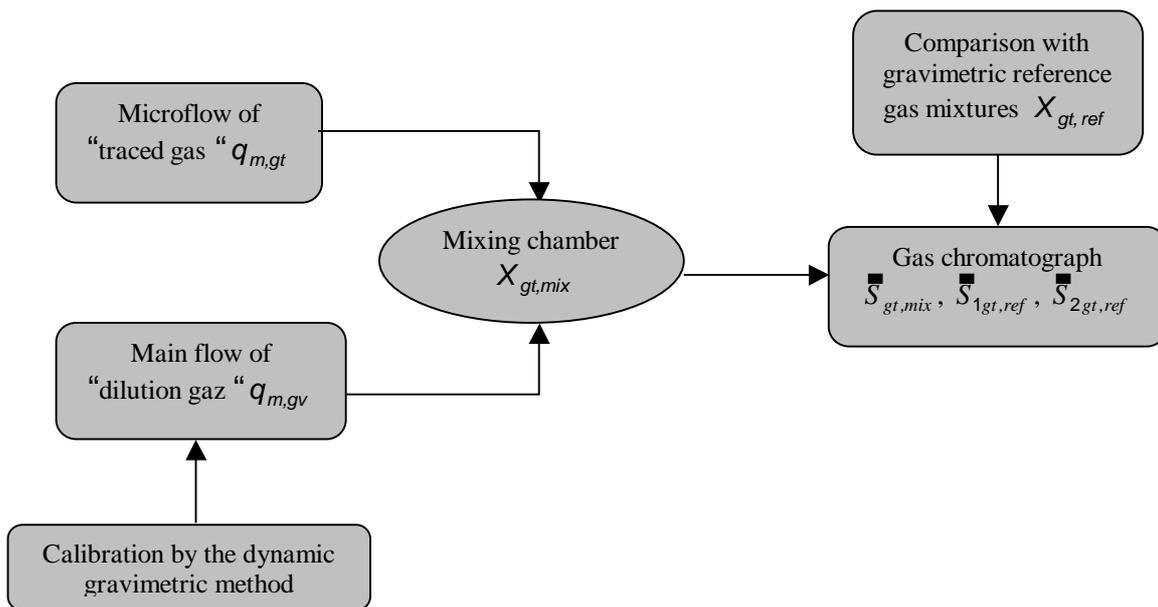The schematic of the measurement principle is shown in figure 1.

Fig. 1 Schematic of the measurement principle for microflow calibration

A detailed description of the method and its uncertainties are given in reference [2]. In this paper, only the specificities of the traced gas method for helium microflow measurements are listed.

2.2 Preparation of the dynamic gas mixture

2.2.1 Mass flowrate of the traced gas ($q_{m,gt}$)

Helium of 99.999% purity is used as traced gas. The helium flow is measured with great accuracy using a standard flowmeter type Molbloc [3], with a measurement range of 0 - 10 cm^3/min full scale, coupled with a Molbox-RFM-M control electronics. The flow is set using a BRONKHORST MFC with a measurement range varying according to the flows measured.

2.2.2 Mass flowrate of the dilution gas ($q_{m,gv}$)

Nitrogen of 99.999% purity is used as dilution gas. The nitrogen flow is measured with a Molbloc 0 - 500 cm^3/min full scale, coupled with a Molbox-1 control electronics. The flow is set using a BRONKHORST MFC of same measurement range.

2.3 Preparation of the reference gravimetric gas mixtures ($X_{gt,ref}$)

The reference gravimetric gas mixtures are pressurized cylinders with different concentrations of helium in nitrogen to cover the range of 0.75 µg/s to 30 µg/s.

As an example, Table 1 gives the list of the nominal flows of helium and nitrogen measured and the mole fractions of the reference gas mixtures.

Table. 1 Nominal flows and mole fractions

Helium flow µg/s	Nitrogen flow mg/s	Mole fraction Reference gas mixture mol/mol
0.75	5.2	1.0×10^{-3}
1.5	2.6	4.0×10^{-3}
3.0	5.2	
6.0	10.5	
9.0	3.1	2.0×10^{-2}
15	5.1	
22	7.5	
30	10.3	

2.3 Calibration procedure

The gas channels are purged before calibration in order to evacuate residual air. The absence of traces of oxygen is verified using the chromatograph.

Before starting the measurements a leak test is performed. It consists in isolating the traced gas channel under an absolute pressure of 3 bar and measuring the residual flowrate.

Then the reference gravimetric gas mixture ($X_{gt,ref}$) is injected into the chromatograph, and the helium peak is measured. This step is repeated 15 times in order to calculate the average of helium surfaces over the last 10 injections ($\overline{S}_{1gt,ref}$).

At the same time, the helium flow is set at the desired value so as to have the same concentration as that of the reference gas mixture. After a period of stabilisation, the dynamic mixture ($X_{gt,mix}$) is injected into the chromatograph 15 times in order to calculate the average helium surfaces over the last 10 injections ($\overline{S}_{gt,mix}$) and to determine the average nitrogen flow.

Finally, the reference gas mixture is injected again in order to take into account a possible drift in the response of the chromatograph. This step is also repeated 15 times, and the average of helium surfaces over the last 10 injections is calculated ($\overline{S}_{2gt,ref}$).

From the two average surfaces of the reference gas mixture and the dynamic mixture, the reference mass flow is calculated.

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3. Results and uncertainty analysis

For a better understanding in the following sections, the equation used to calculate the mass flowrate of the traced gas is given.

$$q_{m,gt} = \frac{M_{gt}}{M_{gv}} \cdot \frac{X_{gt,mix}}{1 - X_{gt,mix}} \cdot q_{m,gv}$$

where

$$X_{gt,mix} = \frac{\overline{S}_{gt,mix}}{(\overline{S}_{1gt,ref} + \overline{S}_{2gt,ref})/2} \cdot X_{gt,ref}$$

and M_{gt} is the molar mass of the traced gas and M_{gv} is the molar mass of the dilution gas.

3.1 Mass flowrate of the dilution gas (N_2)

The major uncertainty sources are : the calibration error and the linearity of the flowmeter, and the stability of the dilution gas during the measurement.

Calibration: the calibration certificate of the flowmeter indicates a small bias error, comparable to the calibration uncertainty. Nevertheless, a calibration function is calculated to correct the bias error. The uncertainty of this function is considered as the calibration uncertainty of the flowmeter. This standard uncertainty is estimated to 0.15% of the reading.

Stability: this source leads to a standard uncertainty of 0.00045 mg/s for the full range.

3.2 Mole fraction of the traced gas (He) in the dynamic mixture

This fraction depends on three quantities : the mole fraction of helium in the reference gas mixture, the average surface of the dynamic mixture and the average surface of the reference gas mixture measured by the chromatograph.

Reference gas mixtures: the relative standard uncertainty of the mixtures varies from 0.15 % to 0.20 % for the mixture with the lowest mole fraction.

Surfaces: the uncertainty comes from the repeatability and a day effect. As repeatability varies from day to day, a day effect must be added to the uncertainty. The reproducibility (repeatability + day effect) is estimed globally. This reproducibility is lower for the reference mixture, which is more stable during the measurement. The relative standard uncertainty is about 0.06 % for the surface of the reference mixture, and varies from 0.16 % to 0.07 % for the surface of the dynamic mixture.

The relative standard uncertainty of $X_{gt,mix}$ is at maximum of 0.27 % and the main contributor to this uncertainty is the mole fraction of helium in the reference gas mixture.

3.3 Helium mass flowrate

The uncertainty on the helium mass flowrate is calculated by propagation of the uncertainties of the nitrogen mass flowrate and of the mole fraction of helium estimated previously.

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The evolution of this uncertainty with the flow is presented in Table 2.

Table. 2 Standard uncertainties of the helium mass flowrate

Helium flow $(q_{m,gt})$ (µg/s)	$u(q_{m,gv})$	$u(x_{gt,mix})$	$u(q_{m,gt})$	$u(q_{m,gt})$ (µg/s)
0.7551	0.15 %	0.26 %	0.30 %	0.0023
1.5515	0.15 %	0.17 %	0.23 %	0.0036
2.9813	0.15 %	0.17 %	0.23 %	0.0068
5.851	0.15 %	0.17 %	0.23 %	0.013
9.217	0.15 %	0.18 %	0.23 %	0.021
14.934	0.15 %	0.18 %	0.23 %	0.035
22.430	0.15 %	0.18 %	0.23 %	0.052
29.965	0.15 %	0.18 %	0.23 %	0.070

The uncertainties of the molar mass of helium and nitrogen are negligible compared to these of the nitrogen mass flowrate and the mole fraction of helium.

Both factors have a contribution respectively of 40 % - 60 % to the mass flow of the traced gas, except for the lowest flow (25 % - 75 %).

The standard uncertainty of the calibration method is modelised by :

$$u(q_{m,gt}) = 0.0024 * q_{m,gt} + 0.0005 \ µg / s$$

4. Calibration of a laminar flow element Molbloc^{TM}

A laminar flow element Molbloc has been calibrated directly with the traced gas method between 1.5 µg/s and 30 µg/s of helium (0.5 cm^3/min to 10 cm^3/min).

The results for the Molbloc are displayed in Figure 2. The relative deviations of the Molbloc are between - 0.3 % and - 0.4 % on the whole range.
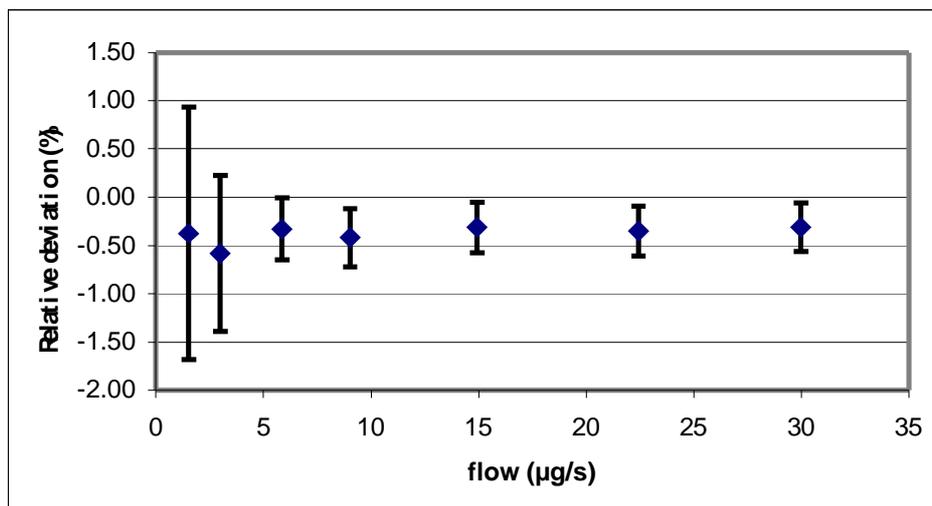

Fig. 2 Relative deviations and uncertainties of the Molbloc between 1.5 µg/s and 30 µg/s

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The calibration uncertainty of the Molbloc is calculated by propagation of the uncertainties of the calibration method, the resolution of the instrument, the repeatability of the measurements and the stability of the helium flow in the dynamic mixture. The leak tests have shown a residual flowrate of 0.0022 µg/s of helium. This value is added to the calibration uncertainty.

The evolution of the Molbloc calibration uncertainty with the flow is presented in Table 3.

Table. 3 Relative standard uncertainties of the Molbloc

$q_{m,Molbloc}$ (µg/s)	$u(q_{m,gt})$ modelised	$u(res)$	$u(rep)$	$u(sta)$	$u(q_{m,Molbloc})$	$u(q_{m,Molbloc})$ (µg/s)
1.515	0.31 %	0.07 %	0.89 %	0.81 %	1.32 %	0.020
2.974	0.27 %	0.03 %	0.49 %	0.38 %	0.71 %	0.021
5.832	0.26 %	0.02 %	0.07 %	0.17 %	0.34 %	0.020
8.976	0.25 %	0.01 %	0.07 %	0.13 %	0.30 %	0.027
14.881	0.25 %	0.01 %	0.07 %	0.07 %	0.27 %	0.040
22.343	0.24 %	0.00 %	0.07%	0.05 %	0.26 %	0.059
29.875	0.24 %	0.00 %	0.07%	0.04 %	0.26 %	0.077

The standard uncertainty of the Molbloc is modelised by :

$$u(q_{m,Molbloc}) = 0.0024 * q_{m,Molbloc} + 0.017 \ \mu g \ / \ s$$

5. Calibration of an industrial laminar flow element ANALYT

The calibration of the ANALYT flowmeter is performed in helium between 1.5 µg/s and 7.5 µg/s of helium (0.5 cm^3/min to 2.5 cm^3/min), by comparison with the Molbloc calibrated with the traced gas method.

The calibration results are shown in Figure 3. The relative deviations of the ANALYT are between - 7 % at 7.5 µg/s and - 10 % at 1.5 µg/s.
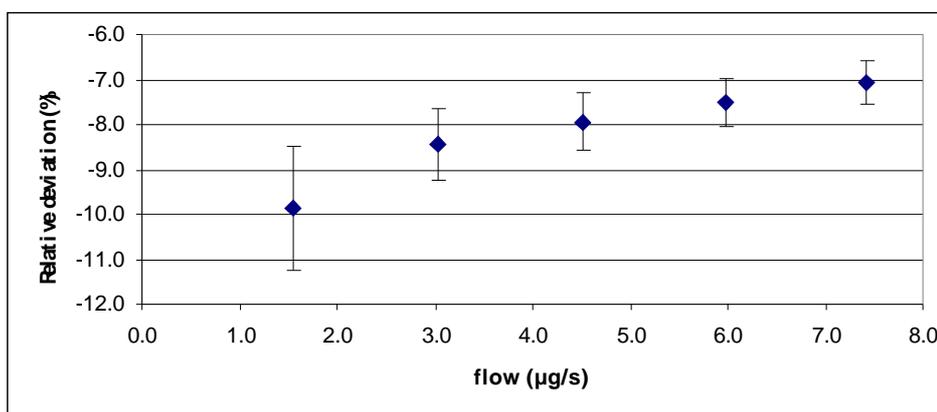

*Fig. 3 Relative deviations and uncertainties of the ANALYT
by comparison to the Molbloc 10 ml/min FS*

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The calibration uncertainty is due to the uncertainties of the Molbloc calibration, the resolution of the instrument and the repeatability of the measurements.

The evolution of the ANALYT calibration uncertainty with the flow is presented in Table 4.

Table. 4 Standard uncertainties of the ANALYT

$q_{m,ANALYT}$ (µg/s)	$u(q_{m,Molbloc})$ modelised	$u(res)$	$u(rep)$	$u(q_{m,ANALYT})$	$u(q_{m, ANALYT})$ (µg/s)
1.543	1.34 %	0.20 %	0.34 %	1.40 %	0.022
3.030	0.80 %	0.10 %	0.12 %	0.82 %	0.025
4.508	0.62 %	0.07 %	0.12 %	0.63%	0.028
5.970	0.52 %	0.05 %	0.12 %	0.54 %	0.032
7.430	0.47 %	0.04 %	0.12 %	0.49 %	0.036

6. ATD/GC application for benzene

In order to determine the mass of component reaching the GC column, it is necessary to measure accurately the GC column flowrate. Indeed, the percentage of components from the sample reaching the GC detector is obtained by the following equation :

$$Mass\ of\ component\ reaching\ the\ Detector = \left(\frac{Column\ Flow}{Column\ Flow + Outlet\ Split\ Flow} \right) \times Mass\ from\ the\ sample$$

Table. 5 Application for the measurement of benzene

Mass from the sample (ng)	Outlet Split Flow (cm³/min)	Reading Column Flow (cm³/min)	Uncorrected mass reaching the detector (ng)	Corrected Column Flow (cm³/min)	Corrected Mass reaching the detector (ng)
504.2 ± 5.6	30.2 ± 0.4	2.19 ± 0.02	34.08 ± 0.8	2.36 ± 0.02	36.58 ± 0.8
		2.19 ± 0.02	34.08 ± 0.8	2.36 ± 0.02	36.58 ± 0.8
		2.18 ± 0.02	33.93 ± 0.8	2.35 ± 0.02	36.43 ± 0.8
		2.17 ± 0.02	33.79 ± 0.8	2.34 ± 0.02	36.29 ± 0.8
		2.17 ± 0.02	33.79 ± 0.8	2.34 ± 0.02	36.29 ± 0.8

The calibration of the flowmeter, used for measuring the GC column flow, has highlighted a deviation of about 7% of the mass of component reaching the detector, while the uncertainty on this mass was estimated at 2.2 %.

7. Conclusion

The works presented here show the performances and advantages offered by the traced gas method: a calibration uncertainty of the flowmeters between 0.5 % and 2 % in the range of 3 µg/s to 30 µg/s of helium and microflow measurements that can be performed more quickly than with the dynamic gravimetric method.

The calibration results of the ANALYT flowmeter have shown a bias between 7 % and 10 % of the reading. The use of the corrected flow has led to a more accurate determination of the mass of compounds quantified by the chromatograph detector.

References

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