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Short communication

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

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ABSTRACT

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.

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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 [5–9]. 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 [9–11] 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].

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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 Sigma–Aldrich 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/NH₂ 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 cm³ of gas is taken by pulling back the syringe plunger.

2.3. Analytical procedure

The analytes retained in the cartridges were extracted with 3 cm³ DCM. The extracts were analysed using a Hewlett Packard 5890 series II gas chromatograph coupled to a Hewlett Packard 5971A mass spectrometer. 1 mm³ volumes were injected. Operating conditions were as follows: initial oven temperature 60 °C, held for 1 min, then increased at 3 °C min⁻¹–105 °C, then increased at 8 °C min⁻¹–250 °C, then increased at 5 °C min⁻¹–260 °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 μm). 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).

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

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 cm³, V_g is the volume of the gas sampled in cm³ 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

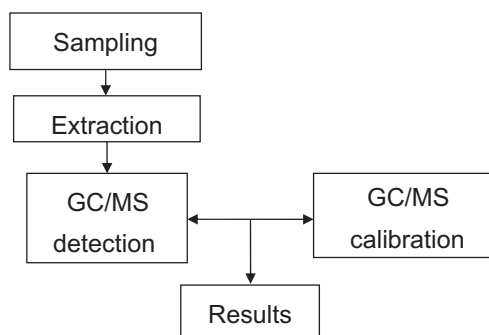


Fig. 1 – Scheme of the analytical procedure.

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