ESTIMATION OF THE UNCERTAINTY IN THE QUANTIFICATION OF H_2, N_2, CO, CO_2 AND CH_4 IN GAS SAMPLES

*GISELA BRUHN, MARÍA ELENA ORTIZ AND CATHERINE TESSINI**

Laboratorio de Análisis Químico e Instrumental, LabQI
Departamento de Química, Universidad Técnica Federico Santa María, Valparaíso, Chile

1. INTRODUCTION

In the production process of H_2, CO and their mixture (synthesis gas), gases such as H_2, N_2, CO, CO_2 and CH_4 must be quantified in the raw material (or reformed gas) and samples, which are obtained at different points in the production lines of the mentioned gases.

The quantification of H_2, N_2, CO, CO_2 and CH_4 in gas samples by gas chromatography is a routine analysis performed in our laboratory according to ASTM D1946-90 (2011) and UOP Method 603-88 [1,2]. In this work, the uncertainty was estimated considering its importance in the determination of the main sources of dispersion in the analytical method and its importance as a requirement in NCh-ISO.17025.

2. Instrumentation and gas chromatography method

The Gas Chromatography (GC) analyses were performed with different equipment. A Gow-Mac gas chromatograph with a VP-Molsieve 5Å column and a TCD detector, which used Nitrogen as the carrier to determine H_2 and Helium, was used to determine N_2. An HP gas chromatograph, which was equipped with a GS-Q column, a methanizer and an FID detector, with Helium as the carrier, was used to determine CO, CO_2 and CH_4. The data were processed using the CSW software.

Different gas standards were used to determine the concentrations of all analytes in the samples using 4 different gas syringes (100-250 [µL], 1-5 [mL]).

2.1 Uncertainty estimation

The general procedure for gas quantification includes the following steps. First, four standards were used to determine the necessary calibration curves. Second, different volumes of sample were injected to quantify every analyte in each sample. In this work, the uncertainty estimation was calculated using the error propagation approach in 3 steps with the bottom-up model: (I) preparation and correction of the standards, (II) calibration curve and (III) precision of the method under intermediate precision [3,4]. These results were used to estimate the uncertainty of the method.

3. RESULTS AND DISCUSSION

To determine five compounds in the sample gas, the uncertainty sources with greater significance were simplified in the following groups:

a) Uncertainty associated with the method precision (*s*): identical samples were analyzed in two different days (n=4)
b) Uncertainty associated with the concentration of standards (*c.a*): evaluated by the certificate of analysis of each standard.
c) Uncertainty associated with the syringe volume (*c.s*): evaluated by the certificate of accuracy of each syringe.
d) Uncertainty associated with the use of different syringes (*iny*): injection of standard with one syringe and comparison to the calibration curve of another syringe.
e) Calibration curve (*calib*): according to Eurachem QUAM:2012 [3]

The main contribution to uncertainty comes from the preparation and correction of the standards and calibration curve for all determined gases. U was estimated by multiplying the combined standard uncertainty by a coverage factor of 2 (95% confidence interval). There is no expanded uncertainty for N_2 because this analyte was always under the detection limit. Table 1 shows the obtained results for all determined gases.

Table 1 Expanded uncertainty calculation for five compounds in the gas sample.

	Relative standard uncertainty						
	Precision	Calibration curve	Standards preparation and correction				
Gas	s	$u_{(calib)}$	$u_{(c.a)}$	$u_{(c.s)}$	$u_{(iny)}$	Concentration (%)	$U_{(K=2)}$ (%)
H_2	$3{,}26\times10^{-4}$	$9{,}72\times10^{-4}$	$8{,}33\times10^{-10}$	$1{,}67\times10^{-5}$	$1{,}33\times10^{-4}$	78	7,6
CO	$2{,}42\times10^{-3}$	$2{,}49\times10^{-4}$	0,015	$1{,}67\times10^{-5}$	$1{,}88\times10^{-4}$	1,9	11
CH_4	$2{,}36\times10^{-3}$	$1{,}24\times10^{-4}$	0,014	$1{,}67\times10^{-5}$	$1{,}88\times10^{-4}$	2,0	11
CO_2	$1{,}32\times10^{-4}$	$9{,}74\times10^{-4}$	0,157	$1{,}67\times10^{-5}$	$1{,}88\times10^{-4}$	17	32
N_2	-	0,718	0,016	$1{,}67\times10^{-5}$	-	< LD*	-

**Detection limit*

CONCLUSION

The gases were determined with direct injection of the samples, which does not involve a sample treatment. The use of different syringes (different volumes) and calibration curves were considered in the uncertainty estimation. In this case, the use of different syringes is a source of uncertainty, but the most important sources of uncertainty are the calibration curves and standards. The highest uncertainty belongs to the CO_2 determination because of the standard certification. The intermediate precision of the method is only high for the determination of CH_4 and CO.

ACKNOWLEDGMENTS

The authors thank the financial support of the Chemistry Department, Universidad Técnica Federico Santa María.

REFERENCES

1.- Standard Practice for Analysis of Reformed Gas by Gas Chromatography, ASTM D1946-90, (2011).
2.- Trace CO and CO_2 in hydrogen and light gaseous hydrocarbons by GC, UOP Method 603-88.
3.- Quantifying Uncertainty in Analytical Measurement, EURACHEM/CITAC, 3rd Edition (2012).
4.- C. Tessini, C. Mardones, L. Rivas, D. von Baer, *Accred. Qual. Assur*, 14, (2009).

e-mail: catherine.tessini@usm.cl