

Assessment uncertainty associated to the analysis of tar from gasification of sewage sludge

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A B S T R A C T

The uncertainty evaluation associated with the quantification of tar from gasification of sewage sludge is present. Each of the sources of uncertainty associated with the wet type sampling method and GC–MS analysis was identified to determine the critical stages of the analytical methodology in order to reduce them. The study shows that major contributions to the overall uncertainty are related to extraction steps. High expanded uncertainties were found for all compounds, due to the segregation of the tar in different samples because of the sampling method. However, the analytical method used was successfully applied for the evaluation of the tar cleaning filter in a real gasification plant.

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1. Introduction

The production of low-heating-value gaseous fuels by gasification of biomass and waste provides a renewable source of electric power. Gasification of sewage sludge produces low-quality combustible gas while reduces the environmental impact caused by fossil fuels and diminishes the waste volume. However, one of the remaining problems still to be solved is the reduction of the high level of tar present in the product gas [1]. Tar is a complex mixture of condensable hydrocarbons consisting mainly of polycyclic aromatic compounds. Tar easily condense on the surfaces of pipes and filters and may cause blockage and corrosion in the engines and turbines used in application of the producer gas [2,3]. Hence, tar removal is one of the most important technical barriers for a successful application of the technology in the power markets [4,5]. Consequently, to minimize tar, development of accurate analytical methods for tar sampling and analysis are essential in gasification research and commercial gas production. The sampling methodology employed consisting in a serial of impinger bottles with an organic solvent, is commonly used for tar measurement but there is not data available of the uncertainty associated with this type of sampling. The aim of this study is to quantify each of the sources of uncertainty associated with this type of sampling to determine the critical stages of the analytical methodology in order to reduce them.

2. Material and methods

2.1. Chemicals

PAHs mixture (2000–100 ppm) and deuterated phenanthrene were obtained from Dr. Ehrenstorfer, GMBH. Dichloromethane and 2-propanol of GC grade were acquired to SDS and Riedel-de Haën respectively. All standards prepared from stocks solutions were placed in sealed flasks and refrigerated at $-4\text{ }^{\circ}\text{C}$ until their analysis.

2.2. Materials and instruments

The sampling system consists of a heated particle filter (25 mm $\times$ 100 mm Spirax Sarco) at $150\text{ }^{\circ}\text{C}$, a series of impinger bottles and a volumetric meter (KROMSCHOEDER, BK-G4). The first impinger bottle was empty and it acted as moisture collector, in which water and tar condensed from the producer gas. The next four impinger bottles contained 75 mL of 2-propanol at ambient temperature and the last two were in a bath at $-20\text{ }^{\circ}\text{C}$. The first had 75 mL of 2-propanol and the second was empty. For tar sampling, 100 L of gas were passed through the sampling system. Three types of samples were collected with this system: filters (F), aqueous solutions (Aq) and organic solutions (O).

For gas chromatography, an Agilent 6890 chromatograph with automatic sampler and coupled to an Agilent 5975 mass spectrometer was employed.

2.3. Analytical procedure

Filters were Soxhlet-extracted with 150 mL of 2-propanol for more than 8 h. The extract was concentrated with a rotary

evaporator to 10 mL. 2 mL of aqueous solution collected in the condenser were extracted with 2 mL of dichloromethane. Organic solutions did not need any extraction procedure and were analyzed without further preparation. All extracts and organic solutions were analyzed using GC/MS. 1 μ L volumes were injected. Operating conditions were as follows: initial oven temperature 90 °C, held 5 min, then increased at rate of 5 °C/min to 300 °C held 13 min; PTV injector had an initial temperature of 100 °C, held 0.10 min, then increased at rate of 150 °C/min to 350 °C, held 5 min; operation mode: splitless; carrier gas: He at flow rate 1 mL/min; capillary column HP-5MS (30 m $\times$ 0.25 mm $\times$ 0.25 μ m), detector operated in electronic impact mode (70 eV), detector mode: SIM, solvent delay: 5 min.

3. Results and discussion

3.1. Quality of analytical methodology

To determine the quality of the analytical results, the following parameters were determined: precision, linearity, sensitivity, selectivity and quantification and detection limits.

To obtain calibration curves, five standard solutions were analyzed in triplicate and the least squares linear fit was performed. Correlation coefficients obtained for all analytes were 0.999 except for naphthalene ($r^2 = 0.994$). Sensitivity defined as the slope of the calibration curve ranged from 0.74 L/mg for acenaphthene to 1.96 L/mg for pyrene. Detection limits ranged from 0.01 to 0.04 μ g/mL and quantification limits ranged from 0.04 to 0.12 μ g/mL.

Due to the characteristic of the samples it was not possible to find a reference material, but in the absence of reference materials bias can be investigated by spiking and recovery [6]. Spiking and recovery tests were performed for filter and aqueous samples. Three filters spiked with 50 μ L of PAHs mixture (2000–100 ppm) were extracted and concentrated like a real sample and four aqueous samples surrogated with 25 μ L of PAHs

mixture (2000–100 ppm) were extracted like non-surrogated samples. Recovery results with the standard deviation are shown in Table 1.

Table 1

Results of spiking and recovery studies. R: recovery, Na: naphthalene, Ac: acenaphthylene, Ace: acenaphthene, Fl: fluorene, Ph: phenanthrene, An: anthracene, Flu: fluoranthene, Py: pyrene, BaA: benzo(a)anthracene, Chr: chrysene, BbF: benzo(b)fluoranthene, BkF: benzo(k)fluoranthene, BaP: benzo(a)pyrene, IcdP: Indene(123-cd)perylene, DBahA: dibenzo(ah)anthracene, BghiP: benzo(ghi)perylene.

Analyte	R (%) filter samples	R (%) aqueous samples
Na	98 $\pm$ 6	115 $\pm$ 7
Ac	102 $\pm$ 5	81 $\pm$ 3
Ace	101 $\pm$ 8	90 $\pm$ 5
Fl	99 $\pm$ 7	70 $\pm$ 4
Ph	100 $\pm$ 3	99 $\pm$ 1
An	99 $\pm$ 3	45 $\pm$ 4
Flu	100 $\pm$ 6	63 $\pm$ 3
Py	90 $\pm$ 5	53 $\pm$ 3
BaA	67 $\pm$ 1	93 $\pm$ 7
Chr	67 $\pm$ 6	83 $\pm$ 6
BbF	91 $\pm$ 5	69 $\pm$ 2
BkF	82 $\pm$ 4	77 $\pm$ 4
BaP	80 $\pm$ 3	72 $\pm$ 3
IcdP	79 $\pm$ 5	67 $\pm$ 2
DBahA	76 $\pm$ 6	83 $\pm$ 2
BghiP	94 $\pm$ 3	61 $\pm$ 3

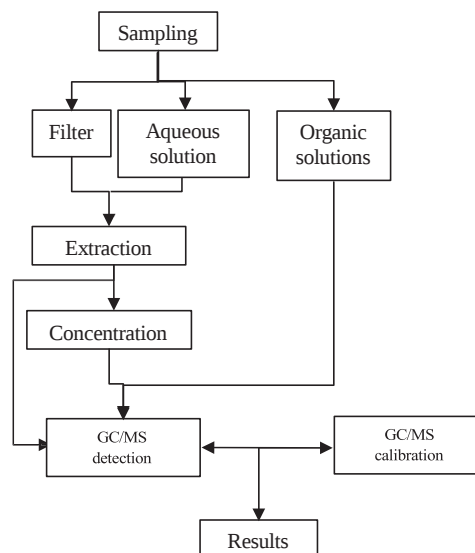


Fig. 1. Diagram of analytical procedure.

3.2. Estimation of uncertainty

To estimate the uncertainty of the results the ISO or bottom-up methodology was used.

This strategy consists to identify and quantify each individual source of uncertainty and then combines them to obtain the total uncertainty. This methodology involves four steps: specify measure, identify sources, quantify components and calculated combined uncertainty.

The tar concentration in the producer gas is the sum of the tar concentration in each type of sample. The analytical procedure scheme is presented in Fig. 1. The expressions used to calculate the concentration of an analyte into the gas stream, expressed in mg/N m³, are shown in Eqs. (1)–(3)

$$C_{aF} = \frac{C_{GC}V_e}{V_gR} \quad (1)$$

$$C_{aAq} = \frac{C_{GC}V_e}{V_gR} \quad (2)$$

$$C_{a0} = \frac{C_{GC}V_e}{V_g} \quad (3)$$

where C_{aF} , C_{aAq} , and C_{a0} are the analyte concentrations in the gas stream retained by each kind of sample; C_{GC} is the analyte concentration obtained from calibration in μ g/L; V_e is sample volume (50 mL for aqueous samples, 10 mL for filter extracts and 75 mL for organics solutions); V_g is the volume of gas sampled (100 L) and R is the recovery. All parameters in Eqs. (1)–(3) are main sources of uncertainty.

3.2.1. Estimation of the uncertainty derived from chromatographic analysis (u_{CGC})

This uncertainty is a combination of three principal uncertainties associated to: standards preparation, calibration curve and equipment repeatability.

In order to estimate uncertainty associated with the standards preparation two contributions were considered: uncertainty of initial standards concentration and uncertainty of the dilution procedure along all analytical process. The certificate values supplied by the manufacturer of PAHs showed an uncertainty of 0.5% for all compounds. So the uncertainty derived from the standard initial

concentration can be calculated with the expression (4). In Table 2

Table 2

Initial concentration of the standards (C_o) and the uncertainty associated (u_{C_o}) was shown.

Analyte	C_o (μg/mL)	u_{C_o} (μg/mL)
Na	1052	3.04
Ac	2103	6.07
Ace	1056	3.05
Fl	209.1	0.60
Ph	103.4	0.30
An	103.7	0.30
Flu	214.2	0.62
Py	96.9	0.28
BaA	104.4	0.30
Chr	104.1	0.30
BbF	210	0.61
BkF	104.1	0.30
BaP	107	0.31
IcdP	101.8	0.29
DBahA	207	0.60
BghiP	206.4	0.60

the initial concentration of the standards and the uncertainty associated was shown.

$$u_{C_o} = \frac{C_o 0.5\%}{\sqrt{3}} \quad (4)$$

where u_{C_o} is the uncertainty derived from the standard initial concentration and C_o is the standard initial concentration.

To estimate the uncertainty of the dilution procedure (u_{dil}) three main sources were considered: temperature, repeatability and volumetric material tolerance.

The contribution of the variations in the temperature (u_{dil1}) was estimated using a rectangular distribution within $\pm 5^\circ\text{C}$ and assumed that the coefficient of volume expansion of the material can be considered against the liquid depreciable. For organic liquids the coefficient of volume expansion (γ) considered was $1 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$ [7]. So the contribution of the variations in the temperature (u_{dil1}) was calculated with the expression (5) as

0.0029 mL.

$$u_{dil1} = \frac{V \Delta T \gamma}{\sqrt{3}} \quad (5)$$

The volumetric repeatability is obtained by the standard uncertainty from the weighing (five times) each volumetric material full of solvent ($u_{dil2} = 0.0032$ mL) and the tolerance of volumetric material was calculated through a triangular distribution within 0.01 mL as minimal division ($u_{dil3} = 0.0041$ mL). The uncertainty of the dilution was $u_{dil} = 0.0059$ mL and the relative standard uncertainty (u_P/C_P) of the standards preparation calculated with the expression (6) were 0.0066 for all compounds.

$$\frac{u_P}{C_P} = \frac{u_{C_o}^2}{C_o^2} + \frac{u_{dil}^2}{V^2} \quad (6)$$

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, usually the most important contribution is the random variations in the signal [7]. Therefore, this contribution can be calculated employing Eq. (7).

$$S = \frac{1}{n-2} \left(\sum_{i=1}^n (y_i - \hat{y}_i)^2 \right)$$

Table 3

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

Analyte	b	S	x_{pred} (μg/mL)	$\bar{x}$ (μg/mL)
Na	1.59	0.55	5.64	7.6
Ac	1.87	1.34	10.71	15.2
Ace	0.99	0.28	5.46	7.6
Fl	0.93	0.085	1.01	1.52
Ph	1.20	0.094	0.91	0.76
An	0.15	0.052	3.15	7.6
Flu	1.66	0.16	0.61	1.52
Py	1.56	0.062	0.91	0.76
BaA	0.092	0.12	11.11	7.6
Chr	1.67	0.077	0.095	0.76
BbF	0.95	0.24	1.15	1.52
BkF	2.03	0.14	0.34	0.76
BaP	1.14	0.043	1.11	0.76
IcdP	1.44	0.070	0.46	0.76
DBahA	0.81	0.10	0.88	1.52
BghiP	1.29	0.077	0.49	1.52

Uncertainty associated to the equipment repeatability (u_r) was calculated as standard uncertainty obtained from five repetitions

of the chromatographic measurement. In Table 4 is shown each uncertainty contribution and the combined uncertainty derived

from chromatographic analysis applying Eq. (8):

$$\frac{u_{C_{GC}}}{C_{GC}} = \sqrt{\frac{u_P^2}{C_P^2} + \frac{u_r^2}{C_r^2} + \frac{u_c^2}{C_c^2}} \quad (8)$$

where $u_{C_{GC}}$ is the uncertainty derived from chromatographic analysis, C_{GC} is the concentration chromatographically determinate, u_P is the uncertainty derived from standard preparation, C_P is the standard concentration, u_r is the uncertainty due to the equipment repeatability, C_r is the concentration used in the repeatability test, u_c is the uncertainty of linear least square calibration and C_c is the

medium concentration used in the calibration.

3.2.2. Uncertainty associated to sample volume (u_{V_e})

The uncertainty derived from the sample volume depends on the type of sample and has three sources: the tolerance of volumetric material (u_t) which is calculated through a triangular distribution ($u_t = \text{tolerance}/\sqrt{6}$), the repeatability (u_r) which is calculated as standard deviation and the temperature (u_T) which is calculated in the same manner described above (using Eq. (5)). Table 5 shows each contribution of the uncertainty and total

Table 4

Contributions and uncertainty of the chromatographic analysis. u_P/p : relative standard uncertainty of standards, u_C : uncertainty due to the linear least squares calibration, u_r : uncertainty due to the repeatability of the GC-MS, u_{GC}/GC : relative

standard uncertainty of the chromatography analysis.

$$u_c = \frac{S}{\sqrt{b^2 + \frac{p}{n} + \frac{\sum (x_i^2) - (\sum x_i)^2/n}{\sum (x_i^2) - (\sum x_i)^2/n}}} \quad (7)$$

where S is the standard error of the estimation; b is the slope; p is the number of repetitions to obtained C_0 and n is the number of points of the calibration curve.

Table 3 shows the parameters of Eq. (7) obtained from triplicates of the calibration curves.

Fl	0.0066	0.048	0.0092	0.034
Ph	0.0066	0.041	0.0047	0.055
An	0.0066	0.18	0.071	0.034
Flu	0.0066	0.051	0.012	0.040
Py	0.0066	0.020	0.0087	0.030
BaA	0.0066	0.71	0.20	0.096
Chr	0.0066	0.026	0.0069	0.081
BbF	0.0066	0.13	0.099	0.121
BkF	0.0066	0.037	0.028	0.097
BaP	0.0066	0.020	0.013	0.031
IcdP	0.0066	0.026	0.022	0.060
DBahA	0.0066	0.067	0.057	0.079
BghiP	0.0066	0.033	0.010	0.031

Table 5

Sample volume uncertainty for each type of sample.

	Filters	Aqueous solution	Organic solution
u_t (mL)	0.017	0.41	0.41
u_r (mL)	0.0034	0.031	0.095
u_T (mL)	0.029	0.030	0.22
u_{V_e} (mL)	0.034	0.41	0.47

uncertainty associated to sample volume, using expression (9), for each kind of sample.

$$u_{V_e} = \sqrt{u_t^2 + u_r^2 + u_T^2} \quad (9)$$

3.2.3. Uncertainty derived from gas volume (u_{V_g})

To measure the volume of the gas sampled (100 L) a volumetric meter was used. Manufacture specifications indicate that it has an accuracy of 0.5%, so the standard uncertainty can be calculated through a rectangular distribution ($u_{V_{g1}} = (0.005/\sqrt{3}) = 0.0029$ L). Not only is the equipment accuracy a source of uncertainty but also the variations on the gas temperature and pressure can be sources of uncertainty. The contribution of the variations in the temperature was estimated using a rectangular distribution within $\pm 15^\circ\text{C}$ and assume that the coefficient of volume expansion of the gas can be considered equal to the air at 20°C ($u_{V_{g2}} = (V \times \Delta T \times \gamma/\sqrt{3}) = 2.95$ L). The variation of pressure during the sampling was considered negligible. The combination of these contributions, considering both independent generates a final standard uncertainty (u_{V_g}) of 2.95 L.

3.2.4. Estimation of the uncertainty derived from liquid extraction of aqueous samples (u_R)

Five recovery experiments were carried out to evaluate the uncertainty of liquid extraction as uncertainty type A. Real samples were spiked with a standard solution, extracted and analysed in the same way that non-spiked ones. The uncertainty obtained ($u_{R_{\text{exp}}}$) included contributions from chromatographic analysis so this contribution must be subtracted to calculate the uncertainty associated to the liquid extraction (u_R). In Table 6 the results are presented.

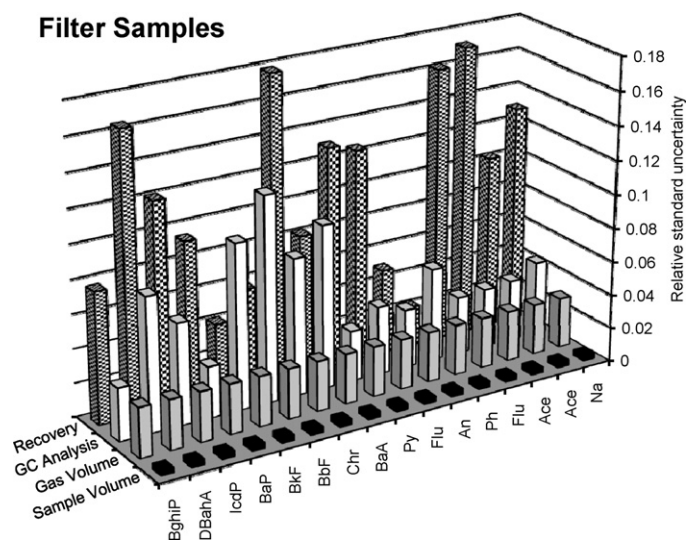
As seen in Fig. 2, the most important contributions to the overall uncertainty for aqueous samples come from the extraction, chromatographic analysis and gas volume measurement.

Table 6Relative standard uncertainties of chromatography analysis (u_{GC}/GC), sample volume (u_{V_e}/V_e), gas volume (u_{V_g}/V_g), recovery of aqueous samples (u_R/R) and recovery – extraction of filter samples ($u_{R+C}/R+C$).

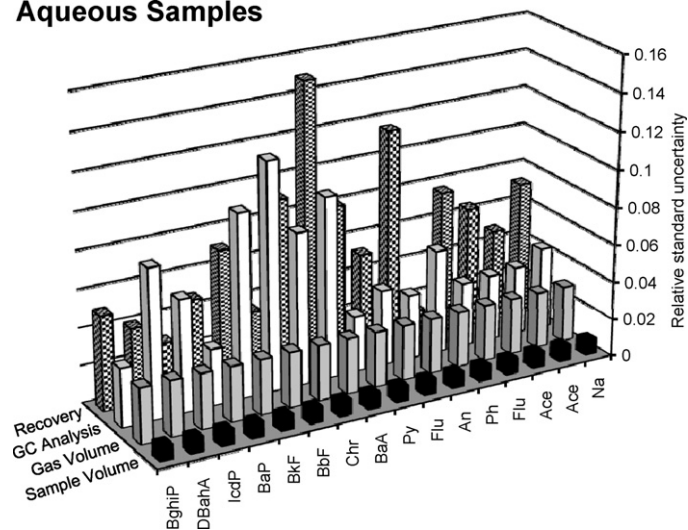
Analyte	u_{GC}/GC	u_{V_e}/V_e ^a	u_{V_e}/V_e ^b	u_{V_e}/V_e ^c	u_{V_g}/V_g	u_R/R	$u_{R+C}/R+C$
Na	0.043	0.0034	0.0082	0.0063	0.030	0.072	0.13
Ac	0.036	0.0034	0.0082	0.0063	0.030	0.049	0.10
Ace	0.035	0.0034	0.0082	0.0063	0.030	0.064	0.17
Fl	0.034	0.0034	0.0082	0.0063	0.030	0.076	0.16
Ph	0.055	0.0034	0.0082	0.0063	0.030	0.01	0.02
An	0.034	0.0034	0.0082	0.0063	0.030	0.115	0.05
Flu	0.040	0.0034	0.0082	0.0063	0.030	0.052	0.13
Py	0.030	0.0034	0.0082	0.0063	0.030	0.081	0.13
BaA	0.096	0.0034	0.0082	0.0063	0.030	0.149	0.08
Chr	0.081	0.0034	0.0082	0.0063	0.030	0.091	0.18
BbF	0.121	0.0034	0.0082	0.0063	0.030	0.03	0.06
BkF	0.097	0.0034	0.0082	0.0063	0.030	0.07	0.04
BaP	0.031	0.0034	0.0082	0.0063	0.030	0.048	0.09
IcdP	0.060	0.0034	0.0082	0.0063	0.030	0.03	0.12
DBahA	0.079	0.0034	0.0082	0.0063	0.030	0.04	0.16
BghiP	0.031	0.0034	0.0082	0.0063	0.030	0.050	0.08

^a Filter.^b Aqueous solutions.^c Organic solutions.

Filter Samples

**Fig. 2.** Diagram of relative standard uncertainty of each contribution for aqueous samples.

Aqueous Samples

**Fig. 3.** Diagram of relative standard uncertainty of each contribution for filter samples.

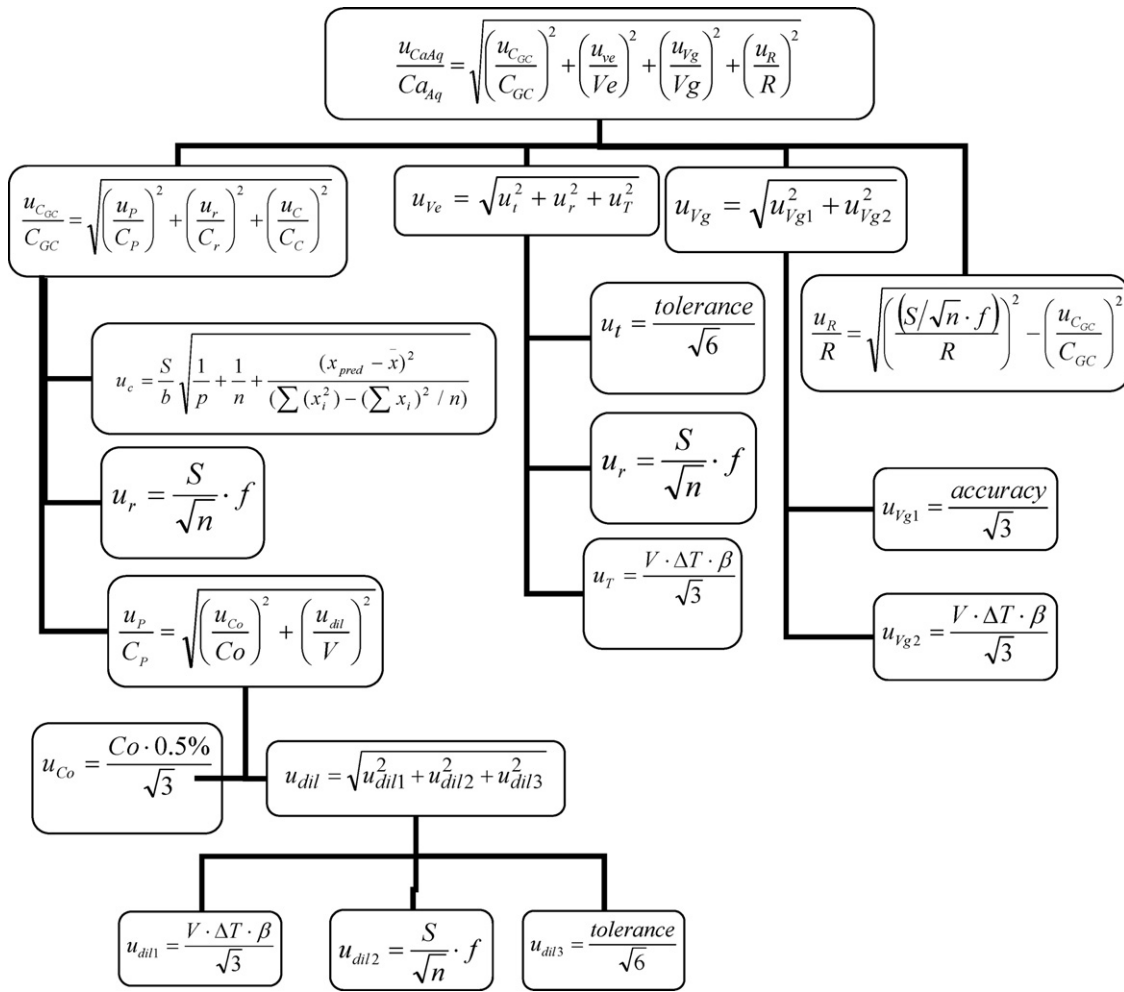


Fig. 4. Schematic for calculated uncertainty of naphthalene in aqueous samples.

3.2.5. Estimation of the uncertainty derived from filters extraction and concentration (u_{R+C})

The uncertainty associated with the Soxhlet extraction and concentration was assessed jointly like type A uncertainty. Four experiments were carried out with the same filters used to collect samples. Filters were spiked with analytes at similar concentrations than those found in samples. However uncertainty associated to this experiment (u_{exp}) included contributions from chromatographic analysis, so this contribution must be subtracted to calculate the uncertainty associated to the Soxhlet extraction and concentration (u_{R+C}). In Table 6 the results are presented.

In Fig. 3, each of the contributions to the overall uncertainty for filters samples are shown. Like in the case of aqueous samples, the most important contributions to the final uncertainty come from the steps of extraction–concentration, chromatographic analysis and gas volume measurement.

3.2.6. Calculating the combined uncertainty

To calculate the combined uncertainty the law of uncertainty propagation was applied (Eq. (10))

$$u_c(y) = y \cdot \frac{u(p)^2}{p^2} + \frac{u(q)^2}{q^2} + \dots \quad (10)$$

To make these calculations, all uncertainties were expressed as relative standards uncertainties (Table 6) and then combined

to obtain the combined uncertainty of each type of sample (Table 7).

To clarify the uncertainty calculations, an example with naphthalene in aqueous samples was shown in schematic way in Figs. 4 and 5.

Table 7

Uncertainty of each type of sample, global uncertainty and expanded uncertainty. u_{CaF} : combined standard uncertainty of filter samples, u_{CaAq} : combined standard uncertainty of aqueous samples, u_{CaO} : combined standard uncertainty of organic samples, u_{Ca} : total combined standard uncertainty, U: expanded total uncertainty.

Analyte	u_{CaF} (%)	u_{CaAq} (%)	u_{CaO} (%)	u_{Ca} (%)	U (%)
Na	14	9	5	17	35
Ac	11	7	5	14	28
Ace	18	8	5	20	40
Fl	17	9	5	20	39
Ph	7	6	6	11	22
An	7	12	5	15	30
Flu	13	7	5	16	32
Py	14	9	4	17	34
BaA	13	18	10	24	49
Chr	20	13	9	25	50
BbF	14	13	12	23	45
BkF	11	12	10	19	39
BaP	10	6	4	13	26
IcdP	14	7	7	17	34
DBahA	18	9	8	22	45
BghiP	9	7	4	12	24

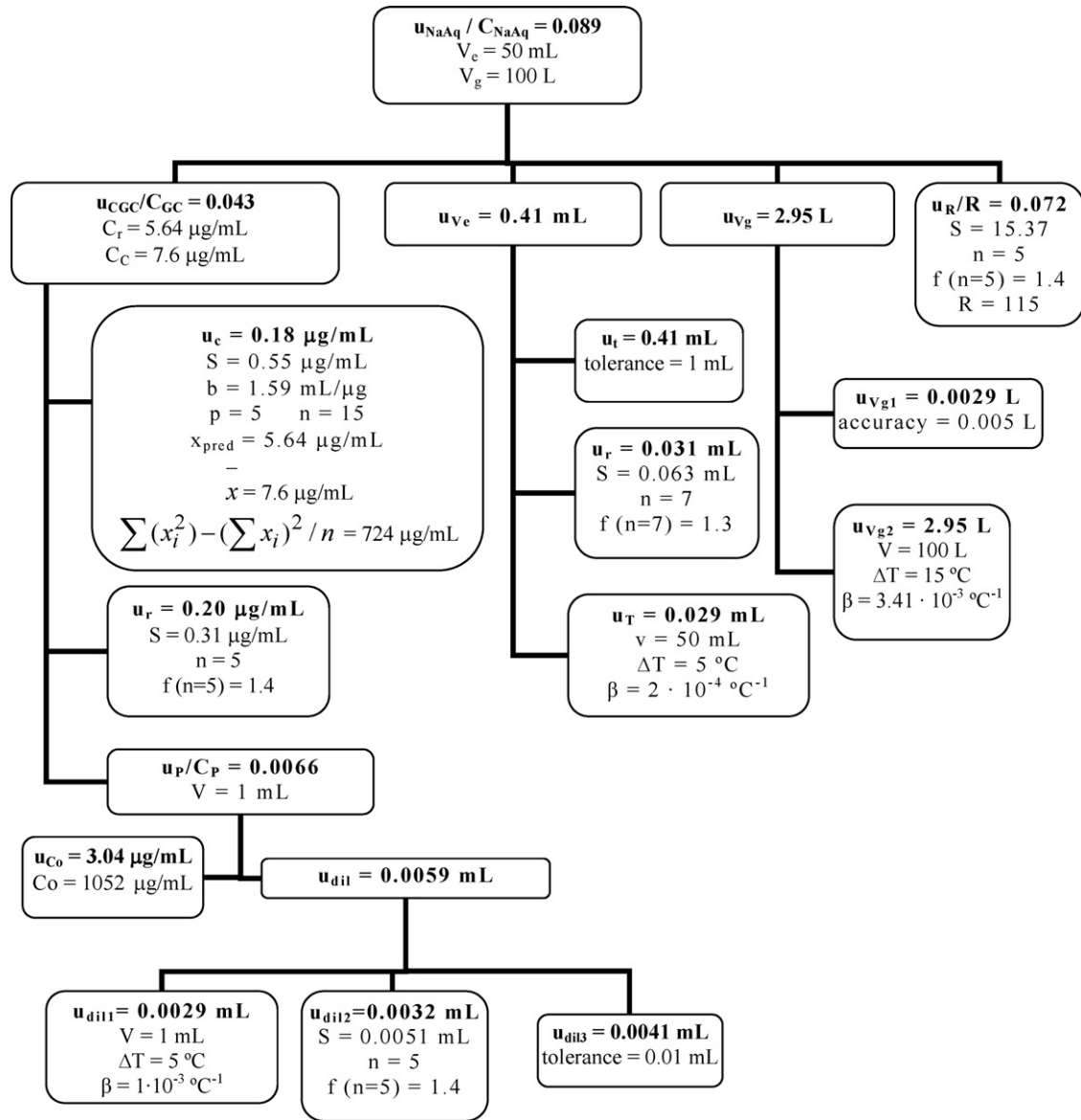


Fig. 5. Schematic with the result of naphthalene uncertainty calculations.

But the global uncertainty of the tar in the producer gas is the sum of the uncertainties of each kind of sample following the Eq. (11).

$$\frac{u_{C_a}}{C_a} = \sqrt{\frac{u_{C_{aF}}^2}{C_{aF}^2} + \frac{u_{C_{aAq}}^2}{C_{aAq}^2} + \frac{u_{C_{a0}}^2}{C_{a0}^2}} \quad (11)$$

Table 7 shows the combined uncertainty for each type of sample, the total combined uncertainty and the expanded uncertainty calculated using a coverage factor of 2 which gives a level of confidence of approximately 95%.

3.3. Application to real samples

To check one of the stages of gas cleaning, real samples from an atmospheric bubbling fluidised bed gasifier with a capacity of 100 kg/h of dried sewage sludge were analysed following the method described above. Table 8 shows the results obtained for

Table 8

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

Analyte	BF (mg/N m ³)	AF (mg/N m ³)
Na	33 (11)	15 (5)
Ac	10 (3)	3 (1)
Ace	0.6 (0.2)	0.3 (0.1)
Fl	4 (2)	1.1 (0.4)
Ph	13 (3)	3.4 (0.8)
An	4 (1)	0.7 (0.2)
Flu	9 (3)	0.6 (0.2)
Py	13 (4)	0.7 (0.2)
BaA	8 (4)	0.2 (0.1)
Chr	13 (7)	0.3 (0.1)
BbF	2 (1)	0.04 (0.02)
BkF	4 (1)	0.05 (0.02)
BaP	4 (1)	0.05 (0.01)
IcdP	1.3 (0.4)	–
DBaHA	0.3 (0.1)	–
BghiP	0.9 (0.2)	–

samples before and after the cleaner filter. Expanded uncertainty is shown in brackets.

Despite the great uncertainty of the results, the removal of tar in the filter is high enough to enable the analysis of the results for all compounds except for acenaphthene in which case the concentration in the gas is so low that no one can say that there is removal in the filter.

4. Conclusions

This work aimed at identifying the main sources of uncertainty associated to determination of main tar components (PAHs) including the expanded uncertainty.

From this study it may be concluded that the step which generates more uncertainty is the extraction stage. Filter samples show a large uncertainty due to the extraction and concentration steps.

Although uncertainties of individual samples have low values, the resulting global uncertainty is very high because

the procedure involves the addition of several types of samples.

To minimize the uncertainty in tar determination, other sampling methods must be studied, especially those that do not involve the segregation of the tar in different matrixes such as solid phase adsorption that allow the capture of tar in a single sample matrix.

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