

## ROUND ROBIN ON BIOMASS FUELS

Thore von Puttkamer, Sven Unterberger, Klaus R.G. Hein  
Institute for Process Engineering and Power Plant Technology (IVD)  
Pfaffenwaldring 23  
70550 Stuttgart, Germany

Phone:+49-711/6853565, Fax:+49-711/6853491,e-mail:puttkamer@ivd.uni-stuttgart.de

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### INTRODUCTION

In order to optimise the use of biomass as a fuel it is essential to have reliable information about its chemical composition. Therefore, it is of great significance to have useful methods for detecting the complete composition of the fuel. By means of Round Robins the commonly used methods can be evaluated and rated.

### OBJECTIVES

The data gained from the Round Robin shall provide a representative overview of the common methods for biomass characterisation used in the laboratories. It will give detailed information about all analysing steps (sample preparation, digestion methods, and analysis). The evaluation will cover in first place the interlaboratory scattering of results. Laboratories using similar methods of analysis will be gathered and evaluated separately. Due to the fact that no reference samples for biomass are available it will not be possible to assess the accuracy of the analytical data.

### IMPLEMENTATION

Two fuel samples of wood and straw were investigated in the Round Robin. The fuels were milled and homogenised by an independent laboratory and then checked for homogeneity by analysing for some major elements (C,N,S,K,Fe). In the Round Robin the probes were analysed for 35 parameters by 39 German and European laboratories. All participating laboratories were free to choose the analytical methods they are used to, only recommendations concerning available experience and possible problems that might occur were supplied. Moreover, the laboratories were free to use several different methods in parallel to compare the obtained results. In order to be able to compare the different methods, the laboratories should fill in a detailed questionnaire to clearly describe each step of preparation, digestion, and analysis itself. Based on this information a comparison of the influence of each single analysis step was possible.

### EVALUATION

The classical evaluation of a Round Robin is based on ISO 5725. The assumption for using this standard is the Gaussian distribution of the data. A normal distribution is based on random mistakes scattering around the accurate value. In a Round Robin where each laboratory was recommended to use its own well proven analytical methods the interlaboratory mistakes will be systematic [1]. In this Round Robin the gained data is very inhomogeneous and therefore, a few data may have a big influence on the location parameters.

Consequently, a distribution free, robust method based on Hampel was used for statistical evaluation. This method does without elimination of so called outliers, which are weighted instead making the results less sensitive to extreme single values [2].

In order to illustrate the statistical calculations the results are shown in evaluation diagrams. Some of the terms mentioned can be defined as follows:

"Wiederholstandardabweichung",  $V_r$ , corresponds to the mean value of all intralaboratory standard deviation  $S_r$ , divided by the "robust" mean value.

"Vergleichstandardabweichung",  $V_R$ , corresponds to the mean value of the interlaboratory standard deviation  $S_R$ , divided by the "robust" mean value.

The values measured by the laboratories are represented in the diagrams by bars. The centreline of each bar shows the robust mean value, the standard deviation corresponds to the distance between the centreline and the outside bounds of the bar.

### RESULTS

As an example for using biomass as a fuel the analysis results for chlorine and ash content that are important for the combustion and slagging/fouling behaviour in furnaces are presented.

KCl in the fuel could be released as KCl or converted into HCl, Potassium silicate and  $K_2SO_4$ . At combustion temperature KCl is released into the gas phase and condenses at the heat surfaces at lower temperatures. Condensed KCl on tube surfaces could form low melting eutectics, leading to an increased corrosion rate [4].

The ash content affects the ashing device and the ash disposal as well as the concept and the cleaning of the heat exchanger.

Figure 1 shows the evaluated chlorine contents of the straw sample. The robust mean value of all laboratories is 1263 mg/kg (db), the range between the single mean values ranges from 745 mg/kg (db) up to 2391 mg/kg (db).

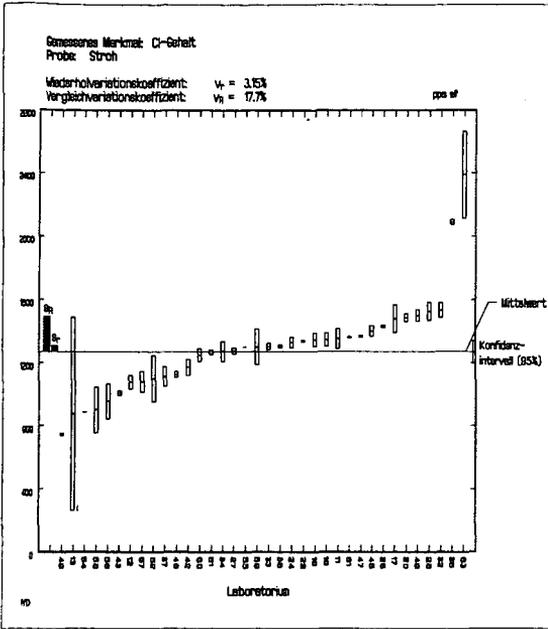


Figure 1: Chlorine in straw

In order to evaluate some single laboratory values the sample preparation, digestion and measurement procedures are shown in Table 1 and 2. Some of the results can be explained as follows:

- Preashing the sample will lead to a loss of volatile matters (Lab 49)
- Using Eschka-mixture (Labs 12, 37) is also not recommended for Cl detection, because volatiles will be lost when putting the probe for 1h in an 675°C heated muffle furnace. This was also reported by [3].

- The low temperature and low pressure of the "Wurzschmitt"-Digestion (Lab 58) may lead to bad results
- Due to a single analysis the results from Lab 54 are not considered.

In order to go one step further, the laboratories were divided into several groups of similar digestion methods. This shows whether the analysis results will be more comparable for laboratories using comparable digestion methods. **This is no classification or benchmarking of the laboratories.**

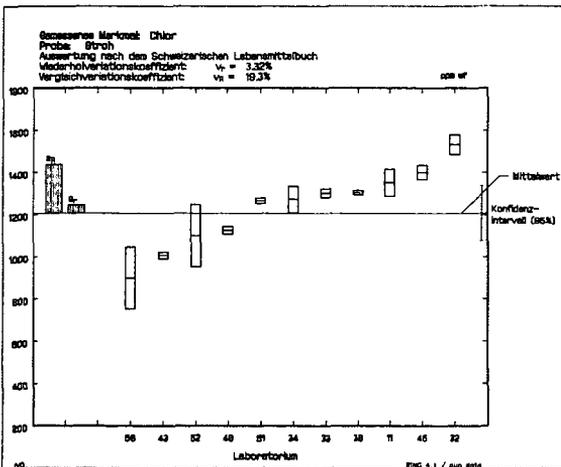


Figure 2: Chlorine in straw analysed by reduced methods

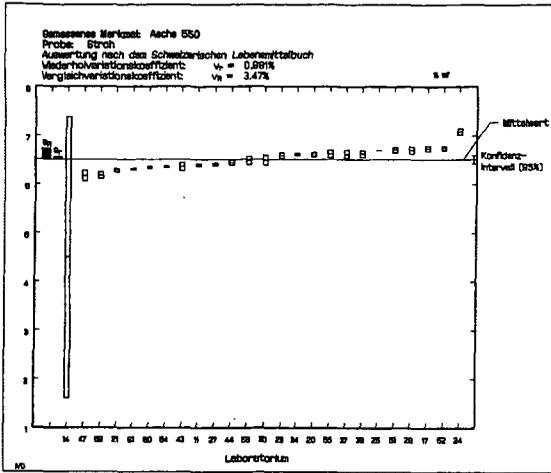


Figure 3: Ashcontent of straw at 550°C

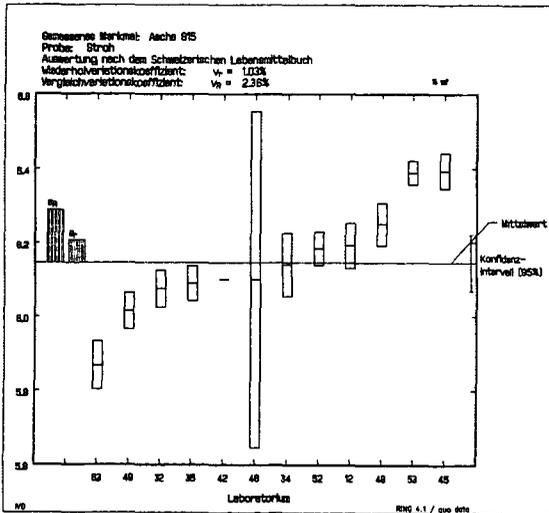


Figure 4: Ashcontent of straw at 815°C

## DISCUSSION AND CONCLUSIONS

One of the major problems when analysing biomass is the non-homogeneity of the fuel and therefore, the collection of a representative probe. The reason for "outliers" is often the small sample-mass taken for the digestion.

Comparing the results from different laboratories using suitable methods for analysing chlorine in the fuel it can be seen that the values scatter in a range of  $\pm 25\%$  around the robust mean value although they were using very different methods. Even digesting the sample by eluting it with water shows very good results. This confirms the assumption that chlorine in Biomass is mostly inorganically bound, whereas the organically bound part is very small. The elution method facilitates to use larger sample quantities for the digestion, with which a better homogeneity can be reached. Reducing the possible digestion methods does not lead to a better comparability of the results. This underlines the previously mentioned problem of the non-homogeneity of the fuel. The ash content of the fuel is strongly connected to the ashing temperature since at higher temperatures more volatile matters are released. The amount of volatiles in biomass (>75%) is very high compared to coal ( $\approx 35\%$ ). It is recommended that ash content should be determined at 550°C, because the volatile elements in a combustion plant condense in the fly ash and therefore must be considered in the ash balance.

Figure 2 shows laboratories using a combustion method collecting the combustion products in an alkali solution.

This makes it clear that reducing the analysis methods for chlorine detection does not lead to more comparable results.

Due to the free choice of analytical methods the ash content was determined in a temperature range of 550°C up

to 900°C. Figure 3 and 4 show the measured results.

The high standard deviation of Laboratory 14 in figure 3 can not be explained. The results from other labs scatter in a range of  $\pm 7\%$  around the robust median value of 6,5% (db). The methods used are all based on the principle of ashing the probes till constant weight. They only differ in sample preparation (milled, unmilled, preashed, or humidified). The ash content determined at 815°C shown in Figure 4 has a mean value of 6,18% (db), which is significantly lower than the 550°C values.

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Table 1: Analysis Methods

Lab	Preparation	Amount	Digestion	Method	Lab	Preparation	Amount	Digestion	Method
		[mg]					[mg]		
11	1000	1100	03b	12	43	1005	300	03b	19
12	1000	1100	05	12	45	1000	20	02e	20
13	1000	200	02d	06	46	1000	20	02d	20
17	2300		03c	12	47	1000	1000	14	06
20	1000	5000	12c	06	48	1000	250	07	06
22	1000	500	20	12	49	1000	500	04	12
24	1000	10000	13	06	51	1000	700-800	03a	06
25	1303	5500	21	14	52	1000	100-200	17	06
27	1000		20	06	54	1002	1000	03c	06
29	1004		21	14	56	1000	400-600	03a	12
32	1000	400	03a	06	57	1000	1000-2000	07	12
33	2302	2-10	02e	12	58	1000	100	16	06
34	1001	15000	03b	06	59	1000	220	03c	06
35	1003	200	03a	06	60	1001	220	03c	06
36	1000	800	02	06	61	1001	1000	14	06
37	2300	1100	05	12	63	1000	130	03a	06
42	1000	2000	04	06					

Table 2: Method-Code

Digestion		Analysis					
2	Combustion in Oxygen	6	IC				
3	Calorimetric Bomb	12	Titration AgNO <sub>3</sub>				
4	Wickbold	14	XRF				
5	Eschka	19	Ion Sensitive Electrode, ISE				
7	Eluting with HNO <sub>3</sub>	20	Mikrocoulometer				
12	Ashing						
13	Aqueous Solution (hot) 10g/250 ml		<b>Chemicals</b>				
14	Aqueous Solution (hot) 5g/250 ml	a	Alkali Solution and H <sub>2</sub> O <sub>2</sub>				
16	Wurzschmitt	b	Alkali Solution				
17	Grote-Kreker	c	In Water				
18	Melting Digestion	d	In Aqueous H <sub>2</sub> O <sub>2</sub> -Solution				
20	Aqueous Solution	e	In Acid and Acetate - Solution				
21	Pellet						
<b>Sample Preparation</b>							
1	As recieved	0	20°	0	Air	0	No extra milling
2	dried	3	105°	1	N <sub>2</sub>	1-5	Extra milling

## REFERENCES

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