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MEASUREMENT UNCERTAINTY EVALUATION ACCORDING TO ISO 17025: LABORATORY OF MMI BOR, SERBIA

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ABSTRACT
One of the important elements to satisfy claims of ISO/IEC 17 025:2006, specifically set forth in paragraph 5.4.6.2, is to assess the uncertainty of testing and/or calibration. For determination of coal technical analysis uncertainty we were used certified reference materials (CRM) benzoic acid and coal marked GBW 11107k. Potential laboratory reference material (RM) is also used for comparison of measurement results and uncertainty in order that, after a sufficient number of measurements and statistical analysis, could be used as a laboratory RM. The results showed that, as well as CRM, also selected potential laboratory RM could be applied to determine the uncertainty of technical analysis of coal, which is significantly cheaper for laboratory work, and is accordance with ISO 17 025.
Keywords: CRM, RM, Benzoic acid, Uncertainty, Coal.

1. INTRODUCTION
Coal is a solid fuel, which dates from ancient times. Technical analysis of coals is actually determination of moisture, ash, combustible and volatile matter, coke residue, C-fix, total sulfur and gross and net calorific values. For technical analysis of coal, are used analytical samples, or samples prepared with specific granulometric composition [1-3]. Chemical analysis of coal is related to determining composition of ash, which includes determination of SiO_2, BaO, Fe_2O_3, TiO_2, Al_2O_3, CaO, MgO, Mn_3O_4, Na_2O_3, SO_3 and phosphorus.
In early 1999 was published international standard ISO/IEC 17 025, which contains general requirements for the competence of testing and/or calibration laboratory. ISO/IEC 17 025 has replaced previous standards EN 45 001 and ISO/IEC Guide 25, who was applied in laboratory work [4]. Last edition of this standard dates from 2006. Application of this standard is important for each laboratory to the accreditation and implementation of management systems in their work. About application and importance of this standard lots of data can be found in the literature [5-7].
Reference materials can be divided into two groups: certified reference materials (CRM) and laboratory (working) reference materials (RM) [8-10]. CRM is a reference material, accompanied by a certificate, whose one or more values of properties confirmed by procedure that establishes traceability for the exact realization of the unit in which are expressed values of characteristics and for

which each certified value is accompanied with measurement uncertainty, with specified confidence level. RM is a working laboratory material available in laboratory, characterized by homogeneity and stability of material which can provide repeatable results, at the same time low-cost and as such are eligible for the laboratory.
Within the estimation of measurement uncertainty, there are two concepts [4]: Nordtest (QC model) and EURACHEM (Full scale model).
The aim of Nordtest principle is to present the most important parameters that contribute to measurement uncertainty: the bias (inaccuracy) and reproducibility (imprecision) of results, while Eurachem includes all the features that influence the measurement uncertainty.
This paper presents the results of using CRM: benzoic acid Ref.: 33 045, with heat of combustion (26461±40)Jg^{-1}, benzoic acid Ref.: C723, heat of combustion (26456±8)Jg^{-1} and coal marked GBW 11 107K in order to test the uncertainty of laboratory equipment for the technical analysis of coal. Also, for checking the possibility of using laboratory RM in the future laboratory work, the results were compared using the same equipment under the same conditions and with the same person, for certified reference materials, and also for potential laboratory RM.

1. EXPERIMENTAL

To determine the gross calorific value of coal according to the standard norms [11] we have used the calorimeter, model C5000, IKA Werke manufacturers from 2008. Calorimeter was used at a constant volume according to the adiabatic type bomb calorimeter method. Calorimeter is equipped with a software program IKA ® C5000 Control, Version 2.21, and a bomb calorimeter C5010-01.490589 with the following characteristics: Ps=230bar, PT=330bar, TS=50°C and V=0,260L. To determine the net calorific value of coal to the same standard norms, it is necessary to determine the hydrogen content in coal [12]. In that purpose we used elemental analyzer, model "vario MACRO cube" from 2010.
For the determination of moisture in the analytical sample of coal by methods described in the standard norms [13,14], was used the dryer with nitrogen stream, model RVT 500, manufacturer Heraus - Hanau, with temperature and time controller NIGOS, model 1012P, factory no.: 7404617 . To determine the ash by the method described in the standard norms [15], volatile matter of coal to the standard norms [16], and total sulfur by the method described in standard norms [17], we used the annealing furnace, type TR f2, manufacturer Iskra. All weight measurements was carried out on an electronic balance, type “Sartorius BP 61S”, manufactured in 2008 with accuracy 0.0001g. To determine the accuracy of laboratory equipment and evaluation of measurement uncertainty were used CRM, benzoic acid powder, manufacturer AlliedSignal Riedel-de Haen, Ref.: 33 045, heat of combustion (26 461±40)Jg^{-1}, (ELINCS-Nr.: 200-618-2), which will be called the BA(1) in this work, also pelleted benzoic acid, IKA Werke manufacturers, Ref.: C723, heat of combustion (26 456±8)Jg^{-1}, (Id. Nr.: 32 430 00), which will be called the BA(2) and coal combustion heat GBW 11 107K (27.54±0.19)$MJkg^{-1}$ which will be called the GBW. As a potential laboratory RM for technical analysis of coal, it is used coal named ASSM. For studying of results was used technique of known values and comparative research technique.

2. RESULTS AND DISCUSSION

By comparing the experimentally obtained results with exact values given in the reference material certificate, accuracy of the method can be determined. Accuracy refers to a particular analytical result and hence represents a combination of systematic and random errors. Systematic error (bias) is the difference between the average value of a large number of measurement results and the exact value of CRM. For determination of correct values were used certified reference materials BA(1), BA(2) and GBW (table 1). To determine the uncertainty of the results were used Nordtest (1) and Eurachem (2) approach.

3.1 Nordtest

Nordtest approach represents a practical approach in the evaluation of methods and laboratories measurement uncertainty. This approach aims to present the most important parameters that contribute to measurement uncertainty, which are: reproducibility (imprecision - random error) and bias (deviation - a systematic error).

Table 1. Certified values of the Gross Combustion Entalphy (GCV) of CRM (benzoic acid BA(1) Ref.: 33045 and BA(2) Ref.: C723, and coal (GBW) and their mean values obtained by calorimeter IKA Werke, Model C5000 and bias

CRM name	GTV CRM*	$\overline{GTV}$ CRM**	bias
BA(1) (Jg^{-1})	26 461±40	26 503	42
BA(2) (Jg^{-1})	26 456±8	26 465	-9
GBW ($MJkg^{-1}$)	27.54±0.19	27.54	0

GTV CRM* - certified or true values of CRM, GTV CRM** - mean value of measurement results

Within the Nordtest concept exist two ways of calculating measurement uncertainty: Method and Method B.

In the method A, combined uncertainty u_c (%), calculated using formula (1). Double value of u_c (%) presents an expanded measurement uncertainty U (%) with a confidence level of 95%, formula (2).

$$u_c(\%) = \sqrt{(U(Rw))^2 + (U(Bias))^2} \quad (1)$$

$$U(\%) = 2 \times u_c(\%) \quad (2)$$

3.2 Eurachem

Eurachem access or full scale model represents a principle that includes everything affecting measurement uncertainty of the results, and as such provides a more accurate range of the estimated results then Nordtest. Parameters that contribute to complete estimatation of measurement uncertainty of coal technical analysis results are:

1) Sampling of coal and sample handling
2) Equipment (balance, calorimeter, the normal courts, standard solutions, pipette)
3) Human factors and environment (housing and environmental conditions).

Table 2. Results summary of combined uncertainty u_c *(%)* and her extended value *U(%)* for Nordtest concepts, methods A and B, and Eurachem method

	Nordtest				Eurachem	
	Method A		Method B		Method	
	u_c(%)	U(%)	u_c (%)	U(%)	u_c (%)	U(%)
1BA	0.61	1.23	0.23	0.46	0.62	1.24
ASSM	-	-	0.24	0.48	-	-

Table 2 are given overview of the results of measurement uncertainty of combustion heat for CRM BA(1) and a potential laboratory RM ASSM. The results of the measurement uncertainty heat of combustion for CRM BA(1) are, for comparison, processed by methods A and B of Nordtest concept.

Based on the results of Nordtest concept (Table 2), it is noted that the measurement uncertainty of CRM BA(1) according to the method A provides higher value than method B. These values are expected, given that the method A provides more accurate results of uncertainty then method B whose uncertainty value is directly calculated from the standard deviation using the same values of benzoic acid heat of combustion (Table 1).

3. CONCLUSION

The results showed that, as certified reference materials, also and selected laboratory RM could be applied for estimating uncertainty of measurement of technical analysis of coal, which is significantly cheaper for laboratory work then CRM, and that is in accordance with ISO 17 025 standard.

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