Evaluation of the uncertainty associated to tar sampling with solid phase adsorption cartridges

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A B S T R A C T

The uncertainty evaluation associated with the quantification of tar with the use of solid phase adsorption for tar sampling and gas chromatography analysis is present. The study shows that the major contribution to the overall uncertainty is related to the extraction step. Relevant tar compounds are selected and used as model to quantify the uncertainty and for comparison with the uncertainty associates to the traditional methodology for tar sampling. The study indicates that the uncertainty associated to the tar sampling with solid phase adsorption cartridges is lower than the uncertainty associated to the tar sampling with impinger bottles.

Keywords:
Uncertainty
Tar sampling
Gasification
Solid-phase adsorption
Gas-chromatography

1. Introduction

Gasification technology is an environmental friendly way to produce energy but one of the remaining problems still to be solved is the reduction of the high level of tar present in the product gas [1,2].

Tar is a very complex heterogeneous mixture of organic molecules which amount in the gas depends on the operating conditions [3,4]. Tar easily condense on the surfaces of pipes and filters and may cause blockage and corrosion in the engines and turbines used in the application of the producer gas [5e9]. Therefore the ability to quantify tar levels in process stream is essential in gasification research and commercial gas production [3].

Traditional methods for tar sampling, based on cold-trapping with solvent absorption in impingers are the most used by researchers but this type of sampling has drawbacks such as the long period for sampling and troublesome preparations. Due to these disadvantages some researchers used solid phase adsorption (SPA) for tar sampling [9e11] because of their simplicity and speed of sampling. But to the best of the author's knowledge, no information is available about the uncertainty associated with this type of sampling.

Stating the uncertainty of a measurement is indispensable in judging the fitness for purpose of a measured quantity value. Measurement uncertainty enables users of a measured quantity value to make decisions about conformity assessment [12].

The aim of this study is to quantify the sources of uncertainty associated with the SPA sampling method to determine the critical stages of the analytical methodology in order to reduce them. Relevant tar compounds [4,13,14] are selected and used as model to quantify the uncertainty and for comparison with the uncertainty associated to the traditional methodology for tar sampling.

2. Materials and methods

2.1. *Chemicals*

Benzene, toluene, phenol, naphthalene and phenanthrene were obtained as pure compounds from Scharlau, Merck and SigmaeAldrich with at least 99.5% purity. Dichloromethane (DCM) was acquired to SDS. Stock solutions were prepared from pure compounds in dichloromethane. As internal standard, 4-bromofluorobenzene 2 kg m^{-3} in methanol was obtained from Supelco. ENVI-Carb/NH_2 cartridges from Supelco were used for tar sampling.

2.2. *Sampling*

The sampling set up consists of a syringe needle, an SPA column without preconditioning and a syringe connected in series. Samples are taken by a septum port of a T-connection located at the outlet pipe of the gasifier. A sample of 100 cm^3 of gas is taken by pulling back the syringe plunger.

2.3. *Analytical procedure*

The analytes retained in the cartridges were extracted with 3 cm^3 DCM. The extracts were analysed using a Hewlett Packard 5890 series II gas chromatograph coupled to a Hewlett Packard 5971A mass spectrometer. 1 mm^3 volumes were injected. Operating conditions were as follows: initial oven temperature 60 °C, held for 1 min, then increased at 3 °C min^{-1}e105 °C, then increased at 8 °C min^{-1}e250 °C, then increased at 5 °C min^{-1}e260 °C, held for 5 min. Operation mode was splitless, the carrier gas was He (21 kPa) and the capillary column was ZB-624 (30 m × 0.25 mm × 1.40 mm). The detector was operated in electronic impact mode (70 eV) and detector mode SIM.

3. Results and discussion

3.1. *Quality of analytical methodology*

Precision, linearity, sensitivity, selectivity and quantification and detection limits were determined to evaluate the quality of the analytical results.

Five standard solutions with internal standard were analysed in triplicate and the least squares linear fit performed to obtain calibration curves. Correlation coefficients for all analytes were 0.999, except for naphthalene ($r^2 = 0.994$). More details can be found elsewhere [15].

3.2. *Estimation of uncertainty*

To estimate the uncertainty each individual source of it was identified and quantified and then these sources were combined to obtain the total uncertainty. This approach is called ISO or bottom-up methodology and involves four steps: specify measure, identify sources, quantify components and calculated combined uncertainty.

3.2.1. *Specify measure*

In this step the relationship between the analytical result and the parameters on which it depends is established by a mathematical expression. To do this, the analytical methodology described above is taken into account. A scheme of the analytical methodology is shown in Fig. 1.

The expression used to calculate the concentration of an analyte into the gas stream, expressed in mg m^{-3}, is shown in Equation (1).

$$C_a = \frac{C_{GC}\$V_e}{R\$V_g}\$10^3 \qquad (1)$$

where C_a is the analyte concentration in the gas stream, C_{GC} is the analyte concentration obtained from calibration in kg m^{-3}, V_e is sample volume in cm^3, V_g is the volume of the gas sampled in cm^3 and R is the recovery.

3.2.2. *Identify sources*

Taken into account Equation (1) and the analytical methodology, the sources of uncertainty have been identified. To detect the sources and avoid repetitions the cause and effect diagram shown in Fig. 2 was used.

3.2.3. *Quantify components*

The uncertainty derived from each branch of the cause and effect diagram is calculated individually.

3.2.3.1. Estimation of the uncertainty derived from chromatographic analysis (u_{GC}). This uncertainty is a combination of three principal uncertainties associated to: calibration curve, equipment repeatability and standards preparation.

The uncertainty of linear least square calibration (u_c) has four sources: random variations in signal measurement, random effects resulting in errors in the assigned reference values, constant unknown offset in reference values and signals, and errors in the assumption of linearity. However, the most important contribution is the random variation in the

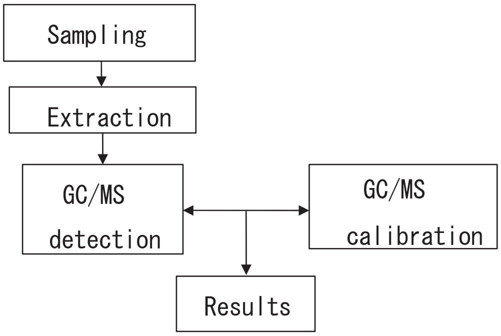

Fig. 1 e Scheme of the analytical procedure.

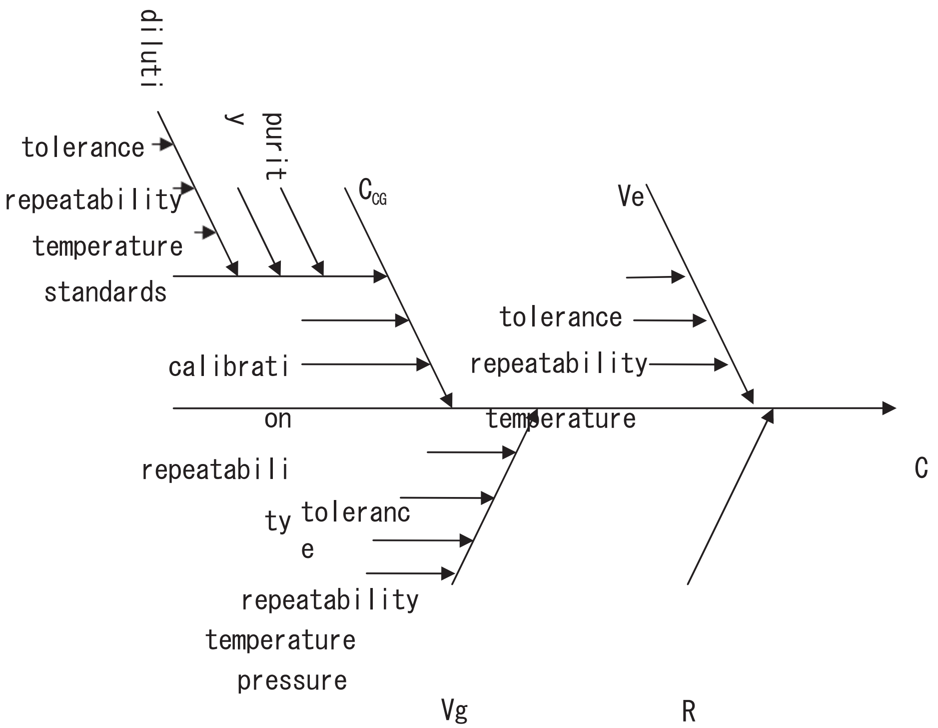

Fig. 2 e Cause and effect diagram.

signal [16]. Therefore, this contribution can be calculated employing Equation (2).

$$u_c = \frac{S}{b}\sqrt{\frac{1}{p}+\frac{1}{n}+\frac{\left(x_{\text{pred}}-\bar{x}\right)^2}{\sum x_i^2-\left(\sum x_i\right)^2/n}} \qquad (2)$$

where S is the standard error of the estimation, b is the slope, p is the number or repetitions to obtain x_{pred} and n is the number of points of the calibration curve.

Table 1 shows the parameters of Equation (2) obtained from triplicates of the calibration curves.

Uncertainty associated to the equipment repeatability (u_r) was calculated as standard uncertainty obtained from five repetitions of the chromatographic measurement. Therefore, to obtain it Equation (3) was used; where S is the standard deviation, n is the number of repetitions and f is a factor that depends on the number of repetitions and is 1.4 for $n = 5$.

$$u_r = \frac{S \cdot f}{\sqrt{n}} \qquad (3)$$

In Table 2 the standard deviation and the uncertainty for each compound is present.

Table 1 e Parameters of the uncertainty associated with the calibration. b: slope, S: standard deviation, x_{pred}: analyte concentration in a sample, $\bar{x}$: analyte concentration media.

Analyte	b	S	x_{pred}	$\bar{x}$	u_C (kg m^{-3})
Benzene	1.71	0.38	131	195	0.12
Toluene	1.61	0.30	129	196	0.11
Phenol	1.42	0.083	9	19	0.032
Naphthalene	2.29	0.18	3	4	0.041
Phenanthrene	1.14	0.0084	25	39	0.078

In order to estimate the uncertainty associated with the standard preparations (u_P) it must be taken into account that all standards were prepared from pure compounds so the uncertainties associated to the purity, to the dilution and to the weight if the compounds are solid have to be considered.

The uncertainty associated to the purity (u_{Pu}) was calculated considering a rectangular distribution using Equation (4). Results are shown in Table 3.

$$u_{\text{Pu}} = \frac{\text{Purity}}{\sqrt{3}} \qquad (4)$$

The uncertainty associated to the analytical balance (u_M) was calculated following the internal quality protocol QM-PT-UC05 [17] as 7.5 × 10^{-5} g. The uncertainty derived from the dilution step (u_{dil}) involves three contributions: variations in the temperature (u_{dil1}), repeatability (u_{dil2}) and volumetric material tolerance (u_{dil3}). The contribution of the variations in the temperature was estimated using a rectangular distribution within 5 °C and assumed that the coefficient of the volume expansion of the material against the liquid can be considered negligible. For organic liquids the coefficient of the volume expansion (b) considered was 1 × 10^{-3} °C^{-1} [16]. So this contribution was calculated with the expression 5 as 0.14 cm^3.

Table 2 e Uncertainty derived from chromatographic determination repeatability.

Analytes	S	u_r (kg m^{-3})
Benzene	5.28	3.30
Toluene	4.66	2.91
Phenol	0.39	0.25
Naphthalene	0.06	0.040
Phenanthrene	1.60	1.00

Table 3 e Purity, purity uncertainty, dilution uncertainty, analytical balance uncertainty and relative standard preparation uncertainty.

Compound	Purity (%)		u_{Pu}	u_{dil} (cm^3)	u_M (g)	u_P/C_P
Benzene	99.7	0.1	0.00058	0.15	e	0.0030
Toluene	99.5	0.1	0.00058	0.15	e	0.0030
Phenol	99.5	0.1	0.00058	0.15	7.5×10^{-5}	0.0030
Naphthalene	99.7	0.1	0.00058	0.15	7.5×10^{-5}	0.0030
Phenanthrene	99.5	0.1	0.00058	0.15	7.5×10^{-5}	0.0030

$$u_T = \frac{V\$DT\$b}{\sqrt{3}} \tag{5}$$

The volumetric repeatability was obtained by the standard uncertainty from the weighing (six times, $f = 1.3$) each volumetric material full of solvent ($u_{\text{dil2}} = 0.012$ cm^3) and the tolerance of volumetric material was calculated through a triangular distribution within 0.05 cm^3 as minimal division ($u_{\text{dil3}} = 0.021$ cm^3)

The dilution uncertainty and the relative uncertainty associated to the standards preparation are shown in Table 3.

The combined uncertainty derived from chromatographic analysis (u_{GC}) calculated applying Equation (6), where C_{GC} is the concentration chromatographically determinate, C_p is the standard concentration, C_r is the concentration used in the repeatability test and C_c is the medium concentration used in the calibration, is shown in Table 6.

$$\frac{u_{C_{\text{GC}}}}{C_{\text{GC}}} = \sqrt{\frac{u_P}{C_P} + \frac{u_r}{C_r} + \frac{u_C}{C_C}} \tag{6}$$

3.2.3.2. Uncertainty associated to sample volume (u_{V_e}). To evaluate this contribution it should be taken into account the tolerance of the volumetric material (u_t), which is calculated trough triangular distribution (u_t = tolerance/O6), the repeatability (u_r) which is calculated as standard deviation of seven replicates ($f = 1.3$) and the temperature (u_T) which manner of estimation is aforementioned. The total uncertainty associated to sample volume was calculated following the law of uncertainty propagation shown in Equation (7). Each contribution and the uncertainty derived from sample volume are shown in Table 4.

$$u_{\text{Ve}} = \sqrt{u_t^2 + u_r^2 + u_T^2} \tag{7}$$

3.2.3.3. Uncertainty derived from gas volume (u_{V_g}). To calculate the uncertainty derived from the measure of the gas volume it must be taken into account the tolerance and repeatability of the equipment used, and the variations on the gas temperature and pressure.

Table 4 e Contributions and sample volume uncertainty.

u_t (cm^3)	u_r (cm^3)	u_T (cm^3)	u_{V_e} (cm^3)
0.010	0.0046	0.0072	0.013

Table 5 e Uncertainty derived from the recovery.

Compound	R (%)	u_{Rexp} (%)	u_R/R
Benzene	87	6	0.07
Toluene	84	7	0.08
Phenol	92	10	0.11
Naphthalene	92	5	0.05
Phenanthrene	90	3	0.04

To measure the gas sampled, a 100 cm^3 syringe was used. It has a minimal division of 2 cm^3 so considering a triangular distribution the uncertainty of the syringe tolerance (u_t) is 2/O6 = 0.82 cm^3

Repeatability (u_r) calculated as standard deviation of five repetitions ($f = 1.4$) is 0.28 cm^3

The contribution of the variations in temperature was estimated using a rectangular distribution within 5 °C and assuming that the coefficient of the volume expansion of the gas can be considered equal to the air at 20 °C ($u_{V_{g2}} = (V \times DT \times b/O3) = 0.98$ cm^3). The variation of the pressure during the sampling was considered negligible. The combination of these contributions, considering both independent generates a final standard uncertainty (u_{V_g}) of 1.31 cm^3

*3.2.3.4. Uncertainty from recovery (*uR*).* Three recovery experiments were carried out to evaluate the uncertainty of the analyte recovery as uncertainty type A. 10 mm^{-3} of a standard solution was added to the cartridges and a stream of nitrogen was applied to simulate the pass of the gas through the cartridge. The uncertainty obtained (u_{Rexp}) like a standard deviation included contribution from chromatographic analysis so this contribution must be subtracted to calculate the uncertainty associated to the analytes extraction. In Table 5 the results are presented.

In Fig. 3 each of the contributions to the overall uncertainty are shown. The most important contribution to the global uncertainty comes from the recovery extraction from the cartridges.

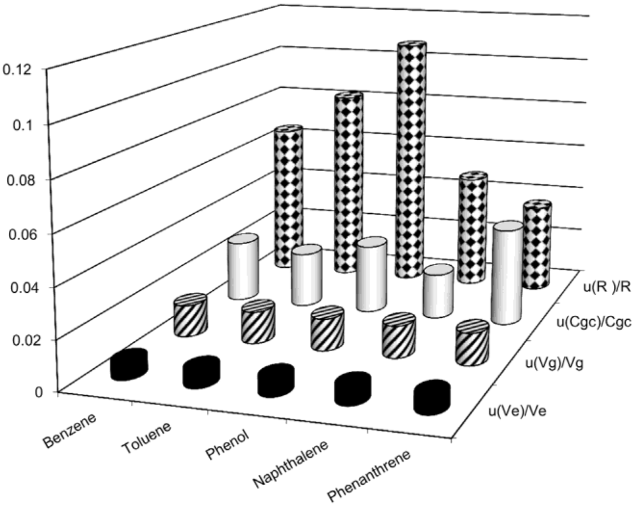

Fig. 3 e Diagram of relative standard uncertainty of each contribution.

Table 6 – Relative standard, combined and expanded uncertainties.

Compound	u_{GC}/GC	u_{V_e}/V_e	u_{V_g}/V_g	u_R/R	u_{Ca} (%)	U_{Ca} (%)
Benzene	0.025	0.0067	0.013	0.07	7	14
Toluene	0.023	0.0067	0.013	0.08	9	17
Phenol	0.029	0.0067	0.013	0.11	11	22
Naphthalene	0.019	0.0067	0.013	0.05	5	11
Phenanthrene	0.040	0.0067	0.013	0.04	6	11

3.2.4. *Calculating the combined uncertainty*

To calculate the combined uncertainty (u_{Ca}) first of all it is necessary to express all uncertainties as relative standards uncertainties and then, combine them following the law of uncertainty propagation shown in Equation (8).

$$u_c(y) = y\sqrt{\left(\frac{u(p)}{p}\right)^2 + \left(\frac{u(q)}{q}\right)^2 + \ldots} \quad (8)$$

Finally, the expanded uncertainty (U_{Ca}) was calculated using a coverage factor of 2 which gives a level of confidence of approximately 95%.

In Table 6 standards uncertainties, the combined uncertainty and the expanded uncertainty are shown.

In order to facilitate the understanding of the calculated performed; a diagram is shown in Fig. 4.

3.3. *Application to real samples*

Table 7 – Concentration and expanded uncertainty. BF: before filter, AF: after filter.

Compounds	BF (g m^{-3})	AF (g m^{-3})
Benzene	2.80 (0.4)	1.51 (0.22)
Toluene	0.99 (0.17)	0.59 (0.10)
Phenol	0.02 (0.004)	–
Naphthalene	0.75 (0.08)	0.03 (0.003)
Phenanthrene	0.03 (0.003)	0.003 (0.0003)

Table 8 – Expanded uncertainty of two types of tar sampling.

Compounds	$U_{\text{Traditional method}}$ (%)	$U_{\text{SPA method}}$ (%)
Benzene	21	14
Toluene	14	17
Phenol	30	22
Naphthalene	35	11
Phenanthrene	22	11

Real samples from an atmospheric bubbling fluidised bed gasifier with a capacity of 100 kg h^{-1} of dried sewage sludge were analysed following the method described above to assess the performance of one of the stages of the gas cleaning system.

Results obtained for samples taken before and after the tar removal filter with the expanded uncertainty in brackets are shown in Table 7.

3.4. *Comparison with uncertainty of traditional method*

In Table 8 the expanded uncertainty associated to both type of sampling, i.e. traditional solvent sampling and SPA sampling,

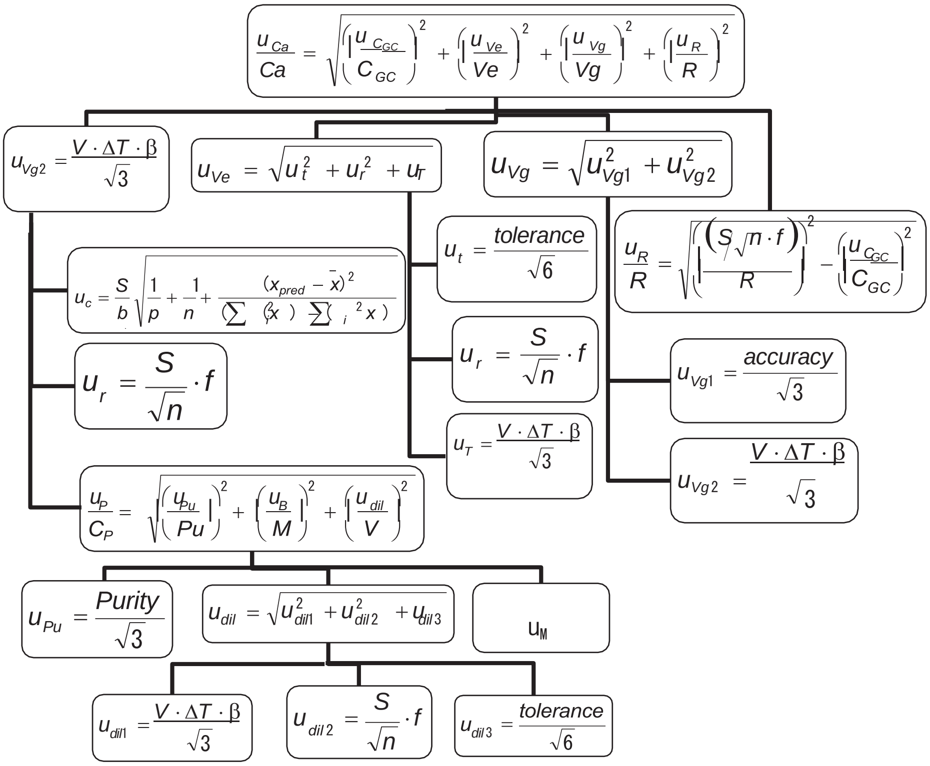

Fig. 4 – Scheme of the uncertainty calculation.

is compared. Uncertainty associated to the traditional method is calculated as described in a previous paper [18].

As shown in Table 8, the uncertainty associated to the use of SPA for tar sampling is lower for all compounds except for toluene.

4. Conclusions

The aim of this work was to identify the main sources of uncertainty associated to the determination of the main tar components including the expanded uncertainty.

As expected, from this study it can be concluded that the step which generates more uncertainty is the extraction stage.

The expanded uncertainty obtained is between 11 and 22 per cent and is low enough to allow assessment of the efficiency of the tar removal filter.

Lower expanded uncertainties were found for SPA tar sampling over traditional tar sampling, what can be regarded as another advantage for this sampling method.

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