An evaluation of analytical quality for selected PAH measurements in ashes/particles from combustion of agricultural and forestry waste biomass

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The environmental measurements of organic compounds still require optimized analytical methods that reliably assess concentration results. This aspect is critical to avoid misunderstanding for behavior interpretation of pollutants in environment. It means it is necessary to continue providing information on quality of analytical data to provide results good enough (García-Alonso, 2011).

As part of a major project devoted to the development of a strategy for emission control and minimization of the combustion of waste biomass (CLEANBIOM), this work has been focused to the determination of selected PAHs by high performance liquid chromatography with fluorescence detection (HPLC/FD). Our main goals are based on minimizing analytical effort and assessing result reliability from ash/particulate matter analyses of real samples involved in the project.

Hence, from analyses of real samples (ashes and particulate matter) our objectives were to evaluate:

- Analytical protocol which has been simplified by using minimal aliquot weights, solvent volumes, handling and taking advantage of high selectivity of fluorescence detection.
- Proportional and constant bias to assess trueness.
- Intermediate precision of analytical results obtained.

Methodology

At Biomass Combustion Pilot Plant at CEDER/CIEMAT, samples of interest were taken from dust collected in purification system from measurement stations during the tests. Agitation of weighted aliquots was performed in closed tubes with 1.5 mL of dichloromethane for three times to assure recovery. Final volume of extract to analyze was 150 µL.

Seventeen PAHs were included for consideration and thirteen of them were quantified in most of the samples: the most volatile PAHs such as naphthalene, 1- methylnaphthalene, acenaphthene and fluorene were rarely quantified, so they were not considered for validation.

Results

The sum of PAHs ranged from:

- Ash sub-samples: 0.9 – 26 µg/g
- Particulate matter: 0.03-3.9 µg/filter

Heavier PAHs were the most abundant which reached concentrations ranged 2-3.5 µg/g and 0.07-0.50 µg/filter for ash and particulate matter, respectively.

For ash measurements, trueness was evaluated by checking proportional and constant bias as recommended Maroto et al (2007). Proportional bias was estimated by analysis of spiked sub-samples and calculating the pooled recovery. Constant bias was estimated with the Youden method by weighting 0.1 g and 0.2 g of sub-samples and analyzing them.

The preliminary results based on intermediate precision calculations (Eurachem/CITAC, 2012; Pantazopoulous, 2001) were very consistent, showing accuracy of over 20 and 30 % for ash and filter sub-sample, respectively. As expected, low levels of concentrations and volatility of the measured compounds increase dispersion in analytical measurements (up to 40%) (Figure1).

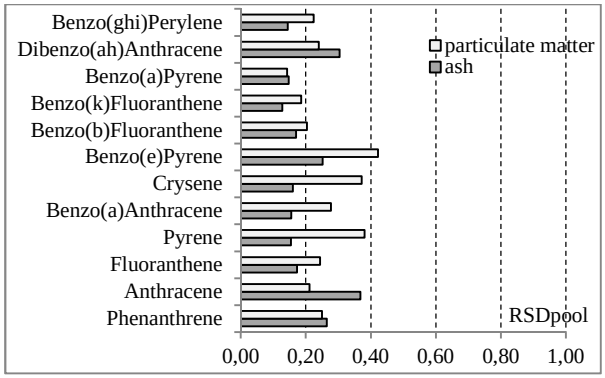

Figure 1 – Intermediate precision of analytical results deduced as pooled relative standard deviation (RSD_{pool}).

Conclusion

The proposed analytical method provides a reduction in extraction time, volume of solvents and sample weight which makes an easier, cheaper and faster method than classical extraction procedures for PAH analyses. This study can be considered of great utility for assessment of analytical quality in PAH determination in samples (ashes and particle matter) of waste biomass combustion.

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