

Paula Teixeira¹, Helena Lopes¹, Ibrahim Gulyurtlu¹, Nuno Lapa²

¹ LNEG-UEZ, Estrada do Paço do Lumiar, Ed.J, 1649-038 Lisboa, Portugal ² UNL-FCT-DCTB-UBiA, Quinta da Torre, 2829-516 Caparica, Lisboa

paula.teixeira@lneg.pt

Abstract

The estimation of uncertainties of measurements was applied to evaluate the recovery ratio of ash and potassium mass in a combustion system. The uncertainty of a measurement for different matrices, namely, coal, biomass, sand and ashes from different streams was based in internal quality control, proficiency tests (PT) or certified reference material (CRM) data. The intra-laboratorial precision and the trueness evaluation allowed to estimate the uncertainties of measurements and consequently to assess if the lack of closure in recovery ratios obtained can be justified by the uncertainties.

Introduction

The uncertainty allows to make a reliable evaluation of the recovery ratio of ash and K in a combustion system, and generally problems of mass recoveries can be justified by uncertainties. The current investigation was performed in a combustion system where the fuel used as input gives rise to four output ashes streams with different physical-chemical characteristics, namely, bottom ashes, BA, ashes from 1st cyclone, 1Cyc, ashes from 2nd cyclone, 2Cyc, and particulate matter, PM. Biomass and coal were used as fuel. Sand was used as fluidizing agent.

Methodology

Specification of the measurand

The measurands were the recovery ratio of ash mass and the recovery ratio of K during the combustion tests performed with biomass and coal, in a pilot fluidized bed scale installation.

$$RR_{Ash} = X_{Output_BA} + X_{Output_1Cyc} + X_{Output_2Cyc} + X_{Output_PM}$$

$$RR_K = X_{Output_BA_K} + X_{Output_1Cyc_K} + X_{Output_2Cyc_K} + X_{Output_PM_K}$$

Where:

$$X_{Output_XYZ_K} = M_{Output_XYZ} \times \%_{Ash_Ignited} \times C_{K_XYZ} \left((M_{Input_Fuel} \times \%_{Ash} \times C_{K_Ash_Fuel}) + (M_{Input_Sand} \times C_{K_Sand}) \right)$$

Identification of uncertainty sources

Uncertainty sources associated with the operations performed **outside the laboratory**: mass of fuel and sand input and mass of three ashes streams: BA, 1Cyc and 2Cyc.

Sources of uncertainty associated with operations performed **inside the laboratory**: fuel ash content, ignited ash from BA, 1Cyc and 2Cyc content, mass of PM, concentration of K in fuels, sand and the four ashes streams.

Quantification of uncertainty components

Uncertainty of operations performed **outside the laboratory** were estimated with base the resolution and repeatability of balances (uncertainty of calibration was not available).

Uncertainty of operations performed **inside the laboratory** were based in intra-laboratorial precision and trueness evaluation. In table 1 is presented the used expressions.

Table 1. Expressions to estimate the uncertainties of operations performed inside the laboratory

| | Precision Evaluation | Trueness Evaluation |
|--|---|---|
| Biomass Coal BA, 1Cyc, 2Cyc | R-Chart according ISO 8258 $u_{R-chart} = RSD = \bar{R}_m / 1.128$ Instrumental Acceptance Criteria (IAC) $u_{IAC} = Accep. Criteria / \sqrt{3}$ | Proficiency Tests $u(\bar{R}_m) = \bar{R}_m \times \sqrt{\left(\frac{s_{\bar{R}}}{\bar{R}_m}\right)^2 + (t(C_{Ref}))^2}$ |
| PM | Instrumental Acceptance Criteria (IAC) $u_{IAC} = Accep. Criteria / \sqrt{3}$ | Certified Reference Material $u(\bar{R}_m) = \bar{R}_m \times \sqrt{\frac{s_{obs}^2}{n \times C_{obs}} + \left(\frac{u(C_{CRM})}{C_{CRM}}\right)^2}$ |
| Sand | Replicate analysis $u_{Replicates} = RSD_{sand_replicates}$ Instrumental Acceptance Criteria (IAC) $u_{IAC} = Accep. Criteria / \sqrt{3}$ | Sample Spike $u(\bar{R}_m) = \bar{R}_m \times \frac{s_{\bar{R}}}{\sqrt{n}}$ |

Combination of standard uncertainty and expanded uncertainty

The uncertainty combined was estimated according to the law of uncertainty propagation.

$$u_c = \sqrt{u_{precision}^2 + u_{\bar{R}_m}^2}$$

The level of confidence used was 95%, a expansion factor of 2 was used.

$$U_c = 2 \times u_c$$

If a bias was statistically evidenced it was included in budget of uncertainties as suggested by IUPAC.

$$U = U_c + \Delta$$

Results

In table 2 is illustrated the ash and K recovery ratio values and uncertainties for the combustion tests performed with biomass and coal.

Table 2. Ash and K recovery ratio values and uncertainties

| Combustion Tests | $RR_{Ash} \pm U(RR_{Ash})$ (%) | $RR_K \pm U(RR_K)$ (%) |
|----------------------|--------------------------------|------------------------|
| Biomass (olive cake) | 103 ± 9 | 117 ± 46 |
| Coal Colombian | 99 ± 3 | 85 ± 40 |

The relative contribution of analytical determination of potassium and ash recovery ratio in the combustion system to the budget of uncertainty was evaluated and the results are presented in Fig.1.

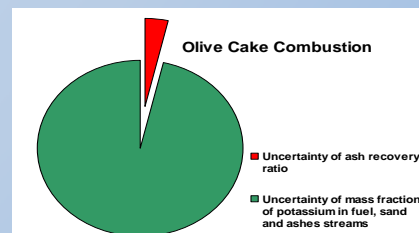


Figure 1. Relative contribution to the uncertainty of ash recovery ratio and mass fractions of K

In the analytical determination of potassium it was verified that the precision was the component that contribute more significantly to the budget of uncertainty as observed in Fig.2.

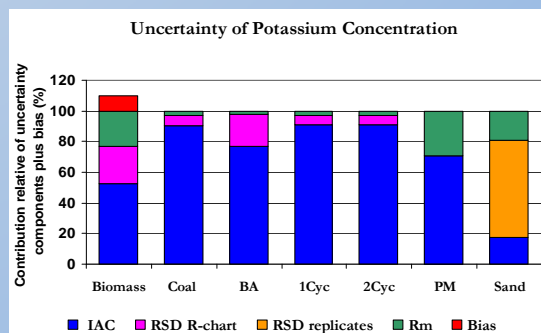


Figure 2. Relative contribution of different components of uncertainty plus bias

Conclusions

- The coal matrix presents values of uncertainty lower than biomass which is reflected in recovery ratios of different combustion tests
- The ash recovery ratio uncertainty do not contribute significantly to the uncertainty of potassium recovery ratio in combustion system
- In analytical determination of potassium the precision is the main component of uncertainty, the decrease of this component could be achieved if the instrumental acceptance criteria is reduced
- The uncertainty of ash and potassium recovery ratio includes a recovery of 100% which allow close the mass balance of the studied combustion system

Bibliography

Eurachem / CITAC Guide, Quantifying Uncertainty in Analytical Measurement, 2nd Edition, 2000.
M. Thompson, S. L. R. Ellison, A. Faigel, P. Willetts, R. Wood, "Harmonised Guidelines for the Use of Recovery Information in Analytical Measurement", IUPAC/ISO/AOAC International/ Eurachem, 2000.
Nordtest Tr 537, Handbook for calculation of measurement uncertainty in environment laboratories, 2nd Edition, 2004.