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Bio-Norm II

Pre-normative research on solid bio-fuels for improved European standards
SPECIFIC TARGETED RESEARCH OR INNOVATION PROJECT
PRIORITY [6-1] – Sustainable energy systems



Contribution to the final conference

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UNIVPM – Università Politecnica delle Marche

SLU – Swedish University of Agricultural Science

Revision 1

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Revisions

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EVALUATION OF METHODS FOR SAMPLING OF SOLID BIOFUELS

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ABSTRACT: Designed sampling experiments were carried out on six different biofuel materials. The aim of the project was to assess the bias that might be introduced when samples are taken from static heaps (for example containers or vehicles) instead of from moving streams, and to define the number and size of increments needed to provide a representative bulk sample. The results showed that bias between the sampling methods was obtained only for a few parameters, in particular parameters where different particle sizes can segregate i.e. particle size distribution of wood chips and mechanical durability in pellets. Individual variances for sub-lots, increments and sub-sample tests were estimated using Analysis of Variance (ANOVA). These variances were then used to determine the minimum number of increments needed to obtain a specified, required precision.

Keywords: BioNorm, solid biofuels, sampling, increment number, bias

1. INTRODUCTION

In the recently-completed BioNorm project, statistically designed sampling experiments were carried out in Sweden with three kinds of wood fuel – sawdust, wood chips from forestry residues consisting of side branches and tops discarded in the tree felling operation and wood pellets in which the moisture content, particle size distribution and ash content were determined. In Denmark similar experiments were carried out with straw bales in which moisture, ash and chloride content were analysed.

Therefore, WP I of the EU-project BioNorm II will extend the already completed work by applying broadly the same methodology to a second selection of materials and test methods, including solid biofuels that are specially relevant for Southern Europe (e.g. agricultural residues from the production and processing of olives and grapes) as well as some others that are of general interest across the EU (other kinds of wood chips and bark). Wood pellets represent the highest grade of solid

biofuel, and the market for them is developing rapidly. Chemical and physical analyses of biofuels are always afflicted with measuring uncertainty also named measuring error. This measuring error may be divided into two types, namely systematic error or bias, and experimental error. Bias affect the accuracy (how close the average of the analytical result is to the “true value”), and is often caused by a single factor like erroneous calibration, inappropriate analytical method, incomplete dissolution of the sample, etc. This error gives rise to an analytical result that is always too low or too large compared to the “true result” and should always be eliminated as far as possible.

Experimental error on the other hand is due to several factors where each factor has small impact on the result

and may affect the result in both positive and negative direction. Examples of such factors are variations in humidity, ambient temperature, pipette volumes, etc. This type of error does not influence the accuracy of the analytical result as the bias does. Instead the experimental error affects the precision, which is the distribution of the analytical results around the “true value”. A low precision means that the results from repeated analyses have a large spread around the “true value” and vice versa. Experimental errors cannot be eliminated, but can be handled by suitable statistical methods.

The objectives of the sampling experiments in this paper were to assess the relative bias of the two studied sampling methods for solid biofuels, heap sampling and conveyor sampling, and to derive recommendations on how to decide the sizes and numbers of sampling increments needed to obtain an accepted sampling error.

2. EXPERIMENTAL

2.1 Experimental design

The experimental design used in this investigation is a nested (hierarchical) design described in [1].

Six different biofuel materials were studied in the sampling experiments, namely olive residue, grape residue, bark from Scots pine, wood chips from Norwegian spruce stem wood including bark, 8mm pellets from stem wood of Norwegian spruce including bark and 6mm pellets from whole trees of beech.

Five lorry loads of olive and grape residue were both sampled from a heap and from a falling stream at the end of a moving conveyor, respectively. From each sub-lot, four increments of three different increment sizes (10L, 5L and 2L) were taken by both methods.

Two sub-samples of each increment were then tested for moisture, ash, nitrogen, and seven major elements (Al, Ca, Mg, Na, P, Si and K).

The wood chips were sampled both from a falling stream at the end of a moving conveyor and from the formed heap. From each sub-lot, four increments of three different increment sizes (10L, 4L and 2L) were taken by both methods. Two sub-samples of each increment were tested for moisture, ash, and particle size distribution.

Five lorry-loads of bark were sampled from the heap and from a stopped conveyor, respectively. From each sub-lot, four increments of three different increment sizes (20L, 10L and 5L) were taken by both methods. Two sub-samples of each increment were tested for moisture, ash, and gross calorific value.

The 6mm pellets were sampled either from a heap formed by collecting pellets from 10 pellets sacks or by random collection of pellet sacks from a conveyor during production. For each method, four increments of three different increment sizes (8L, 4L and 2,5L) were taken. Two sub-samples of each increment were tested for moisture, ash, and mechanical durability.

The 8mm pellets were sampled both from a falling stream at the end of a moving conveyor and from the formed heap. From each sub-lot, four increments of three different increment sizes (8L, 4L and 2,5L) were taken by both methods. Two sub-samples of each increment were tested for moisture, ash, and mechanical durability.

2.2 Statistical analyses

2.2.1 Evaluation of bias

No method of sampling biofuels is considered to be a reference method, so the data can be used only to assess the bias of one method relative to another.

The bias is calculated by using a paired comparison design, where the difference between the mean values of the two sampling methods for each sub-lot and increment size is calculated. The mean value of these differences is then tested by the Student's t-test ($\alpha = 0.05$) for the hypothesis that the difference is not significant different from zero. If the mean of the differences is significant different from zero there is a bias between the sampling methods, otherwise not. The bias testing was also performed for the three increment sizes separately. To ensure that the significant test is valid, the difference values were tested for normality with $\alpha = 0.05$. In addition, a graph was constructed where the average of the conveyor sampling results for each sub-lot was plotted against the corresponding heap sampling results. If there is no bias between the sampling methods, a relatively even distribution of the points on both sides of the diagonal line in the graph should be seen for each sample size.

2.2.2 Evaluation of variances

Analysis of variance (ANOVA)

Basic information on the variability between sub-lots, increments and sub-sample tests due to sampling was provided by Analysis of Variances (ANOVA).

From the individual analytical results of the sub-samples A and B, y_{bst} , the average of each increment, \hat{y}_{bs} , was calculated. The averages of the increments were then used to calculate the average of each sub-lot, \hat{y}_b , and finally the grand average, \hat{y} , was calculated from the results of all sub-samples A and B.

The values for \hat{y} , \hat{y}_b , \hat{y}_{bs} and y_{bst} were then used together with the number of sub-lots N, the number of increments I and the number of sub-sample test T for the calculation of Sum of Squares (SoS) for the sub-lots, the increments and the sub-sample tests according to table 2.2.2.1

Table 2.2.2.1 Formulas for calculation of Sum of Squares (SoS).

	SoS	DoF
Sub-lots	$IT\sum(\hat{y}_b-\hat{y})^2$	N-1
Samples	$T\sum\sum(\hat{y}_{bs}-\hat{y}_b)^2$	N(I-1)
Test	$\sum\sum\sum(y_{bst}-\hat{y}_{bs})^2$	NI(T-1)

These SoS were then divided by the Degrees of Freedom (DoF) to give the Mean Square (MS) of the sub-lots, the increments and the sub-sample tests, respectively.

From the MS-values the individual variances σ_N^2 , σ_I^2 , σ_T^2 and the corresponding standard deviations s_N , s_I , s_T for the sub-lots, the increments and the sub-sample tests were estimated from the formulas (1) to (3).

$$MS_N = IT \sigma_N^2 + T \sigma_I^2 + \sigma_T^2 \quad (1)$$

$$MS_I = T \sigma_I^2 + \sigma_T^2 \quad (2)$$

$$MS_T = \sigma_T^2 \quad (3)$$

Significance tests of variances

Significance tests of differences in variances between increment sizes were performed on Mean Square-values since these have well defined Degrees of Freedom. The differences in MS between the increment sizes were tested for their significance by using the F-distribution with $\alpha = 0.05$. If no significant difference is found between increment sizes within a sampling method an average of the variance may be calculated and the differences between the methods are then tested for their significance as before. If there is a significant difference in variances between increment sizes an average value cannot be calculated and the significance test of the difference between sampling methods has to be performed for the individual increment sizes.

Repeatability

For the analytical methods where a general analysis sample is used for the determination, a repeatability standard deviation was calculated. This was accomplished by repeating the analysis 5-6 times for one single general analysis sample. The result was used to assess the significance of the repeatability of the analytical method compared to the overall analytical variability.

3 RESULTS

3.1 Evaluation of bias

No bias between the sampling methods was found for olive residue except for the 2L-increments of Aluminium and Magnesium, where the heap sampling showed higher values than the conveyor sampling (see figure 3.1.1). The t-values were 3.3 and 3.7 for Al and Mg, respectively compared to a t_{crit} of 2,78.

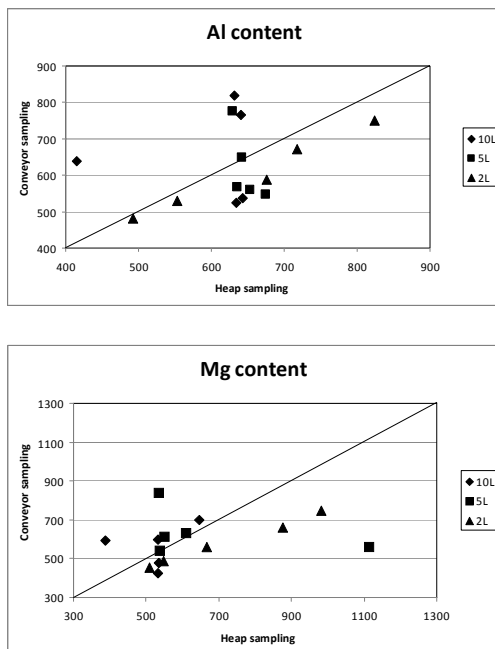


Figure 3.1.1 Test of bias between sampling methods for aluminium and magnesium in olive residue by plotting conveyor sampling vs. heap sampling. The unit is mg/kg DM.

For grape residue a bias between the sampling methods was found for the 2L increment of potassium, where the conveyor sampling gave higher potassium content than the heap sampling (see figure 3.1.2). The t-value was 5.78 compared to a t_{crit} of 2,78. In all other cases no difference between the sampling methods was found.

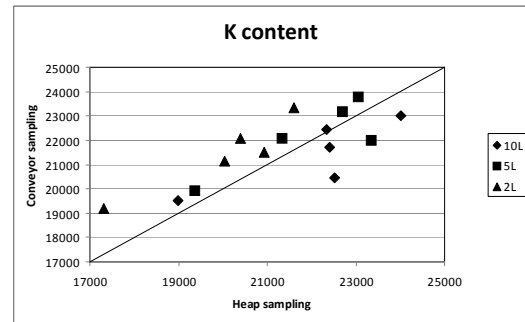
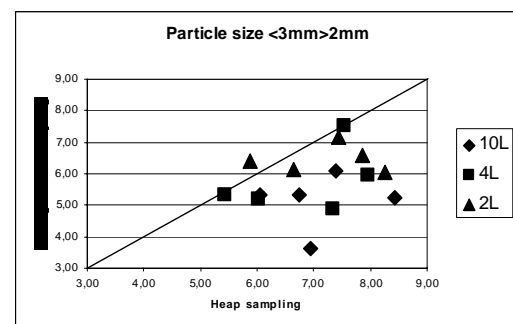
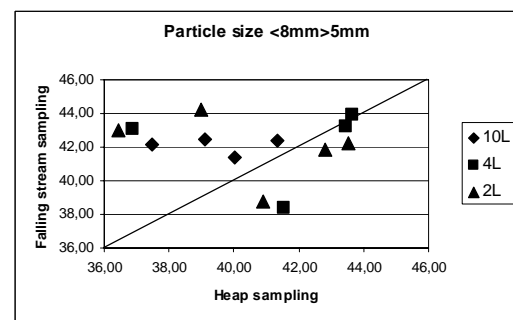
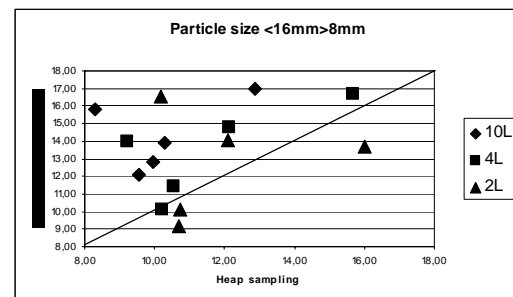


Figure 3.1.2 Test of bias between sampling methods for potassium in grape residue by plotting conveyor sampling vs. heap sampling. The unit is mg/kg DM.

No bias between the sampling methods was found for the moisture content and ash content in wood chips. For the particle size distribution, on the other hand, a pronounced bias is found which is significant for the 10L increment size (see figure 3.1.3). From the graphs one can see that the largest particle sizes are overrepresented in the conveyor sampling while the smallest particle sizes are overrepresented in the heap sampling.



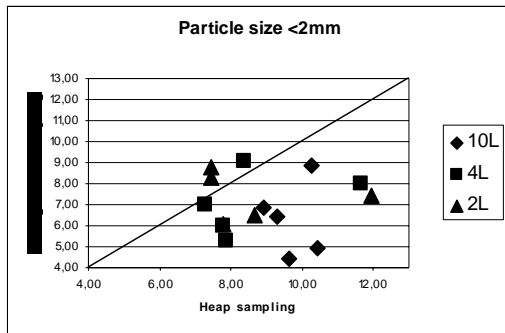


Figure 3.1.3 Test of bias between sampling methods for particle size distribution in wood chips by plotting conveyor sampling vs. heap sampling. The unit is % DM.

A significant bias between the sampling methods for the mechanical durability was observed for all increment sizes for the 8mm pellet material. The t-value was 4,94 compared to a t_{crit} of 2,14. The result is shown in figure 3.1.4.

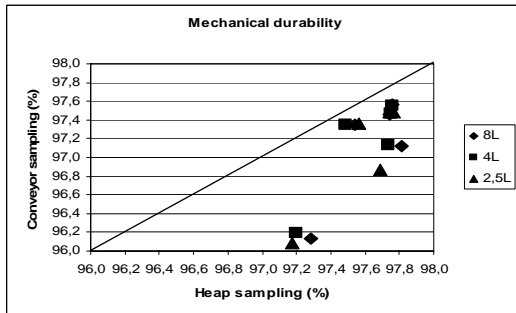


Figure 3.1.4 Test of bias between sampling methods for mechanical durability in 8mm pellets by plotting conveyor sampling vs. heap sampling. The unit is %.

3.2 Evaluation of variances

For bark, wood chips and the pellet materials easy interpretable results for most analytical parameters have been obtained with small differences in variance both between increment sizes and sampling methods. For the olive and grape residue a much more complicated situation was observed with differences in variance between both increment sizes and sampling methods that in many cases was contradictory. This was true especially for the major metallic elements. In table 3.2.1 the individual “pure” variance for moisture and ash content for the various biofuel materials are summarized according to equations (1) to (3).

Table 3.2.1 Individual variances for sub-lots (σ^2_N), increments (σ^2_I) and sub-sample tests (σ^2_T).

Biofuel	Moisture (%)			Ash (%)		
	σ^2_N	σ^2_I	σ^2_T	σ^2_N	σ^2_I	σ^2_T
Bark	3,12	4,89	0,68	0,383	0,026	0,019
Wood chips	1,98	10,5	0,05	0,027	0,023	0,000
Pellets (8mm)	0,80	0,15	0,00	0,005	0,000	0,000
Pellets 6(mm)	0,00	0,01	0,01	0,000	0,000	0,007
Olive residue	0,12	0,10	0,02	0,832	0,658	0,527
Grape residue	6,06	0,74	1,88	0,198	0,519	0,202

4. DISCUSSION

4.1 Bias

No explanation has been found for the bias between heap and conveyor method when sampling aluminium and magnesium in olive residue, and potassium in grape residue, even if a small increment size is more sensitive to inherent heterogeneity of the biofuel material. The bias found for particle size distribution and mechanical durability for wood chips and 8mm pellets, respectively, is probably caused by segregation of different particle sizes in the heap.

4.2 Variances

An explanation to the odd behaviour of grape and olive residue might be the high degree heterogeneity of these materials.

4.3 Calculation of number of increments

The minimum number of increments to be taken from a lot or a sub-lot of a biofuel material to obtain a specified precision of the analytical parameter of interest depends on the heterogeneity of that parameter in the material in combination with the design of the sampling method. Some energy companies are analysing every single sub-lot, i.e. lorry load, and uses the result for the payment of each individual sub-lot of the biofuel. Other companies are using the average of a number of sub-lots, i.e. all lorry loads during one month, as the bases for the analyses of the original lot. Still other companies are dealing with much larger lots, i.e. shipments of 30 000 tonnes, which are usually divided into sub-lots of about 2 500 tonnes from which the sample increments are collected. This means that specific formulas for the various sampling situations are needed for the calculation of number of increments. Below two sampling designs are described in detail

together with the corresponding formula for the calculation of minimum increment number.

4.3.1 Analysis of one sub-lot (10-50 tonnes)

The sub-lot, i.e. a lorry load, is sampled by a specified number of increments. These increments are aggregated to give a laboratory sample which is sent to the analytical laboratory. This laboratory sample is then divided into a number of sub-samples, which are then analysed for the specified parameter.

The uncertainty of this analysis may be calculated by the following equation

$$e = t^* \sqrt{(\sigma_I^2/I + \sigma_T^2/T)} \quad (4)$$

where e is the uncertainty of the analysis; σ_I^2 and σ_T^2 are the increment and the sub-sample variances, respectively; I is the number of increments, T is the number of sub-sample tests and t is the Student's value for $\alpha = 0.05$ which is approximately 2.

By rearranging equation (4) the minimum number of increments needed (I) to obtain a specified precision (e) for a specified parameter is determined by the increment variance (σ_I^2) and the sub-sample variance (σ_T^2) of that parameter together with the number of sub-samples analysed (T) according to the following formula

$$I = \frac{4\sigma_I^2}{e^2 - \frac{4\sigma_T^2}{T}}, \text{ where} \quad (5)$$

I = minimum number of increments needed for the required precision

e = required precision (twice the standard deviation) for the specified analytical parameter

σ_I^2 = increment variance for the specified parameter

σ_T^2 = sub-sample variance for the specified parameter

T = number of sub-sample tests for the specified parameter

The required precision, e , and the number of sub-samples, T , may be decided by the producer and the customer in agreement. The values for σ_I^2 and σ_T^2 may be determined by the company for the material under study or may be determined from earlier experience.

In addition, by constructing a graph where the precision, e , is plotted versus the number of increments, I , for certain values of sub-sample tests, the minimum number of increments for a certain required precision may also be determined.

To demonstrate the effect of the relation between σ_I^2 and σ_T^2 on the sampling error, three different situations are described in figure 4.3.1.1.

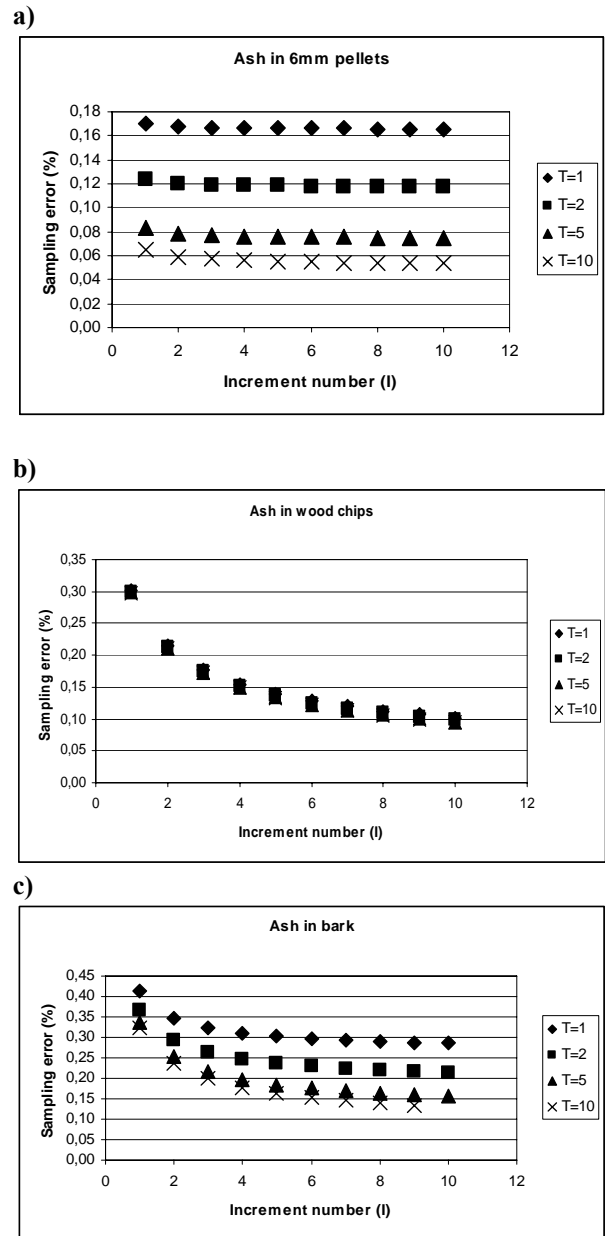


Figure 4.3.1.1 The effect of the relation between σ_I^2 and σ_T^2 on the number of increments needed to obtain a required precision. a) ash in 6mm pellets, b) ash in wood chips c) ash in bark,.

As can be seen from figure 4.3.1.1 the relation between the increment and the sub-sample variance is of great importance how the increment number influence the sampling error. For ash in 6mm pellets, where $\sigma_T^2 \gg \sigma_I^2$ the number of increments have almost no effect on the sampling error.

On the other hand, for wood chips where $\sigma_T^2 \ll \sigma_I^2$ the increment number alone determine the sampling error without influence of the number of sub-sample tests.

For ash in bark where σ_T^2 and σ_I^2 are of the same order both the increment number and the number of sub-sample tests determine the sampling error.

4.3.2 Analysis of several sub-lots (10-50 tonnes each)

A number of sub-lots, i.e. all lorry loads during one month, are sampled by a specified number of increments per sub-lot. The increments from each sub-lot are aggregated to give a laboratory sample which is sent to the analytical laboratory. Each laboratory sample is then divided into a number of sub-samples, which are analysed for the specified parameter. The final result is obtained by averaging the results from each sub-lot which is then an estimation of the studied parameter in the original lot.

The uncertainty of this analysis may be calculated by the following equation

$$e = t^* \sqrt{(\sigma^2_N/N + \sigma^2_I/NI + \sigma^2_T/NT)} \quad (6)$$

where e is the uncertainty of the analysis; σ^2_N , σ^2_I and σ^2_T are the sub-lot, the increment and the sub-sample variances, respectively; N is the number of sub-lots averaged, I is the number of increments, T is the number of sub-sample tests and t is the Student's value for $\alpha = 0.05$ which is approximately 2.

As in section 4.3.1, the minimum number of increments needed (I) to obtain a specified precision (e) for a specified parameter is determined by the sub-lot variance (σ^2_N), the increment variance (σ^2_I) and the sub-sample variance (σ^2_T) of that parameter, respectively, together with the number of sub-lots averaged (N) and the number of sub-samples analysed (T) according to the following formula

$$I = \frac{4\sigma^2_I}{Ne^2 - 4\sigma^2_N - \frac{4\sigma^2_T}{T}}, \text{ where}$$

I = minimum number of increments per sub-lot needed for the required precision

N = number of sub-lots averaged

e = required precision (twice the standard deviation) for the specified analytical parameter

σ^2_N = sub-lot variance for the specified parameter

σ^2_I = increment variance for the specified parameter

σ^2_T = sub-sample variance for the specified parameter

T = number of sub-sample tests for the specified parameter

The required precision, e , the number of sub-lots, N , and the number of sub-samples, T , may be decided by the producer and the customer in agreement. The values for σ^2_N , σ^2_I and σ^2_T may be determined by the company for the material under study or may be determined from earlier experience.

In a similar way as in section 4.3.1, the minimum number of increments for a certain required precision may be determined by constructing a graph where the precision, e , is plotted versus the number of increments, I , for certain numbers of sub-sample tests.

Even in this case the relation between the individual variances determine the influence of the increment number on the sampling error. As can be seen from table 3.2.1 for ash content in bark, that the sub-lot

variance is much larger than both the increment variance and the sub-sample variance. This means that the increment number and the number of sub-sample tests are of little importance for the uncertainty of the overall analytical result.

For the ash content in wood chips and 6mm pellets the increment number and the number of sub-sample tests are the most important factors for the sampling error.

5 CONCLUSIONS

The following conclusions can be drawn from this work:

- Bias between the sampling methods was obtained only for a few parameters, in particular particle size distribution in wood chips and mechanical durability in 8mm pellets

- Bark, wood chips and the pellet materials showed small differences in variance both between increment sizes and sampling methods.

- For the olive and grape residue a much more complicated situation was observed with differences in variance between both increment sizes and sampling methods that in many cases was contradictory. This discrepancy was probably caused by a high heterogeneity of the materials.

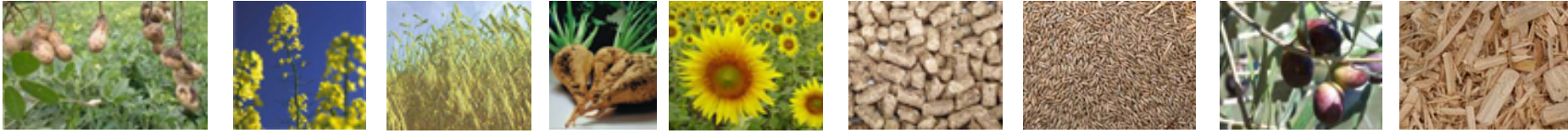
- The individual sub-lot, increment and sub-sample variances estimated by the ANOVA method was used to evaluate the minimum increment number needed to obtain a specified required precision.

6 REFERENCES

- [1] Box, G.E.P., Hunter, W.G. & Hunter, J.S., STATISTICS FOR EXPERIMENTERS. An Introduction to Design, Data Analysis and Model Building. John Wiley & Sons, Inc. 1978, p. 571-583.

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BioNorm 2

Pre-normative research on solid biofuels for improved European standards

Final conference

4th November 2009

UFZ – Centre for Environmental Research,
Leipziger KUBUS



Evaluation of methods for sampling and sample reduction of solid biofuels

Results from BioNorm II, Working Package I

Dr. Robert Samuelsson

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Leipzig, November 4, 2009



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Disposition

- Introduction
- Objectives of BioNorm II, WP I
- Description of experimental design
- Choices of statistical methods
- Results
- Conclusions



BioNorm (2002 – 2004)

Materials

- Sawdust from pine and spruce
- Logging residue from pine and spruce
- Pellets from stemwood of pine
- Straw from wheat



BioNorm (2002 – 2004)

Analytical parameters

- Moisture, ash and particle size distribution in the wood materials
- Moisture, ash and chloride content in the straw material



Sampling scheme

Analytical error

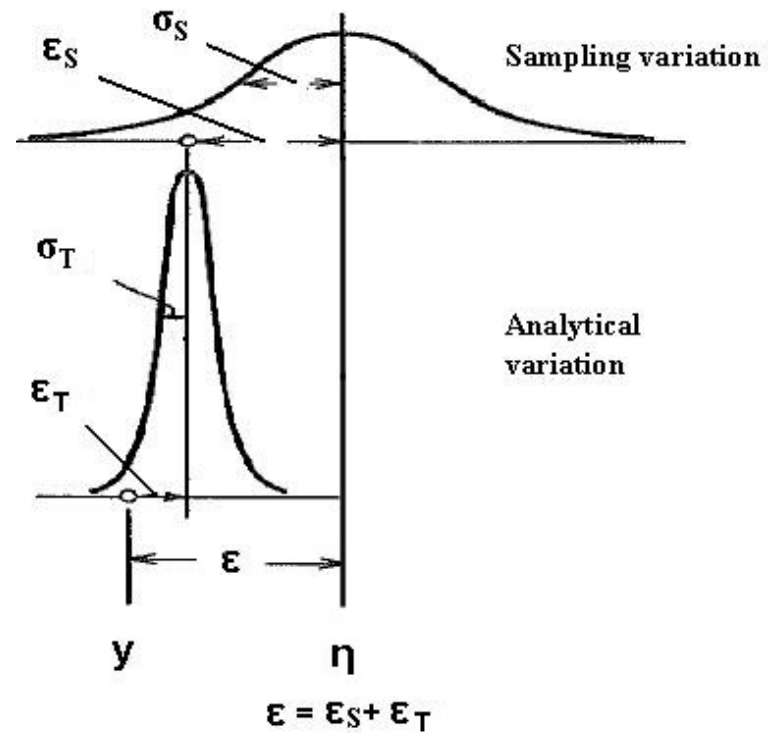
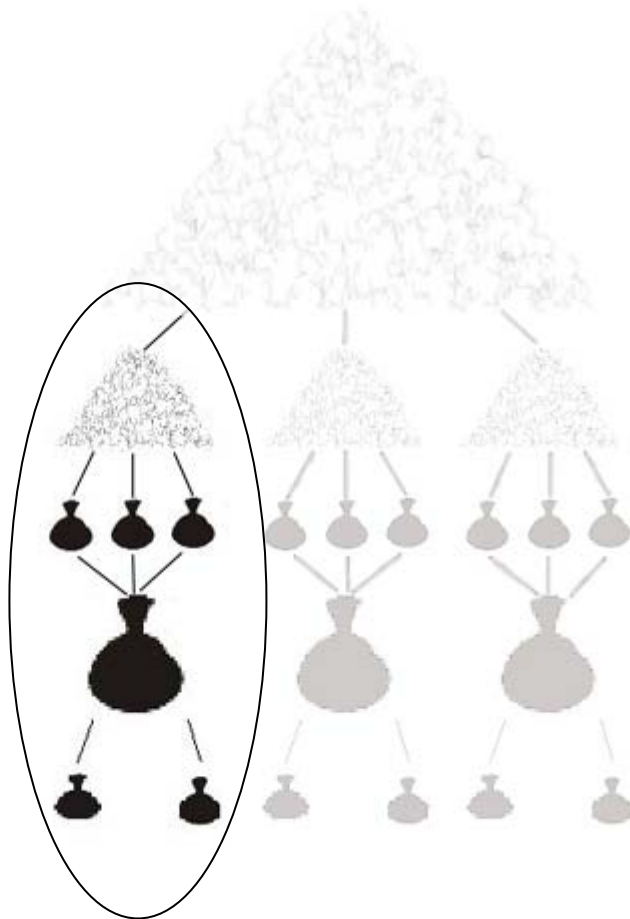
Lot

Sub-lot

Increments

Laboratory sample

Sub-sample



Objectives of BioNorm II, WP I

- Studies of other biofuel materials and analytical parameters
- Assess the bias introduced in samples taken from heap compared to moving streams
- Define the numbers and size of increments needed to provide a representative bulk sample
- Assess methods for sample reduction



Materials

- Bark of pine (< 45mm)
- Wood chips (< 16 mm)
- Pellets (6 and 8 mm diameter)
- Olive residue (< 3 mm)
- Grape residue (< 16 mm)



Experimental design for sample reduction

- 16 subsamples
- 2-3 sample reduction methods
- 2-4 test methods/material
- 1 determination/subsample and test

∑ 64-192 determinations/material

	Reduction methods	Test methods
Bark	Coning & quartering, long pile	Moisture, ash, gross calorific value
Wood chips	Coning & quartering, long pile, riffle box	Moisture, ash, particle size distribution
Pellets	Coning & quartering, long pile, riffle box	Ash, mechanical durability
Olive residue	Coning & quartering, long pile, riffle box	Moisture, ash, Potassium, Nitrogen
Grape residue	Coning & quartering, long pile, riffle box	Moisture, ash, Potassium, Nitrogen



Results from sample reduction

- The table shows the reduction method with the highest precision for each material and parameter

Material	Moisture	Ash	Gross calorific value	Particle size distribution	Nitrogen	Potassium	Mechanical durability
Olive residue	LP	RB	-	-	RB	C&Q	-
Grape residue	RB	C&Q	-	-	LP	LP	-
Bark	C&Q	LP	LP	-	-	-	-
Wood chips	RB	RB	-	RB	-	-	-
Pellets (8mm)	-	RB	-	-	-	-	LP
Pellets (6mm)	-	RB	-	-	-	-	RB

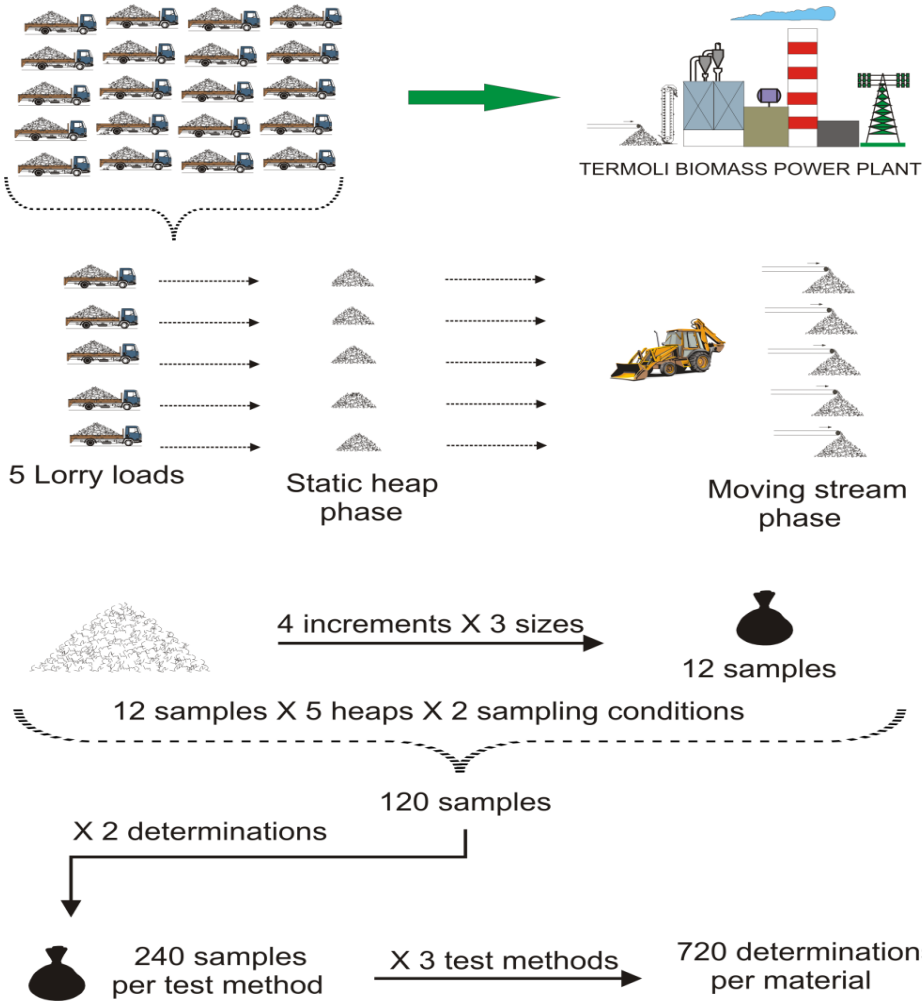


FUNCTIONAL DIAGRAM OF SAMPLING PROCEDURE IN BIOMASS POWER PLANT

EXPERIMENTAL DESIGN FOR SAMPLING

- 5 sub-lots
- 2 sampling methods
- 4 increments
- 3 increment sizes
- 3-10 test methods
- 2 determinations/increment and test methods

Σ 720-2400 determinations/material



Choices of methods

	Sampling methods	Test methods	Increment sizes	Reduction method
Bark	Heap, stopped conveyor	Moisture, ash, gross calorific value	20L, 10L and 5L	Coning & quartering
Wood chips	Heap, falling stream	Moisture, ash, particle size distribution	10L, 4L and 2L	Riffle box
Pellets (6 and 8mm diameter)	Heap, bag/ falling stream	Moisture, ash, mechanical durability	8L, 4L and 2,5L	Coning & quartering/ riffle box
Olive residue	Heap, falling stream	Moisture, ash, 8 major elements (Al, Ca, Mg, Na, P, Si, K, N)	10L, 5L and 2L	Riffle box
Grape residue	Heap, falling stream	Moisture, ash, 8 major elements (Al, Ca, Mg, Na, P, Si, K, N)	10L, 5L and 2L	Coning & quartering



Evaluating bias between sampling methods

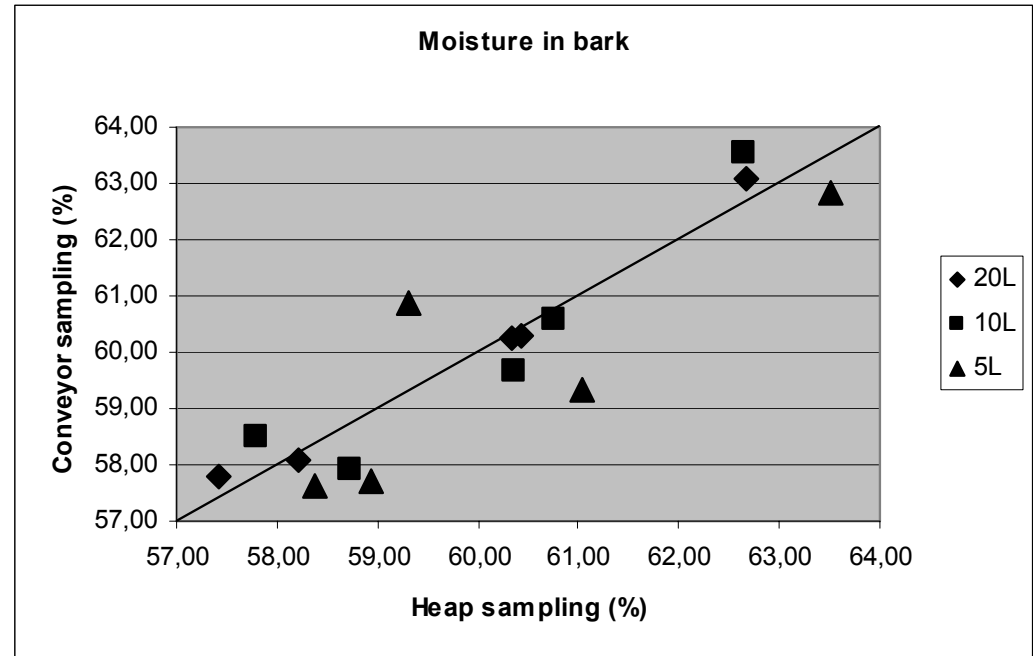
- Paired comparison design of differences
- Significance test of average of differences
- Graphical presentation



Bias between sampling methods

Moisture in bark:

	Heap	Conv- eyor	Diff
20L	62,68	63,08	-0,40
	58,22	58,06	0,16
	57,41	57,79	-0,38
	60,42	60,28	0,14
	60,34	60,24	0,11
10L	62,65	63,55	-0,90
	58,73	57,90	0,83
	57,79	58,48	-0,69
	60,37	59,66	0,71
	60,76	60,58	0,18
5L	63,51	62,84	0,67
	58,95	57,71	1,23
	58,39	57,63	0,75
	61,05	59,34	1,70
	59,31	60,85	-1,55
Average	60,04	59,87	0,17
Std.dev.	1,875	2,033	0,856
		t=	0,78
		t _{crit} =	2,14



Evaluating differences in variance between increment sizes and sampling methods

Analysis of variance (ANOVA)

- F-test of mean square between increment sizes
- F-test of mean square between sampling methods
- Graphical presentation of confidence interval of analytical error vs sub-lot numbers, increment numbers and sub-sample tests



Differences in variances between increment sizes

MS_N = mean square for sub-lots

MS_S = mean square for increments

MS_T = mean square for sub-sample tests

Moisture in bark:

	20L	10L	5L
Heap	$MS_N = 34,4$ $MS_S = 9,61$ $MS_T = 0,293$	$MS_N = 28,4$ $MS_S = 8,78$ $MS_T = 0,459$	$MS_N = 34,7$ $MS_S = 12,2$ $MS_T = 0,773$
Conveyor	$MS_N = 36,4$ $MS_S = 10,6$ $MS_T = 0,680$	$MS_N = 39,5$ $MS_S = 9,74$ $MS_T = 0,728$	$MS_N = 39,2$ $MS_S = 11,9$ $MS_T = 1,148$



Differences in variances between sampling methods

Moisture in bark:

	20L	10L	5L
Heap	$MS_{p,N} = 32,50$		
	$MS_{p,S} = 10,18$		
	$MS_T = 0,293$	$MS_T = 0,459$	$MS_T = 0,773$
Conveyor	$MS_{p,N} = 38,35$		
	$MS_{p,S} = 10,72$		
	$MS_T = 0,680$	$MS_T = 0,728$	$MS_T = 1,148$



Individual variances

Moisture in bark:

$$MS_N = ST\sigma^2_N + T\sigma^2_S + \sigma^2_T \longrightarrow \sigma^2_N = 3,12$$

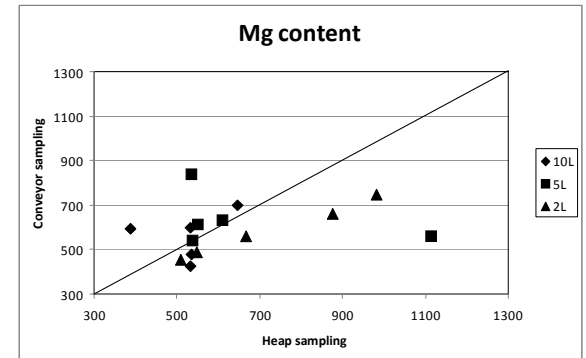
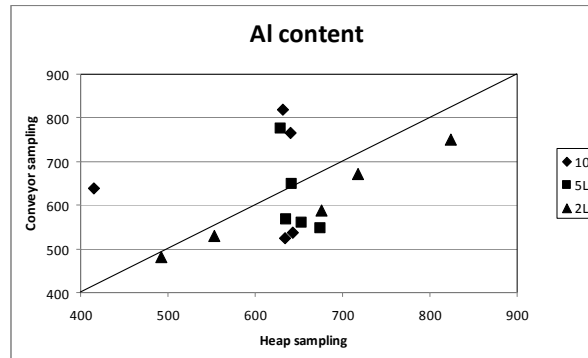
$$MS_S = T\sigma^2_S + \sigma^2_T \longrightarrow \sigma^2_S = 4,89$$

$$MS_T = \sigma^2_T \longrightarrow \sigma^2_T = 0,68$$

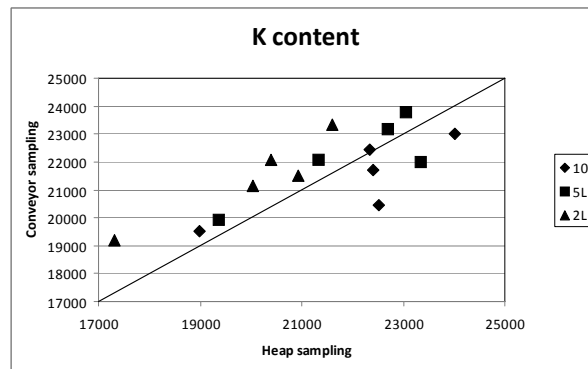


Bias between sampling methods for Al, Mg and K in olive and grape residue

Olive residue:

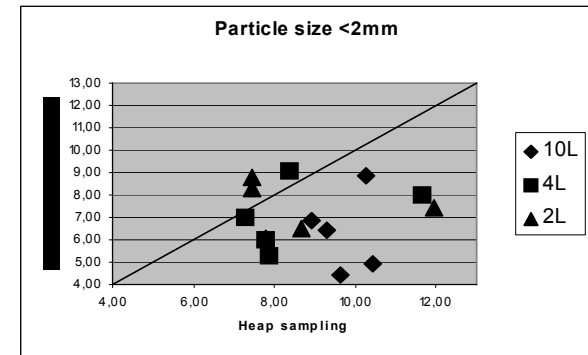
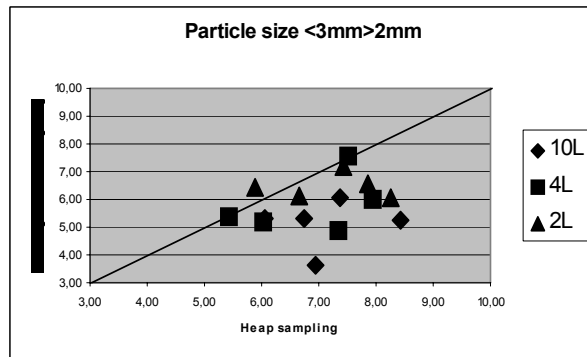
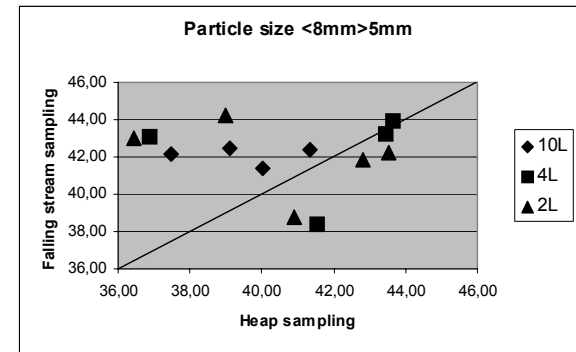
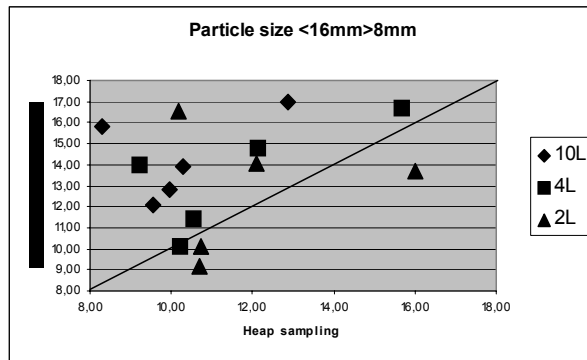


Grape residue:



Bias between sampling methods for particle size distribution in wood chips

Wood chips:



Differences in variances

- **Varying differences in variances were found between increment sizes and sampling methods**
- **In many cases the results were contradictory**

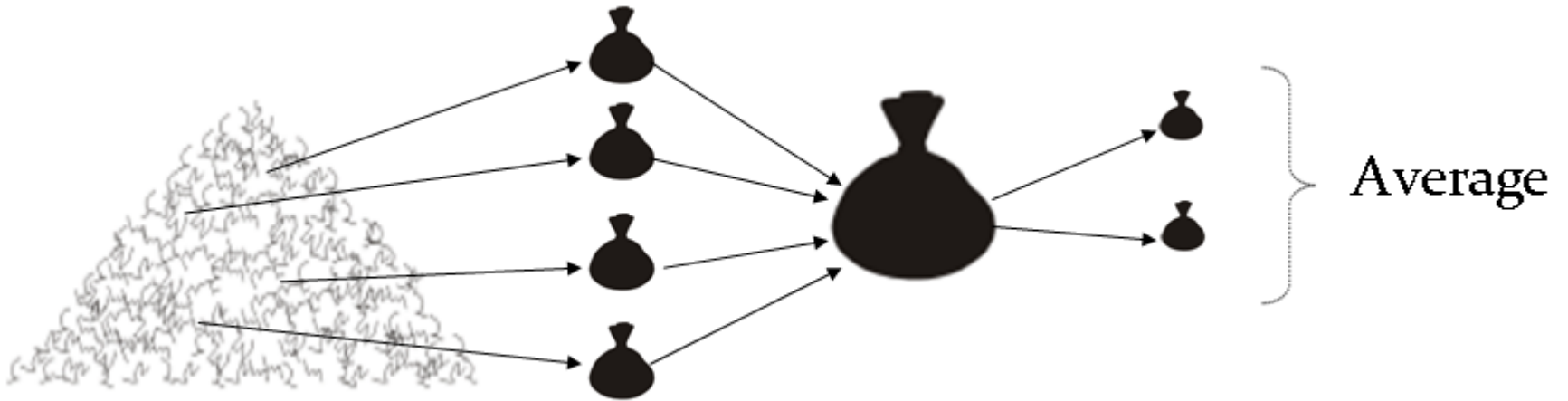


Individual variances for moisture and ash

	Moisture (%)			Ash (%)		
Biofuel	σ^2_N	σ^2_S	σ^2_T	σ^2_N	σ^2_S	σ^2_T
Bark	3,12	4,89	0,68	0,383	0,026	0,019
Wood chips	1,98	10,5	0,058	0,027	0,023	0,0004
Pellets (8mm)	0,800	0,158	0,003	0,0050	0,0004	0,0003
Pellets (6mm)	0,008	0,016	0,014	0,0004	0,0004	0,0071
Olive residue	0,120	0,105	0,028	0,832	0,658	0,527
Grape residue	6,06	0,746	1,88	0,198	0,519	0,202



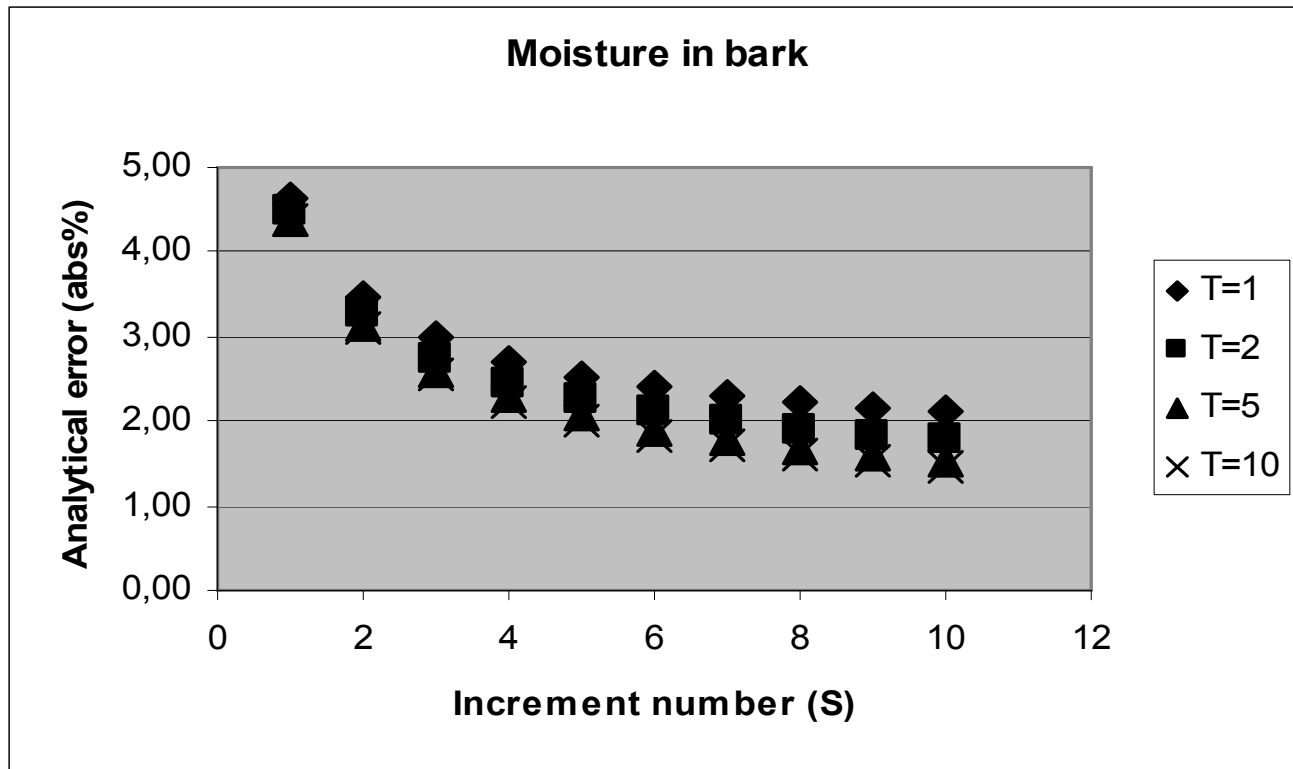
Analysis of one sub-lot



$$e = t^* \left(\sqrt{\sigma^2_S/S + \sigma^2_T/T} \right)$$



Effect of increment and test numbers on analytical error

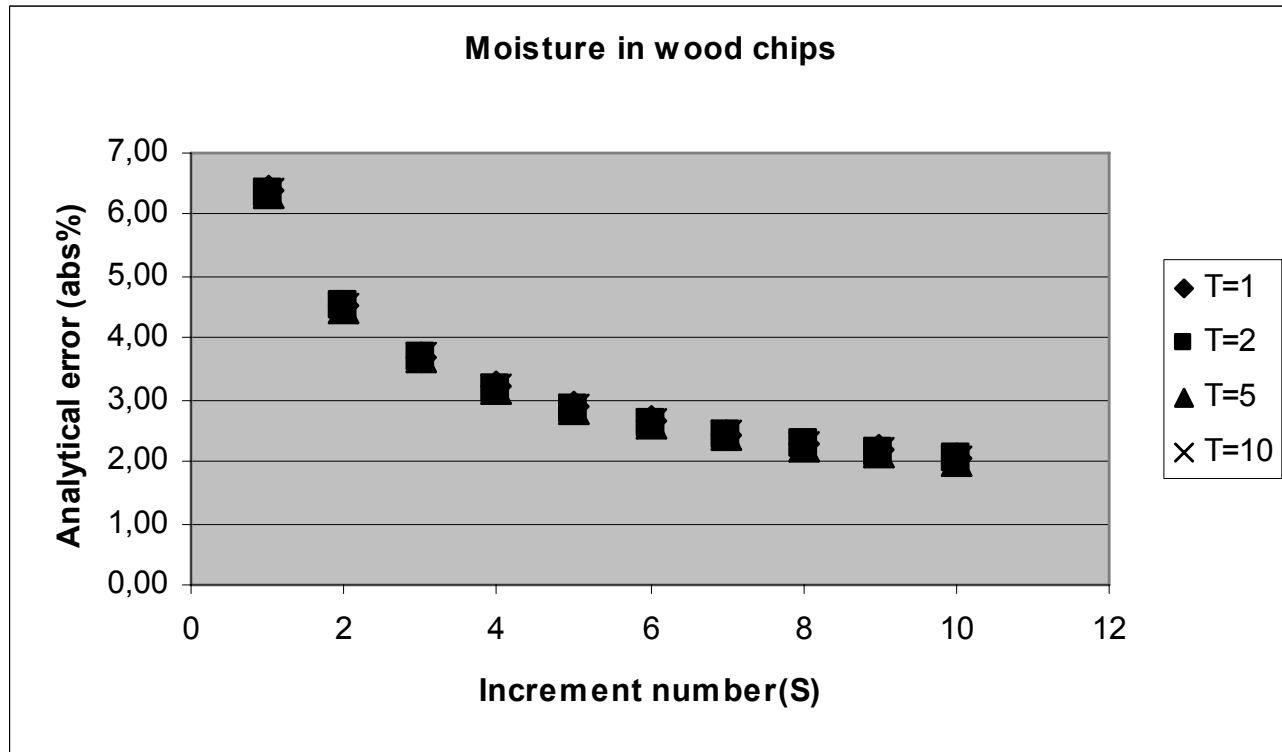


$$\sigma_s^2 = 4,89$$

$$\sigma_T^2 = 0,68$$



Effect of increment and test numbers on analytical error

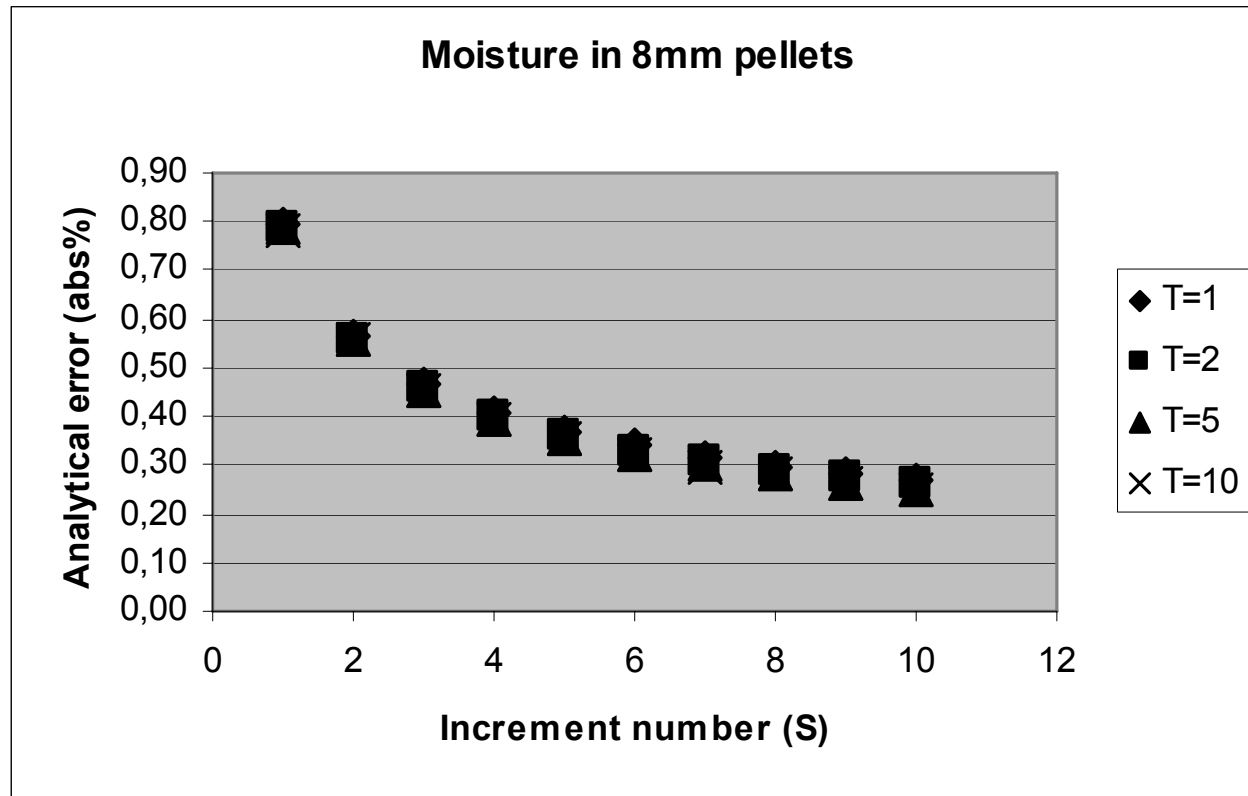


$$\sigma^2_S = 10,5$$

$$\sigma^2_T = 0,0587$$



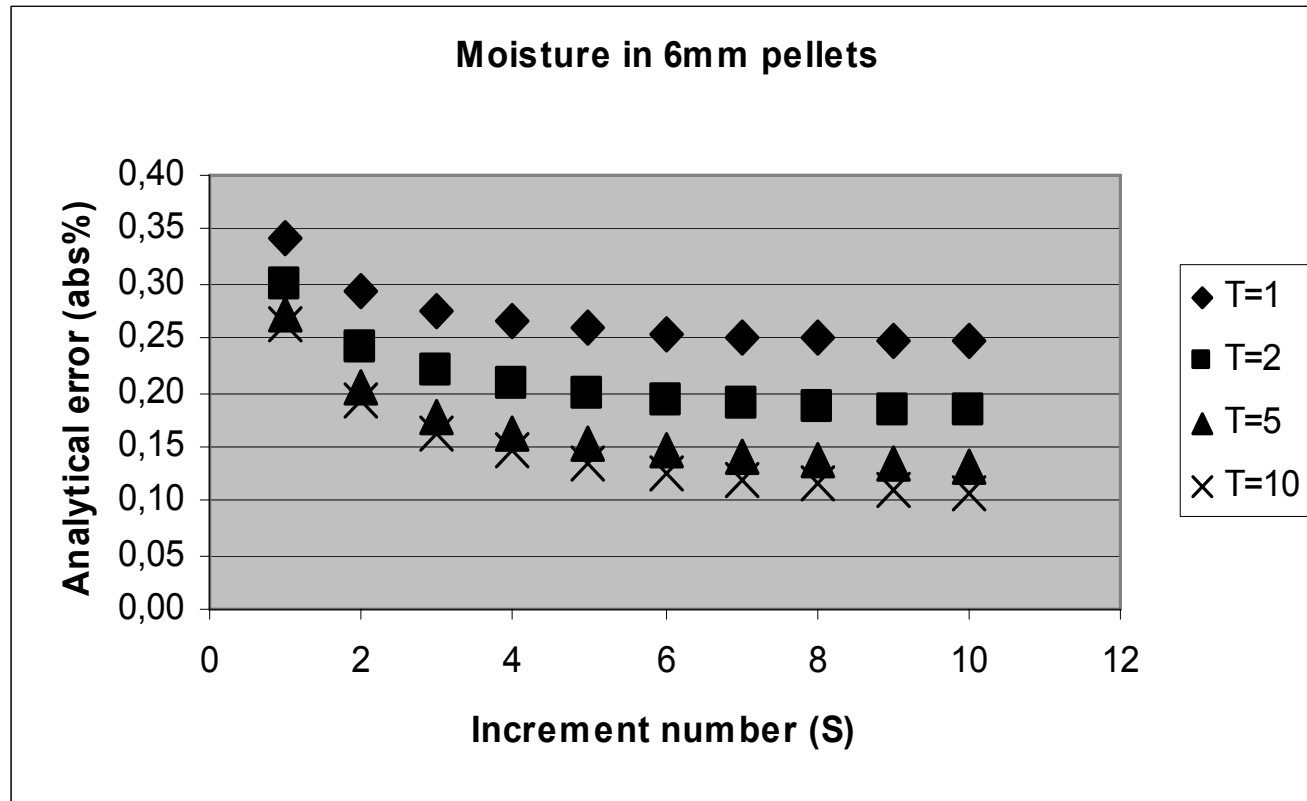
Effect of increment and test numbers on analytical error



$$\sigma^2_S = 0,158$$
$$\sigma^2_T = 0,0032$$



Effect of increment and test numbers on analytical error

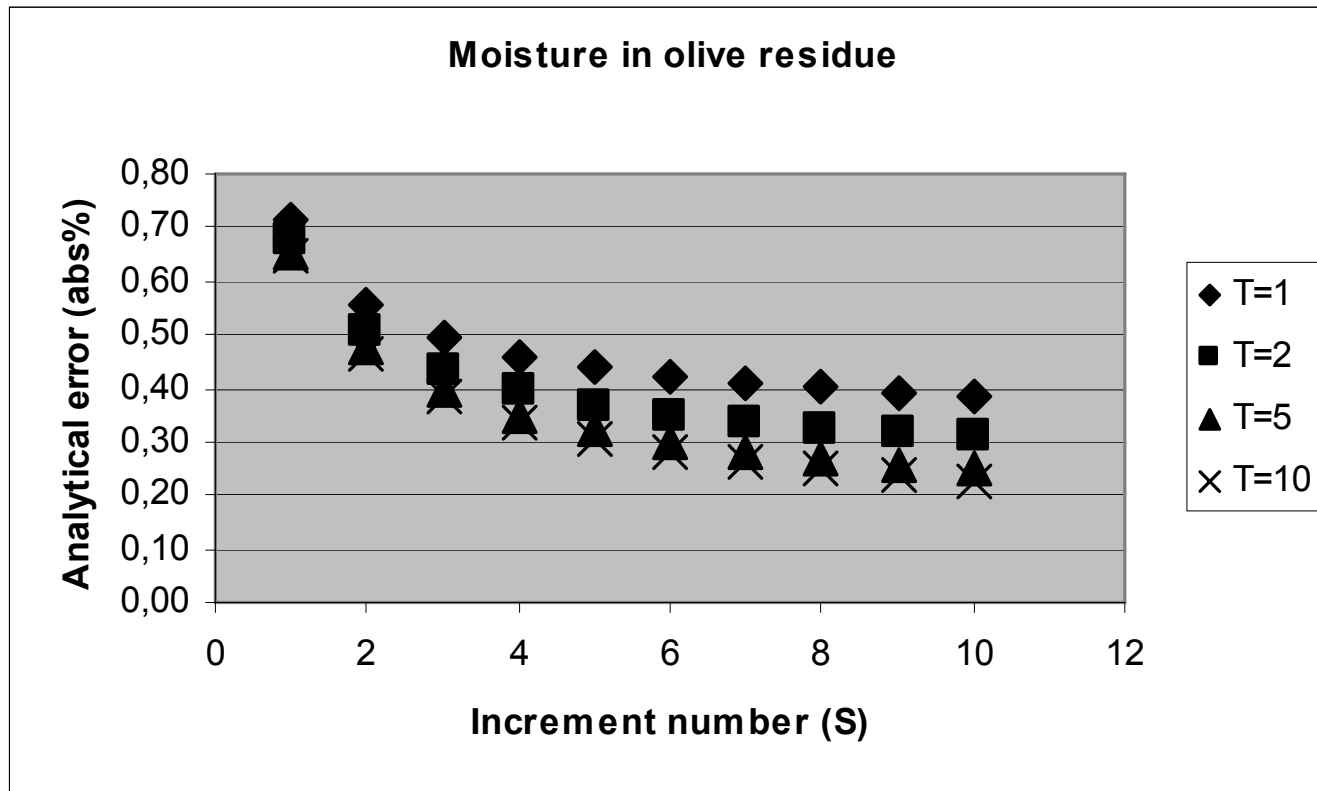


$$\sigma^2_s = 0,0164$$

$$\sigma^2_T = 0,0141$$



Effect of increment and test numbers on analytical error

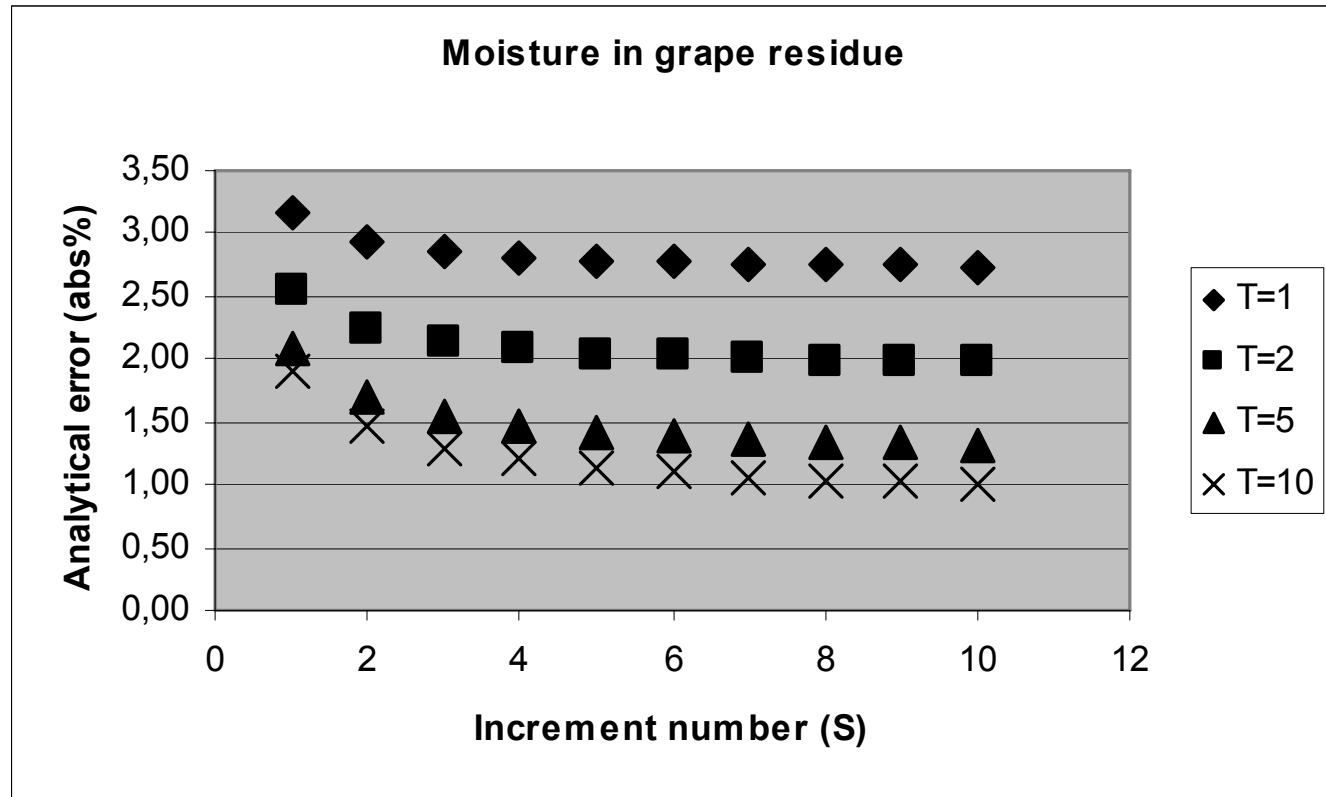


$$\sigma^2_S = 0,105$$

$$\sigma^2_T = 0,029$$



Effect of increment and test numbers on analytical error

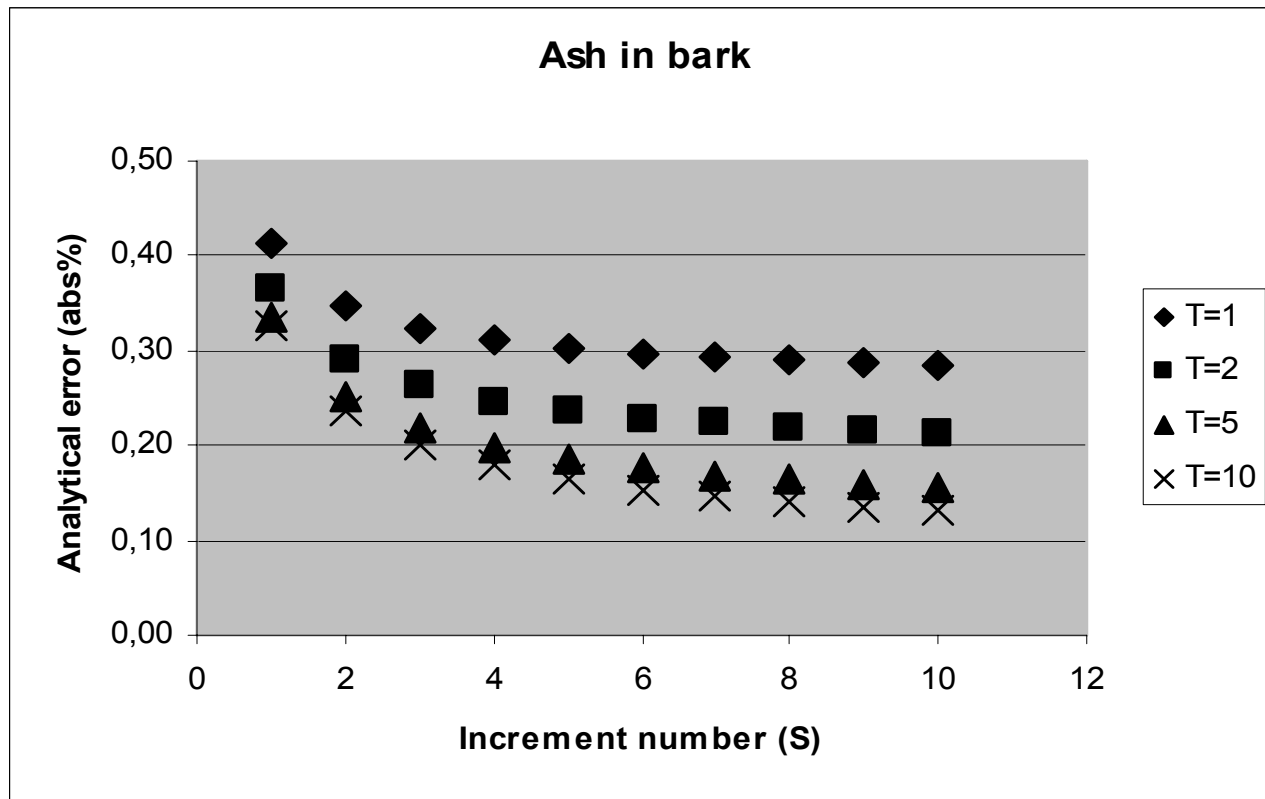


$$\sigma^2_s = 0,746$$

$$\sigma^2_T = 1,88$$



Effect of increment and test numbers on analytical error

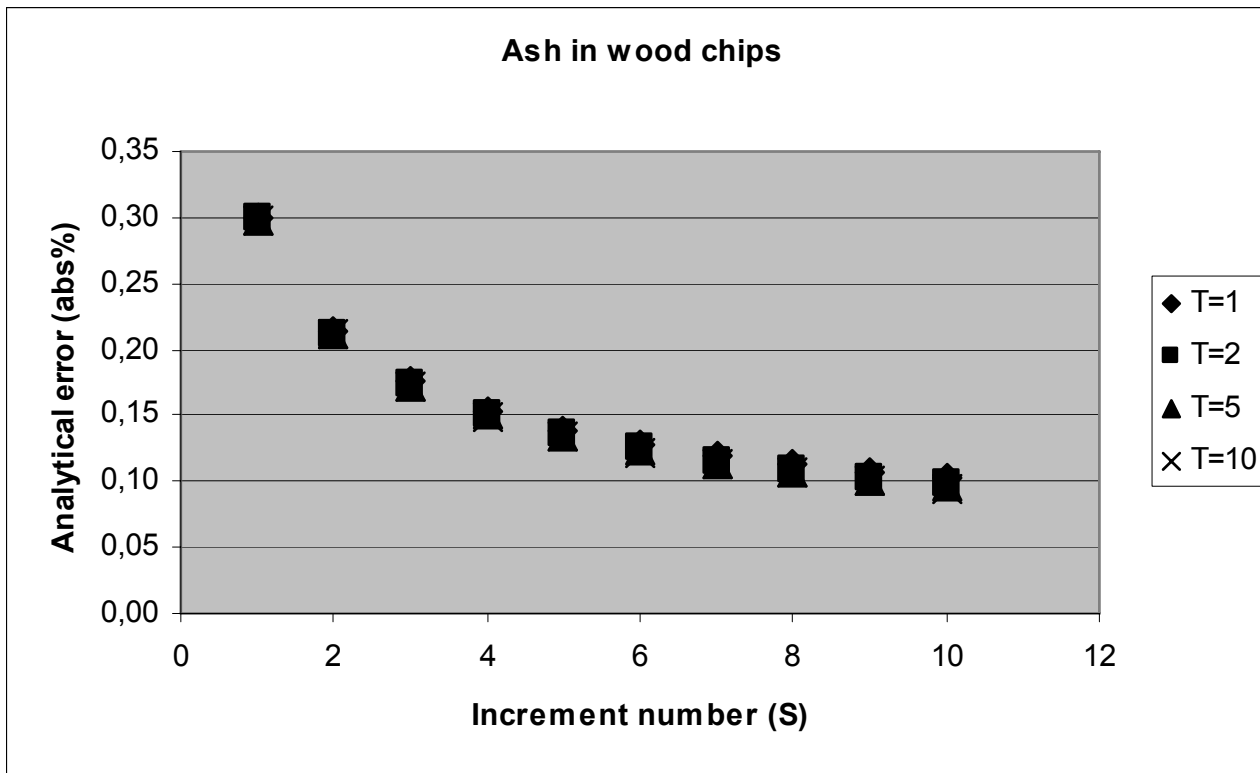


$$\sigma_s^2 = 0,0256$$

$$\sigma_T^2 = 0,0187$$



Effect of increment and test numbers on relative sampling error

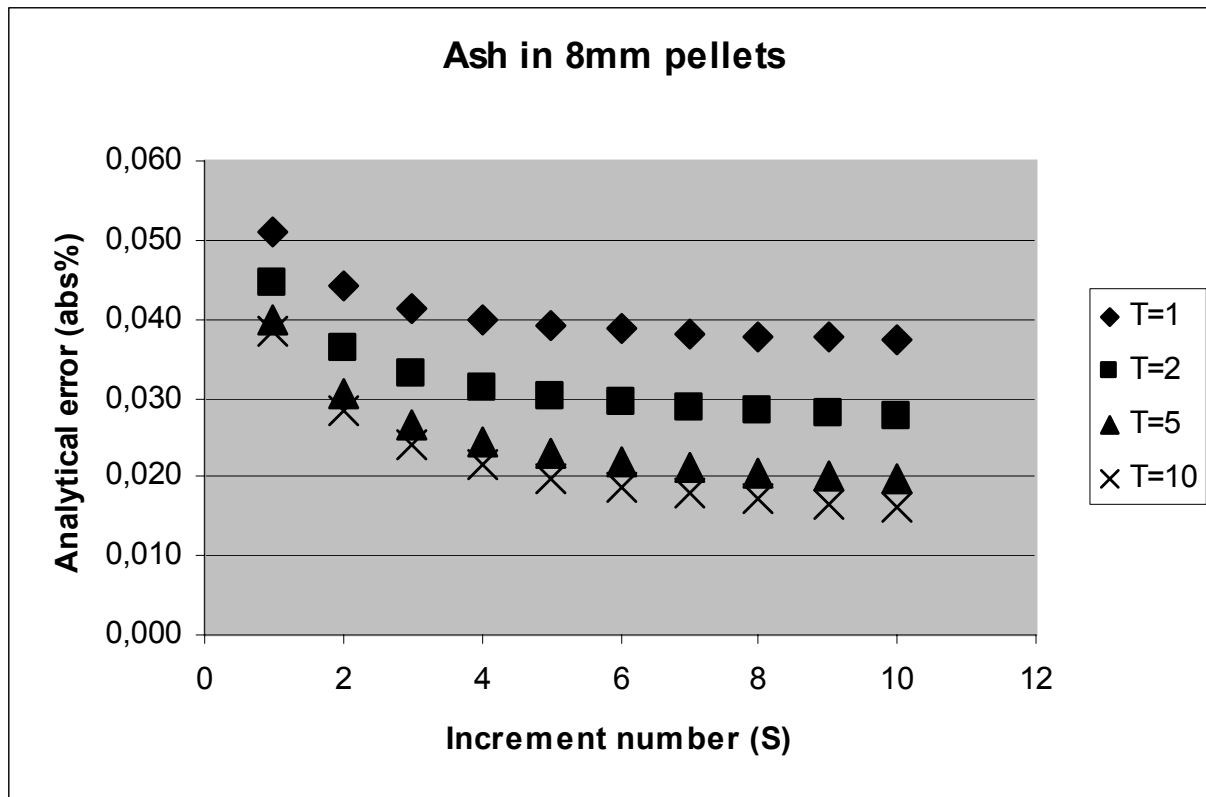


$$\sigma^2_s = 0,0231$$

$$\sigma^2_T = 0,00040$$



Effect of increment and test numbers on analytical error

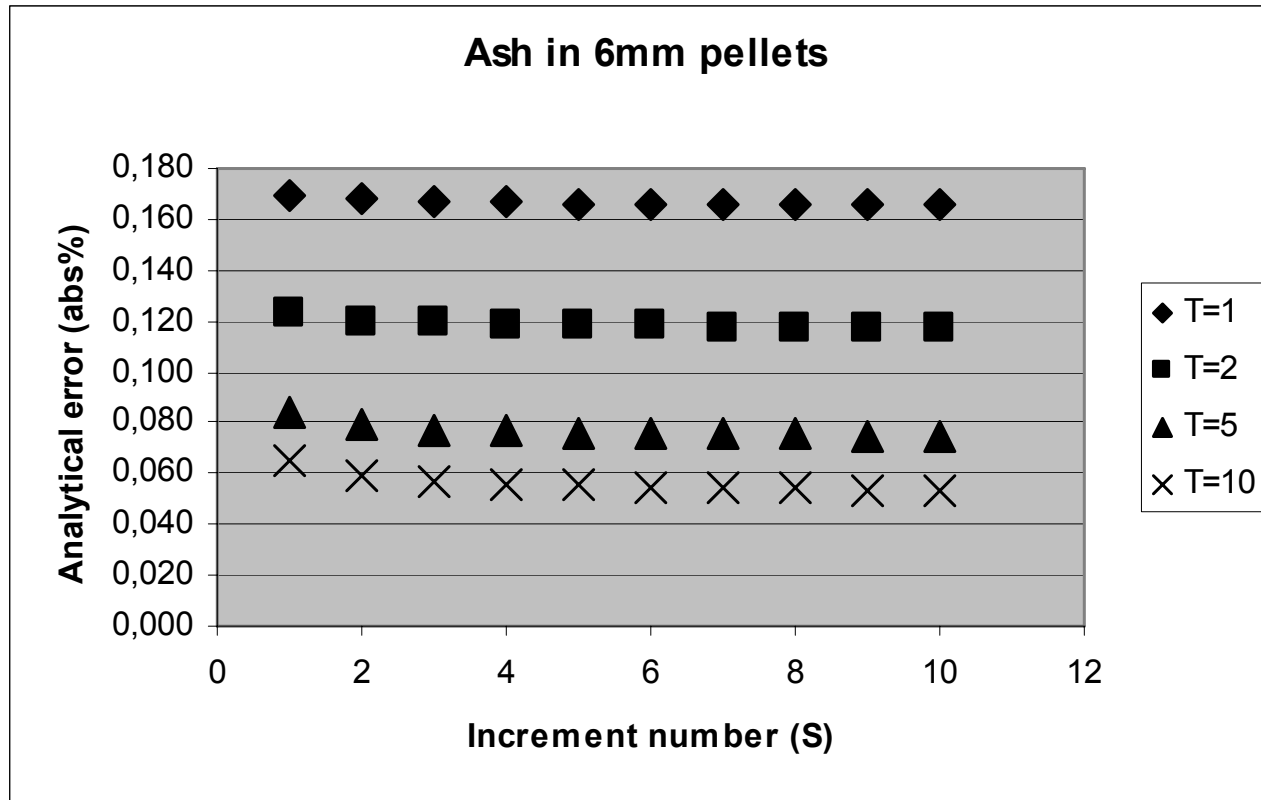


$$\sigma^2_s = 0,00035$$

$$\sigma^2_T = 0,00033$$



Effect of increment and test numbers on analytical error

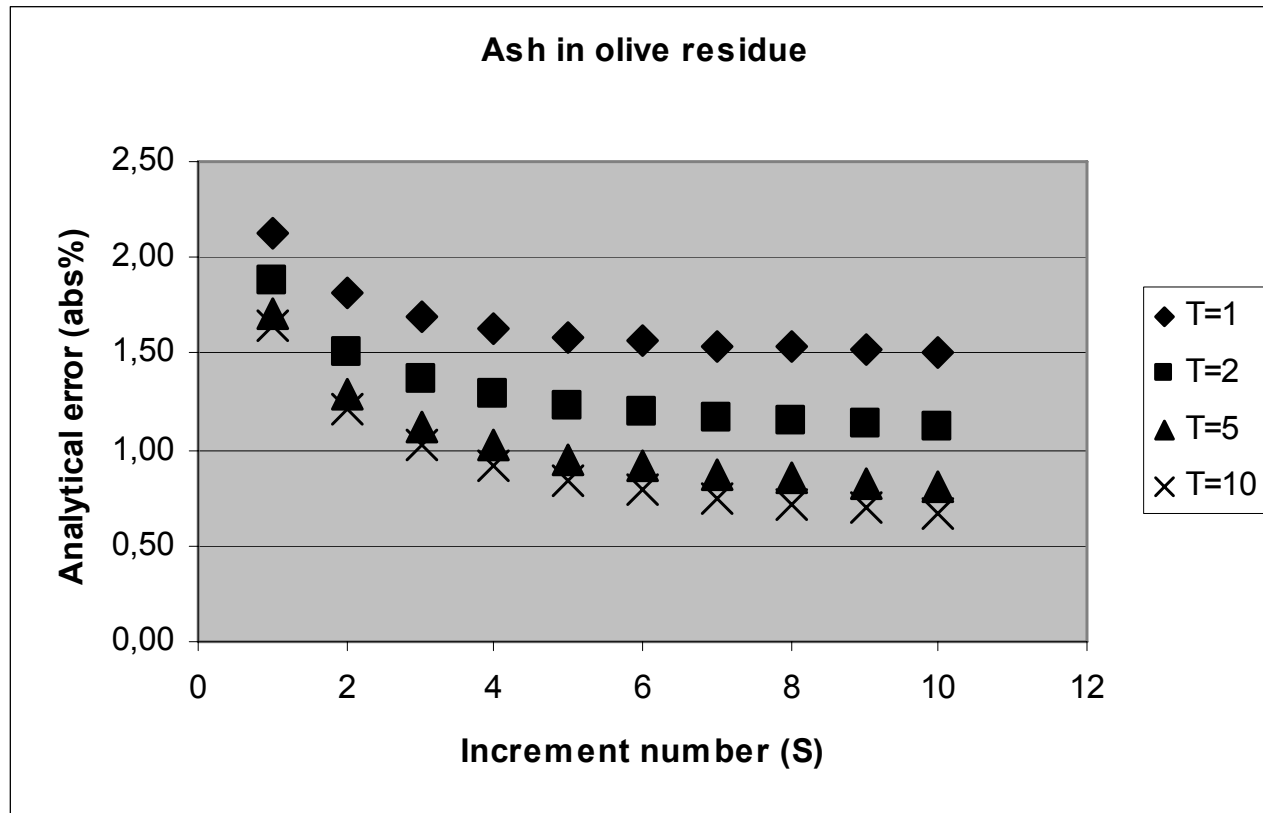


$$\sigma^2_S = 0,000399$$

$$\sigma^2_T = 0,00711$$



Effect of increment and test numbers on analytical error

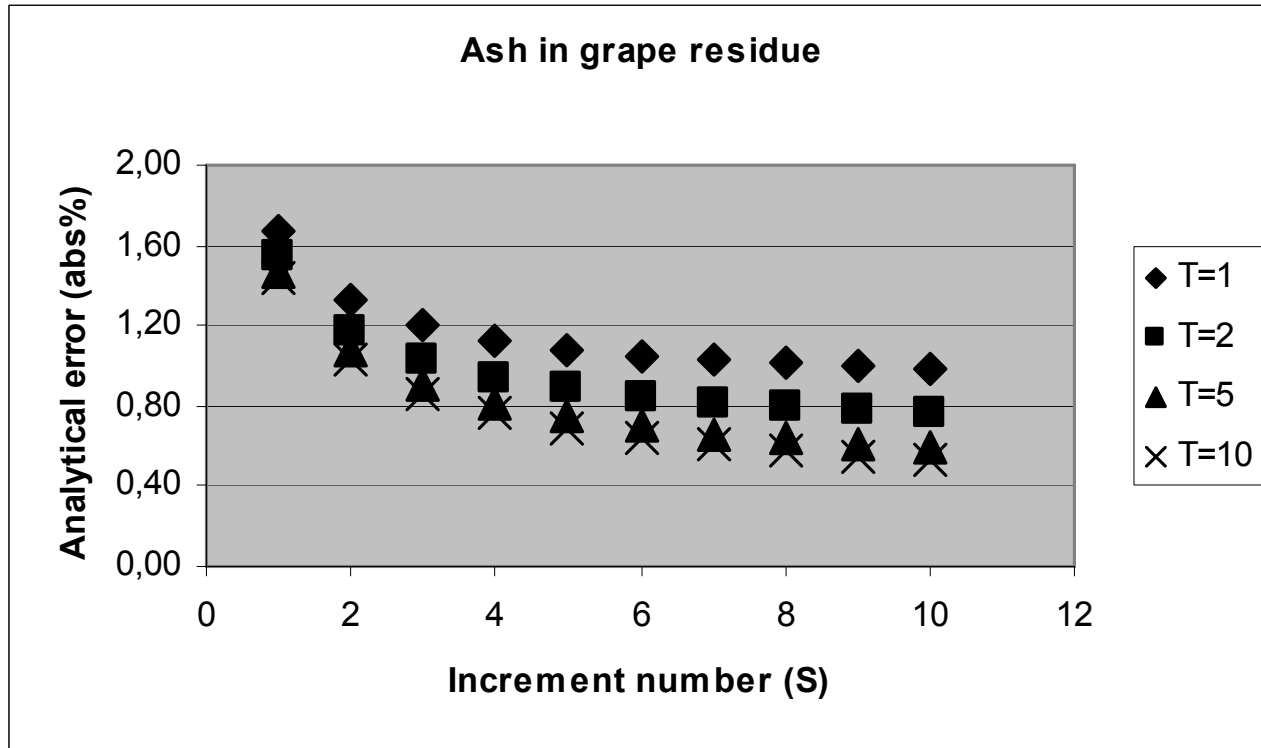


$$\sigma^2_s = 0,658$$

$$\sigma^2_T = 0,527$$



Effect of increment and test numbers on analytical error



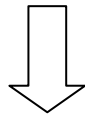
$$\sigma^2_s = 0,519$$

$$\sigma^2_T = 0,202$$



Calculation of increment number

$$e = t^* \left(\sqrt{\frac{\sigma^2_S}{S} + \frac{\sigma^2_T}{T}} \right)$$



$$S = \frac{4\sigma_S^2}{e^2 - \frac{4\sigma_T^2}{T}}$$

S = minimum number of increments needed for the required precision

e = required precision (twice the standard deviation) for the specified analytical parameter

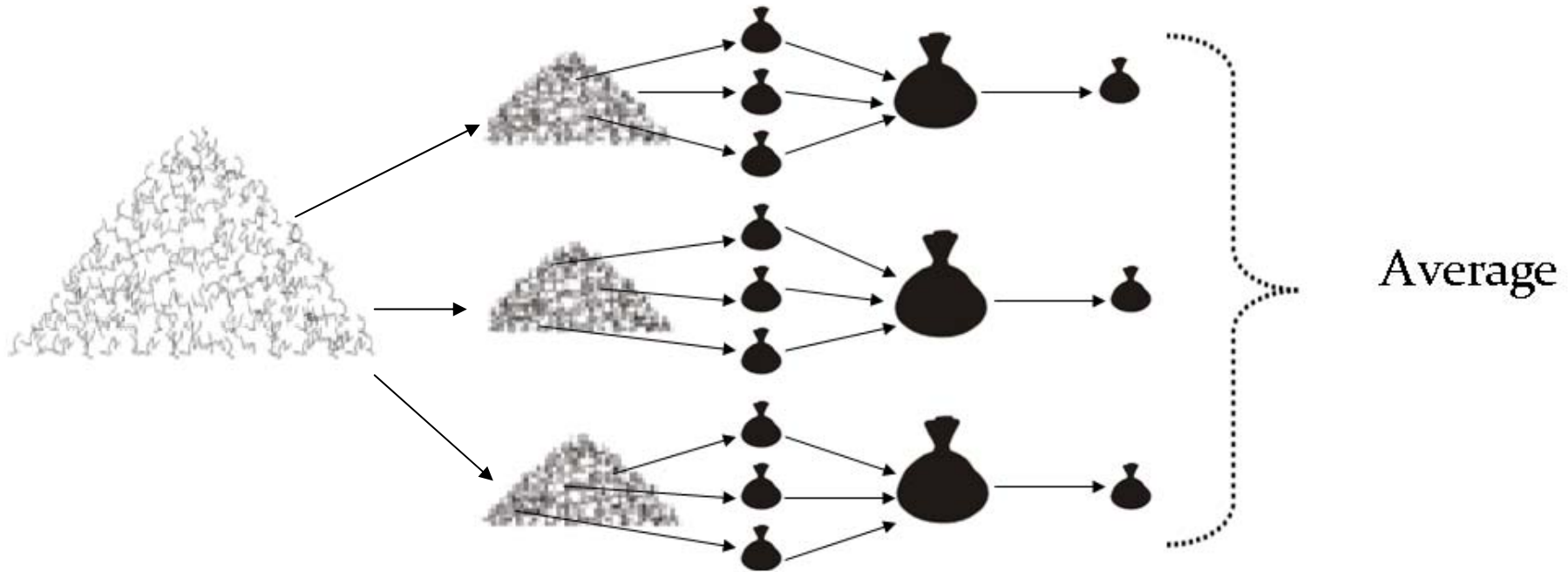
σ^2_S = increment variance for the specified parameter

σ^2_T = sub-sample test variance for the specified parameter

T = number of sub-sample tests for the specified parameter



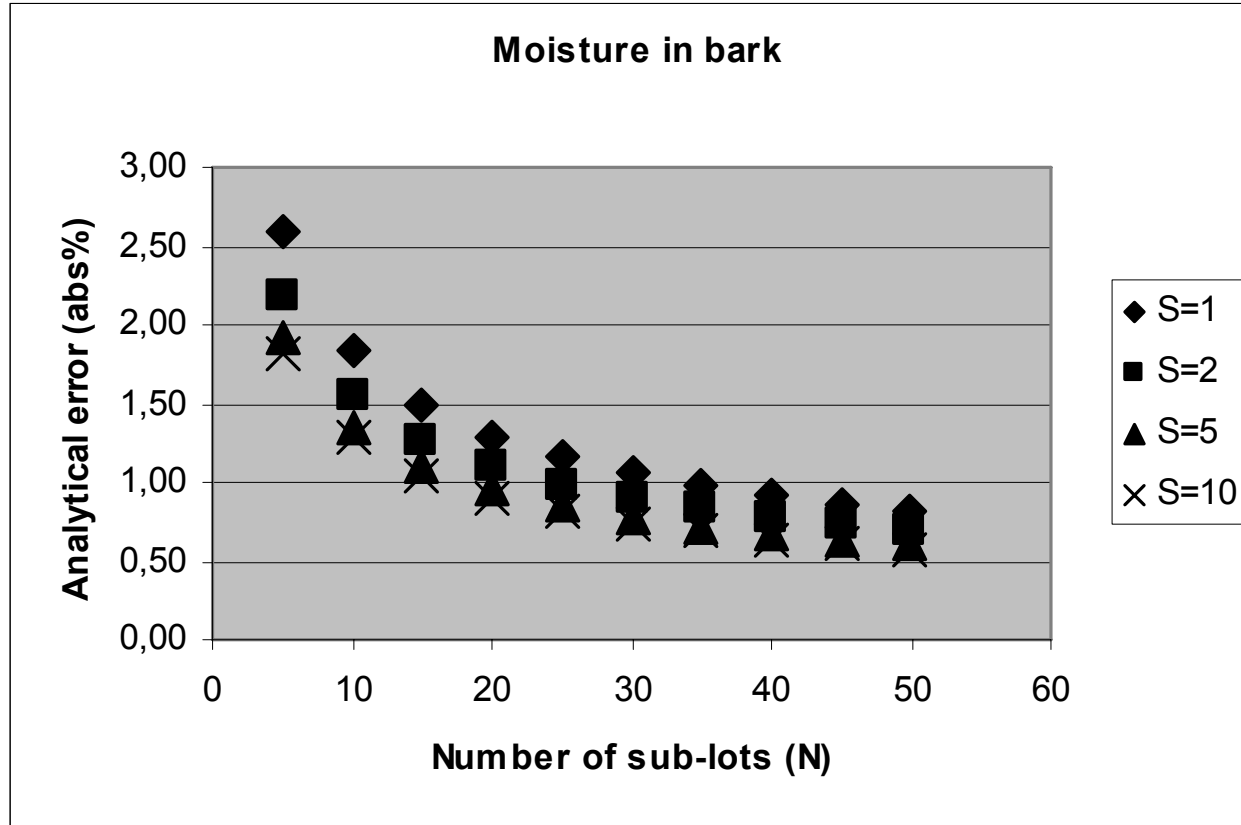
Average of several sub-lots



$$e = t^* \left(\sqrt{\sigma^2_N/N + \sigma^2_S/NS + \sigma^2_T/NT} \right)$$



Effect of sub-lot and increment numbers on analytical error



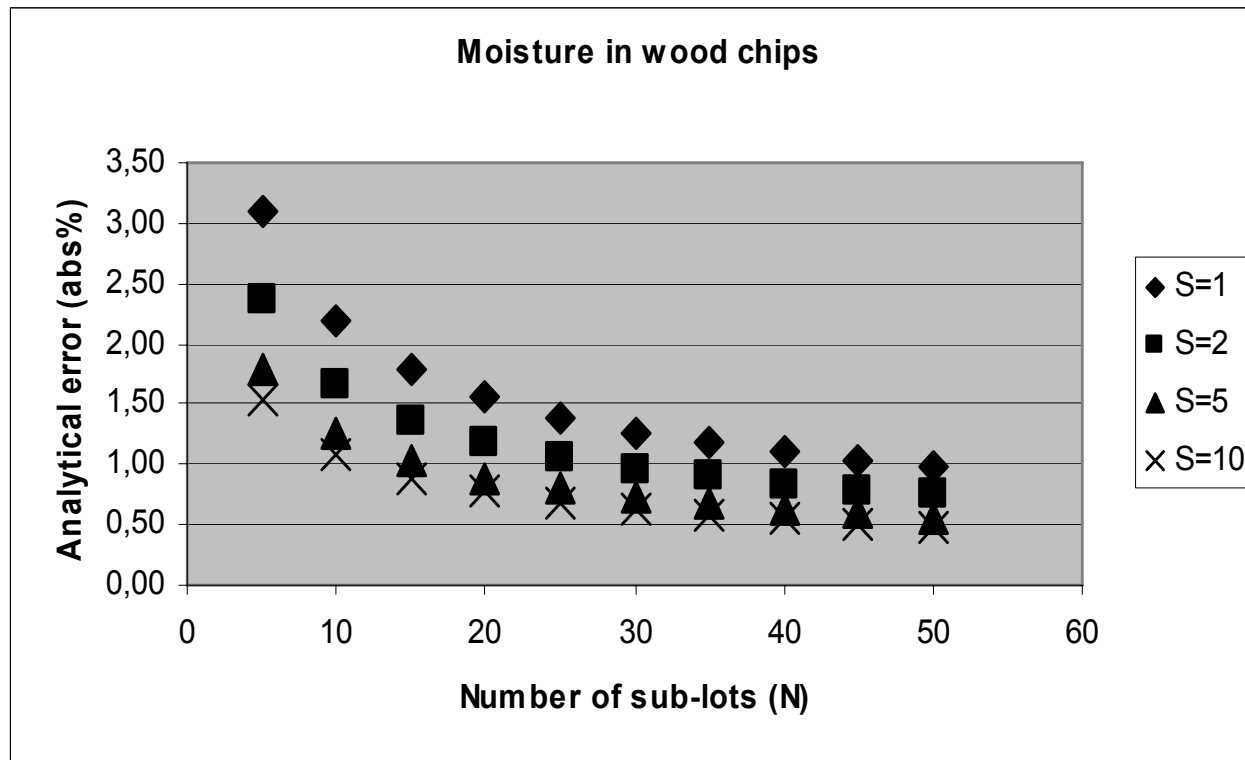
$$\sigma^2_N = 3,12$$

$$\sigma^2_S = 4,89$$

$$\sigma^2_T = 0,68$$



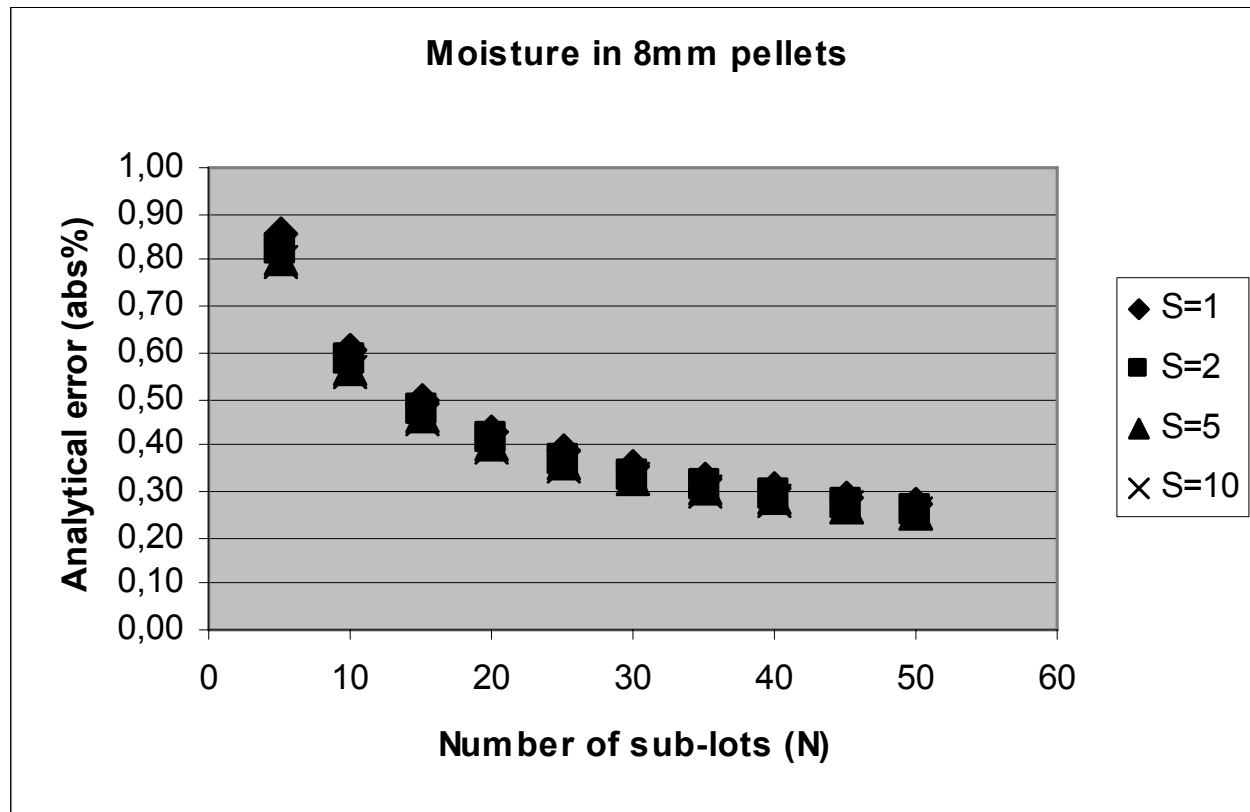
Effect of sub-lot and increment numbers on analytical error



$$\sigma^2_N = 1,98$$
$$\sigma^2_S = 10,5$$
$$\sigma^2_T = 0,059$$



Effect of sub-lot and increment numbers on analytical error



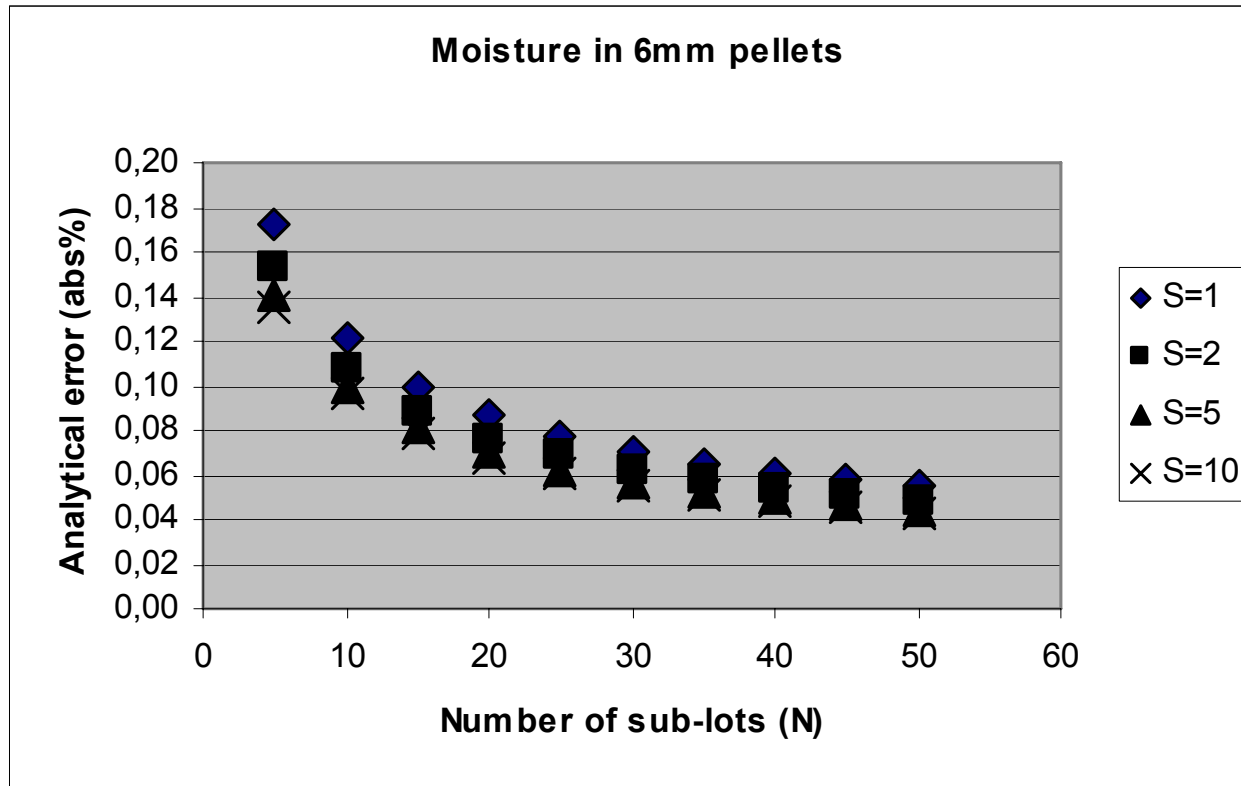
$$\sigma^2_N = 0,800$$

$$\sigma^2_S = 0,158$$

$$\sigma^2_T = 0,0032$$



Effect of sub-lot and increment numbers on analytical error



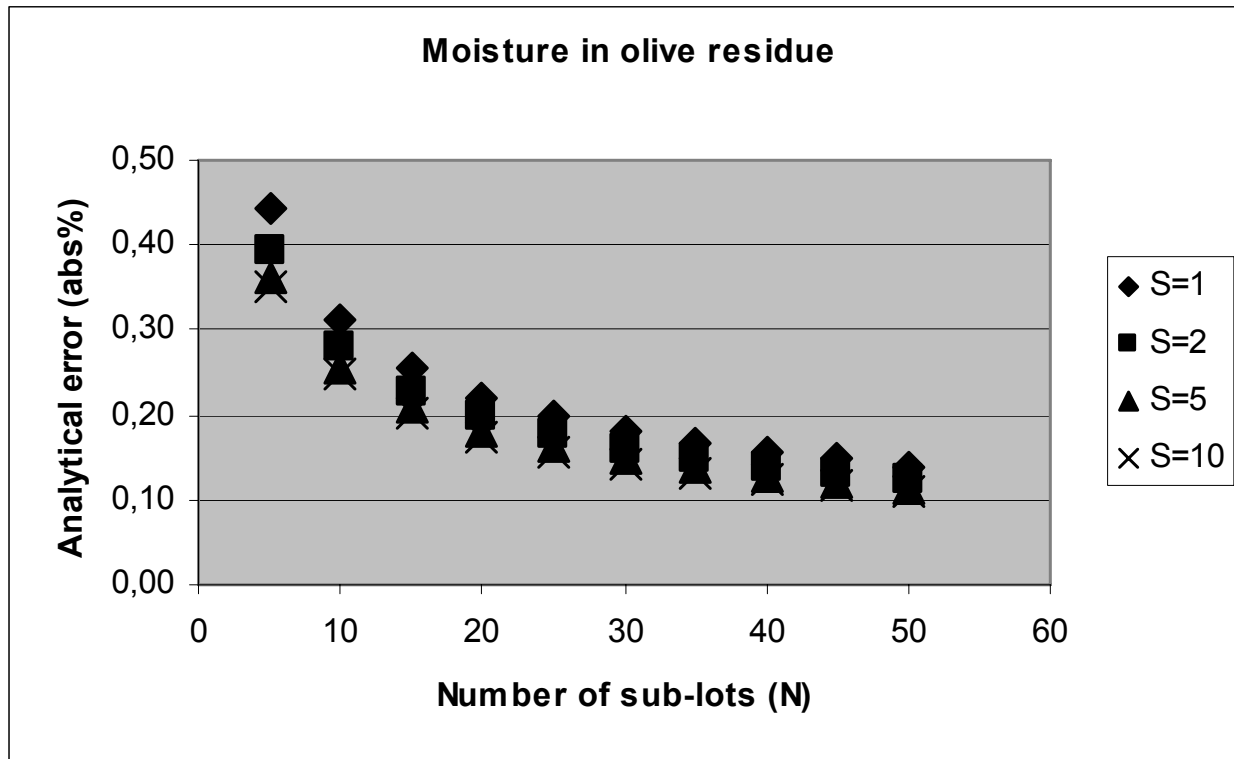
$$\sigma^2_N = 0,0082$$

$$\sigma^2_S = 0,0164$$

$$\sigma^2_T = 0,0141$$



Effect of sub-lot and increment numbers on analytical error



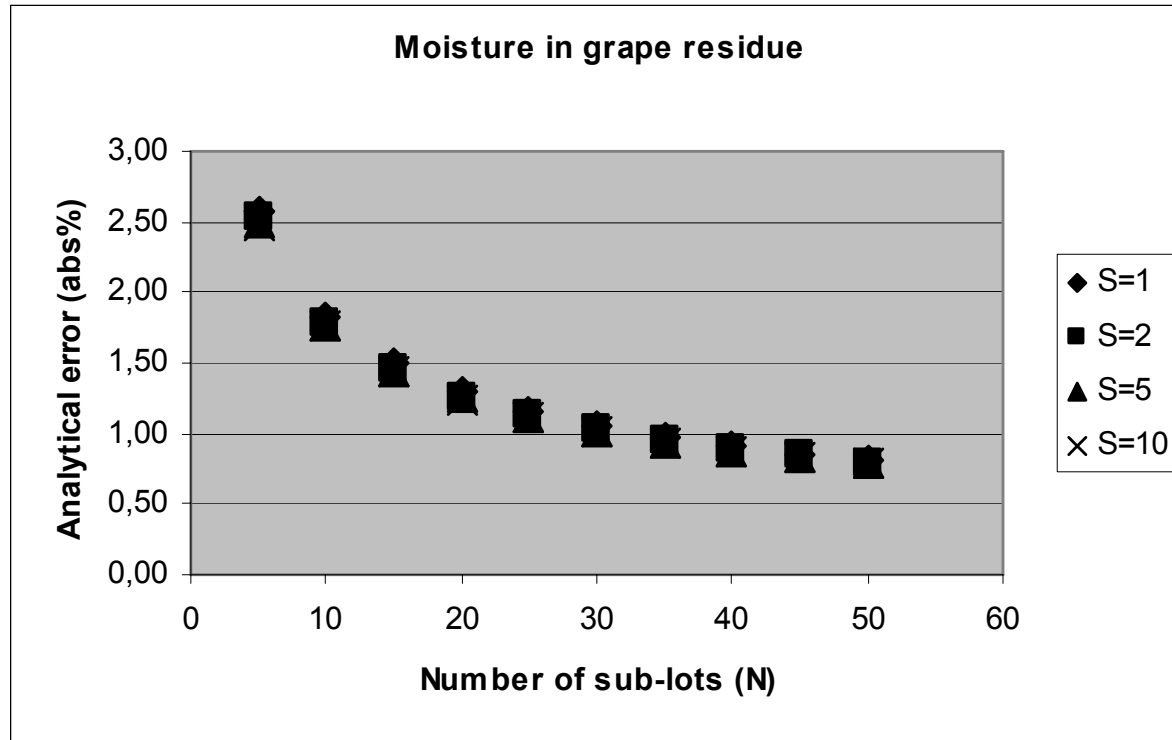
$$\sigma^2_N = 0,121$$

$$\sigma^2_S = 0,105$$

$$\sigma^2_T = 0,029$$



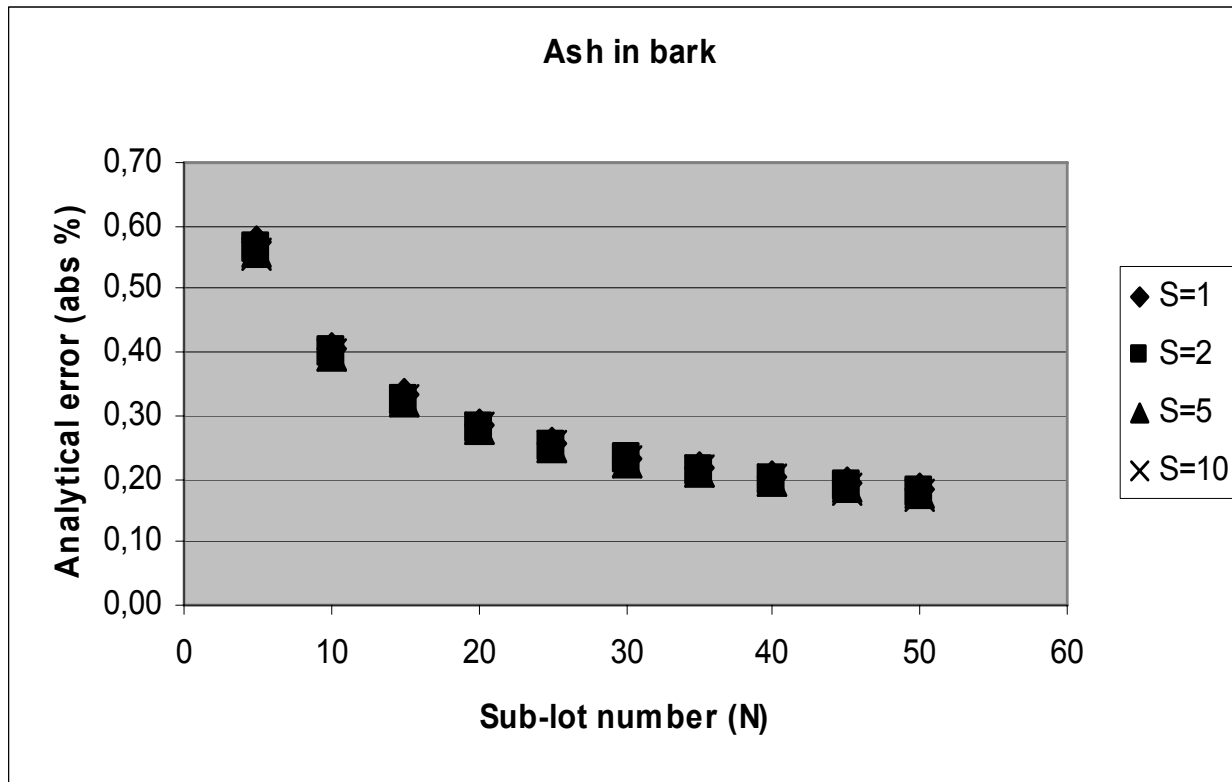
Effect of sub-lot and increment numbers on analytical error



$$\sigma_N^2 = 6,06$$
$$\sigma_S^2 = 0,746$$
$$\sigma_T^2 = 1,88$$



Effect of sub-lot and increment numbers on analytical error



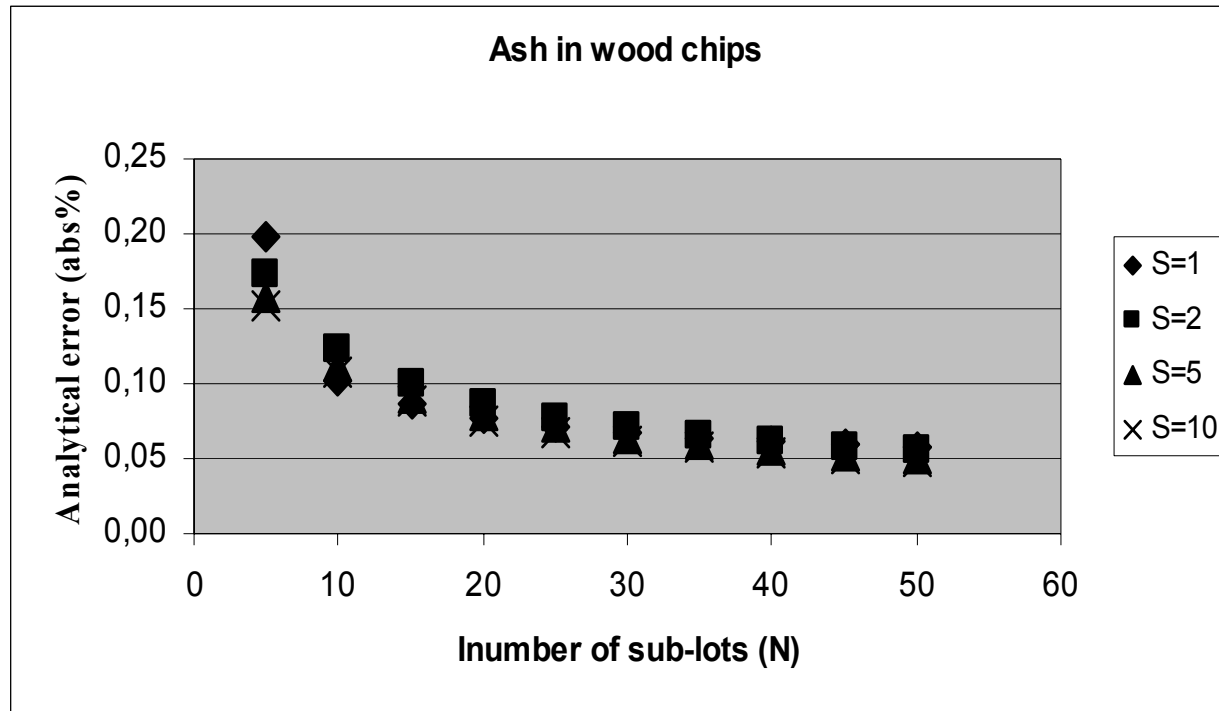
$$\sigma^2_N = 0,383$$

$$\sigma^2_S = 0,026$$

$$\sigma^2_T = 0,019$$



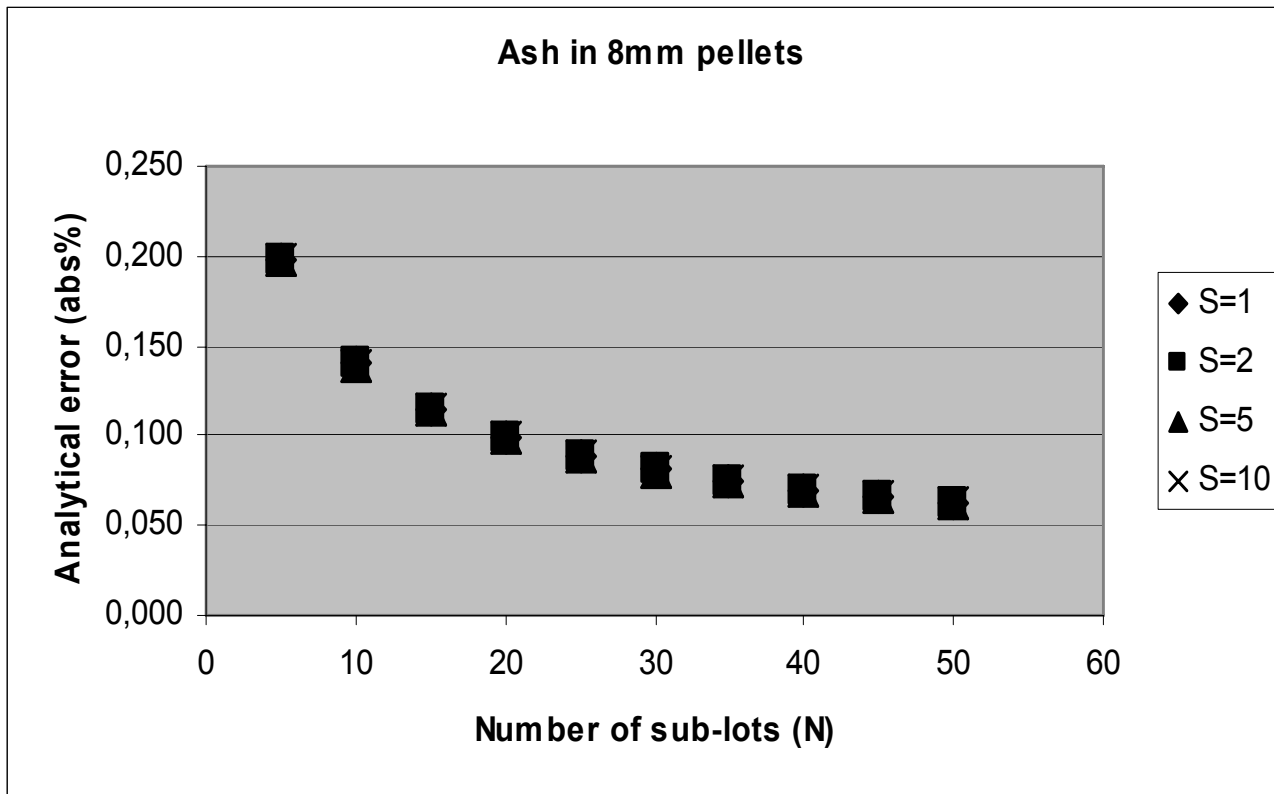
Effect of sub-lot and increment numbers on analytical error



$$\sigma^2_N = 0,0273$$
$$\sigma^2_S = 0,0231$$
$$\sigma^2_T = 0,00040$$



Effect of sub-lot and increment numbers on analytical error



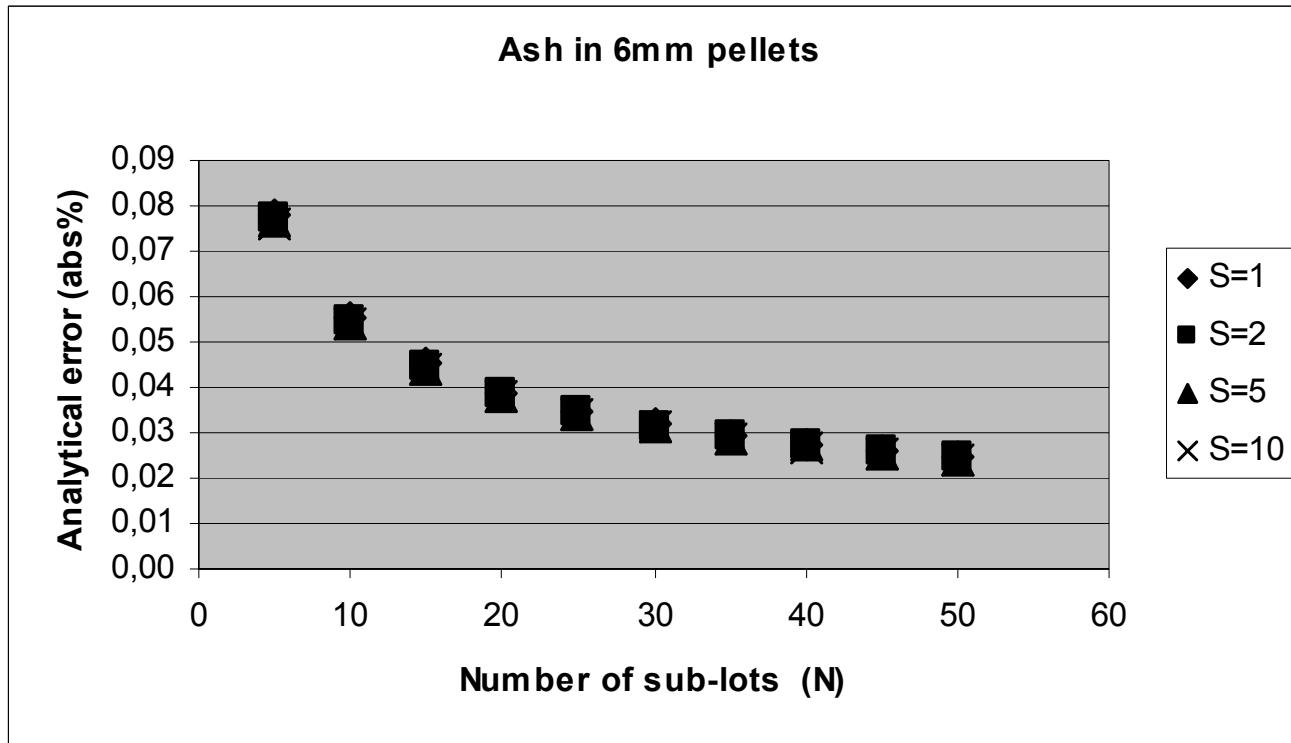
$$\sigma^2_N = 0,00504$$

$$\sigma^2_S = 0,00035$$

$$\sigma^2_T = 0,00033$$



Effect of sub-lot and increment numbers on analytical error



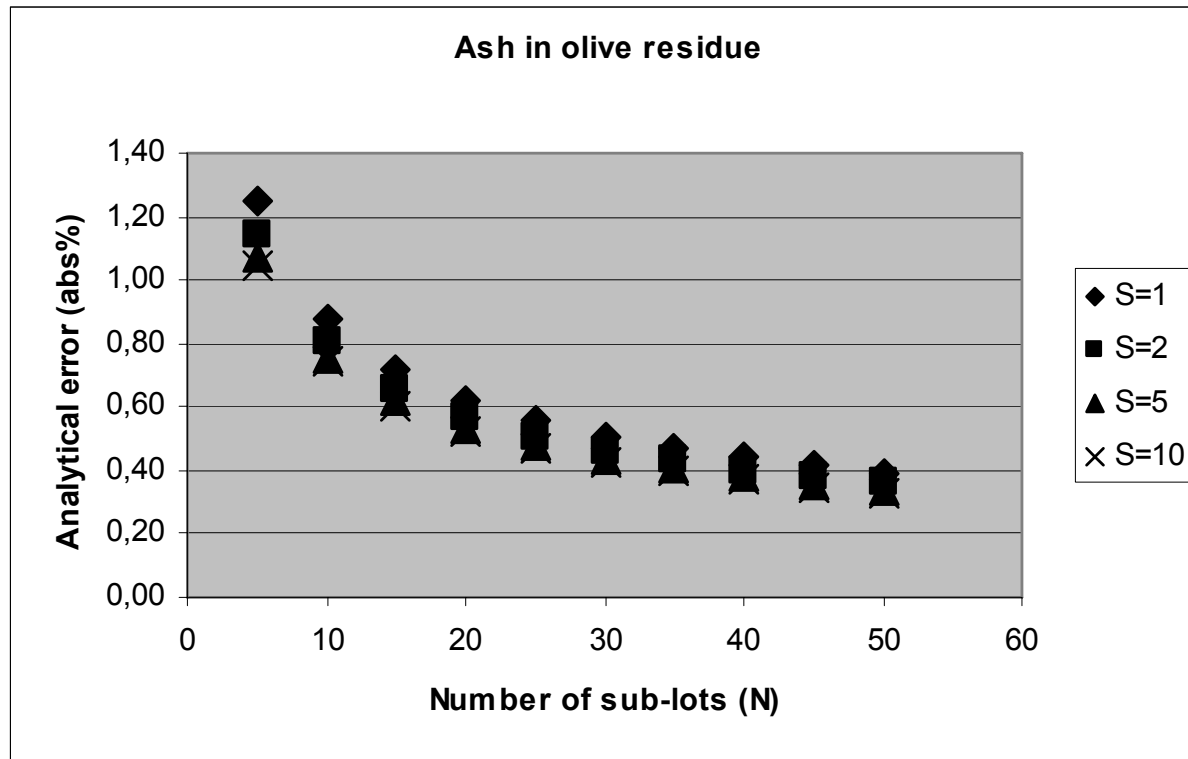
$$\sigma^2_N = 0,000408$$

$$\sigma^2_S = 0,000399$$

$$\sigma^2_T = 0,00711$$



Effect of sub-lot and increment numbers on analytical error



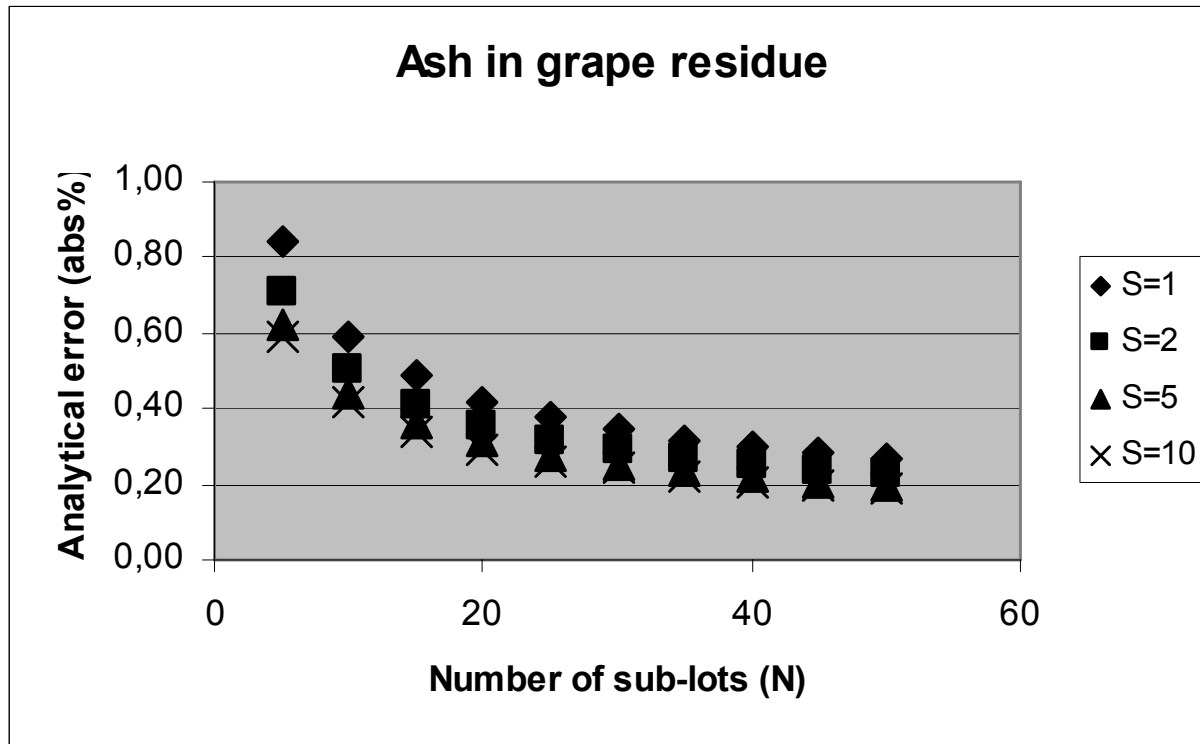
$$\sigma^2_N = 0,832$$

$$\sigma^2_S = 0,658$$

$$\sigma^2_T = 0,527$$

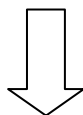


Effect of sub-lot and increment numbers on analytical error



Calculation of increment number

$$e = t^* \left(\sqrt{\sigma_N^2/N + \sigma_S^2/NS + \sigma_T^2/NT} \right)$$



$$S = \frac{4\sigma_S^2}{Ne^2 - 4\sigma_N^2 - \frac{4\sigma_T^2}{T}}$$

S = minimum number of increments per sub-lot needed for the required precision

N = number of sub-lots averaged

e = required precision (twice the standard deviation) for the specified analytical parameter

σ_N^2 = sub-lot variance for the specified parameter

σ_S^2 = increment variance for the specified parameter

σ_T^2 = sub-sample variance for the specified parameter

T = number of sub-sample tests for the specified parameter



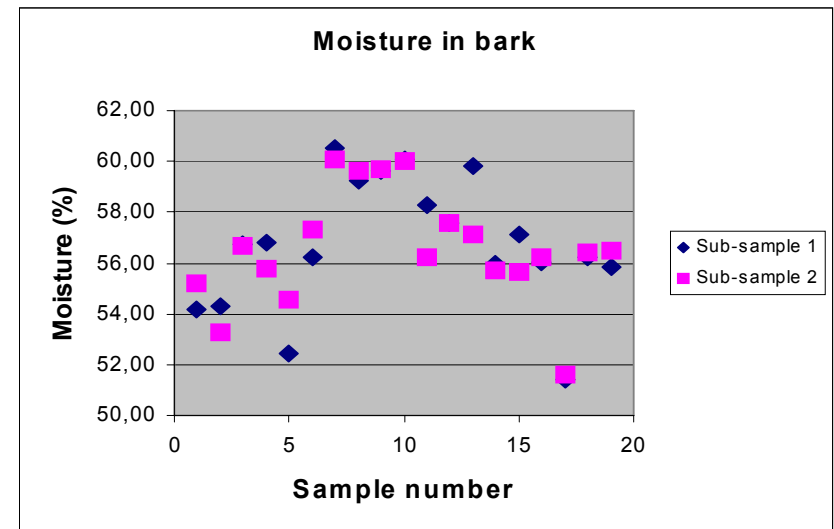
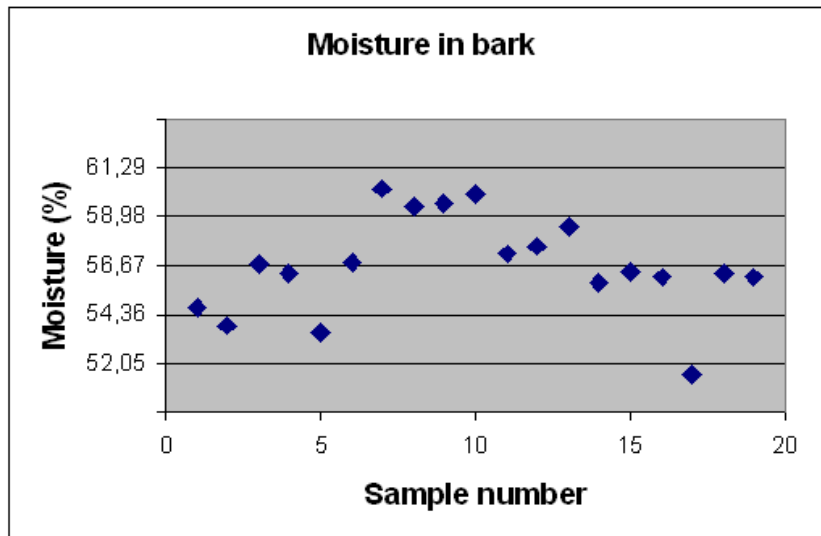
Experimental design for verification of individual variances

Material	Sampling method	S_{incr}	T_{test}	Increment size	Reduction method
Bark	Heap	4	2	5L	Coning & Quartering
Wood chips	Falling stream	4	2	2L	Riffle box
Pellets (8mm)	Heap	4	2	2,5L	Riffle box
Pellets (6mm)	Bag	4	2	2,5L	Riffle box
Grape residue	Heap	4	2	5L	Coning & Quartering
Olive residue	Heap	4	2	5L	Riffle box



Long time variances

Moisture in bark:



Comparison of results from Task I.1 and I.2

Bark:

Parameter	Overall std.dev. Task I.1	Overall std.dev. Task I.2	F-value overall variation	F _{crit}	Sub-sample std.dev. TaskI.1	Sub-sample std.dev. TaskI.2	F-value Sub-sample std.dev.	F _{crit}
Moisture	2,21	2,31	1,1	2,9	0,88	0,79	1,2	2,1
Ash	0,63	0,42	2,3	5,8	0,11	0,14	1,6	2,1
Calorific value	0,26	0,18	2,1	5,8	0,085	0,083	1,0	2,1



Comparison of results from Task I.1 and I.2

Wood chips:

Parameter	Overall std.dev. Task I.1	Overall std.dev. Task I.2	F-value overall variation	F _{crit}	Sub-sample std.dev. Task I.1	Sub-sample std.dev. Task I.2	F-value Sub-sample std.dev.	F _{crit}
Moisture	2,53	4,18	2,7	5,86	0,25	0,18	1,9	2,3
Ash	0,16	0,13	1,5	3,06	0,022	0,013	2,9	2,3
Particle size <16mm>8mm	3,03	3,67	1,5	5,86	1,57	0,89	3,1	2,3
Particle size <8mm>5mm	2,02	3,13	2,4	5,86	1,02	0,63	2,6	2,3
Particle size <5mm>3mm	3,22	3,43	1,1	5,86	1,1	0,66	2,8	2,3
Particle size <3mm>2mm	0,45	1,2	7,1	5,86	0,26	0,21	1,5	2,3
Particle size <2mm	1,16	2,16	3,5	5,86	0,49	0,2	6,0	2,3



Comparison of results from Task I.1 and I.2

8mm pellets:

Parameter	Overall std.dev. Task I.1	Overall std.dev. Task I.2	F-value overall variation	F _{crit}	Sub-sample std.dev. Task I.1	Sub-sample std.dev. Task I.2	F-value Sub-sample std.dev.	F _{crit}
Moisture	0,71	0,27	6,9	2,9	0,084	0,063	1,8	2,1
Ash	0,07	0,04	2,9	2,9	0,017	0,016	1,1	2,1
Mechanical durability	0,24	0,13	3,4	2,9	0,068	0,081	1,4	2,1



Comparison of results from Task I.1 and I.2

6mm pellets:

Parameter	Overall std.dev. Task I.1	Overall std.dev. Task I.2	F-value overall variation	F _{crit}	Sub-sample std.dev. Task I.1	Sub-sample std.dev. Task I.2	F-value Sub-sample std.dev.	F _{crit}
Moisture	0,087	0,69	63	5,8	0,14	0,12	1,4	2,1
Ash	0,04	0,24	36	5,8	0,089	0,11	1,5	2,1
Mechanical durability	0,03	0,81	729	5,8	0,026	0,42	261	2,1



Comparison of results from Task I.1 and I.2

Olive residue:

Parameter	Overall std.dev. Task I.1	Overall std.dev. Task I.2	F-value overall variation	F _{crit}	Sub-sample std.dev. Task I.1	Sub-sample std.dev. Task I.2	F-value Sub-sample std.dev.	F _{crit}
Moisture	0,5	0,29	3,0	3,6	0,18	0,12	2,3	2,8
Ash	0,39	0,56	2,1	6,0	0,58	0,67	1,3	2,3
Aluminium	18	185	106	6,0	143	136	1,1	2,8
Calcium	344	1468	18	6,0	1018	1892	3,5	2,3
Magnesium	250	121	4,3	3,6	846	147	33	2,8
Sodium	43	40	1,2	3,6	45,6	42,6	1,1	2,8
Phosphorous	30	158	28	6,0	38,7	172	20	2,3
Silicon	264	1203	21	6,0	1326	992	1,8	2,8
Potassium	526	1068	4,1	6,0	549	1081	3,9	2,3
Nitrogen	0,091	0,088	1,1	3,6	0,071	0,2	7,9	2,3



Comparison of results from Task I.1 and I.2

Grape residue:

Parameter	Overall std.dev. Task I.1	Overall std.dev. TaskI.2	F-value overall variation	F _{crit}	Sub-sample std.dev. TaskI.1	Sub-sample std.dev. TaskI.2	F-value Sub-sample std.dev.	F _{crit}
Moisture	2,64	2,26	1,4	3,6	1,48	1,79	1,5	2,3
Ash	0,30	0,39	1,7	6,0	0,41	0,24	2,9	2,8
Aluminium	54	30	3,2	3,6	54,6	16,9	10,4	2,8
Calcium	1542	669	5,3	3,6	1291	1112	1,3	2,8
Magnesium	100	149	2,2	6,0	86,8	141	2,6	2,3
Sodium	95	110	1,3	6,0	19,1	49,8	6,8	2,3
Phosphorous	203	277	1,9	6,0	195	333	2,9	2,3
Silicon	146	288	3,9	6,0	294	147	4	2,8
Potassium	1643	1837	1,3	6,0	1152	1717	2,2	2,3
Nitrogen	0,056	0,072	1,7	6,0	0,062	0,029	4,6	2,8



Conclusions (Task I.1)

- No reduction method was significant better than the others
- No bias between sampling methods except for particle size distribution and mechanical durability
- Varying results in the comparison of the variances for increments and tests



Conclusions (Task I.2)

- Similar variances between Task I.1 and Task I.2 were obtained for bark, wood chips and grape residue.
- Significant differences were found for olive residue and the pellet materials.





Thank you for listening!



