



Project no. 038644
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



Report on the statistical analysis of Task I.1

Deliverable D.I.8

Due date of deliverable: 31/07/2008

Actual submission date: 01/08/2008

Start date of project: 1/1/2007

Duration: 36 month

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 UNIVPM – Università Politecnica delle Marche
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Revision 1

Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)		
Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
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Revisions

Version	Date	Author(s)	Change
1	24/07/2008	SLU	-
2	28/10/2008	SLU	Completing

Part I. Sampling

1. Introduction

Chemical and physical analyses of biofuels are always “behäftad” 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 affects 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 Task I.1 in BioNorm II WP I were to assess the relative bias of the two studied sampling methods, 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. In the following sections the design of the experiments is described and the statistical methods used for the evaluation are presented. In addition, the statistical analysis of moisture content in bark is given as a practical example.

1.1 Experimental design

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 batch, four increments of three different increment sizes each 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 batch, four increments of three different increment sizes each 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 batch, four increments of three different increment sizes each 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 pellet sacks or by random collection of pellet sacks from a conveyor during production. For each method, four increments of three different increment sizes were taken. Two sub-samples of each increment were tested for 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 batch, four increments of three different increment sizes each were taken by both methods. Two sub-samples of each increment were tested for ash, and mechanical durability.

2 Statistical analyses

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 batch 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 batch 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. An example on how the bias testing was performed is given in table 2.1.1 and figure 2.1.1 for the moisture content in bark.

Table 2.1.1. Significance test of the difference between heap and conveyor sampling for moisture content (wt-%) in bark

			Heap	Conveyor	Difference
20L	Mean diff	-0,07	62,68	63,08	-0,40
	Stddev	0,29	58,22	58,06	0,16
	t-value	-0,56	57,41	57,79	-0,38
	tcrit	2,78	60,42	60,28	0,14
			60,34	60,24	0,11
10L	Mean diff	0,03	62,65	63,55	-0,90
	Stddev	0,79	58,73	57,90	0,83
	t-value	0,07	57,79	58,48	-0,69
	tcrit	2,78	60,37	59,66	0,71
			60,76	60,58	0,18
5L	Mean diff	0,56	63,51	62,84	0,67
	Stddev	1,25	58,95	57,71	1,23
	t-value	1,01	58,39	57,63	0,75
	tcrit	2,78	61,05	59,34	1,70
			59,31	60,85	-1,55
Overall	Mean		60,09	59,80	0,29
	Stddev		1,875	2,033	0,856
				t-value	1,33
				tcrit	2,14

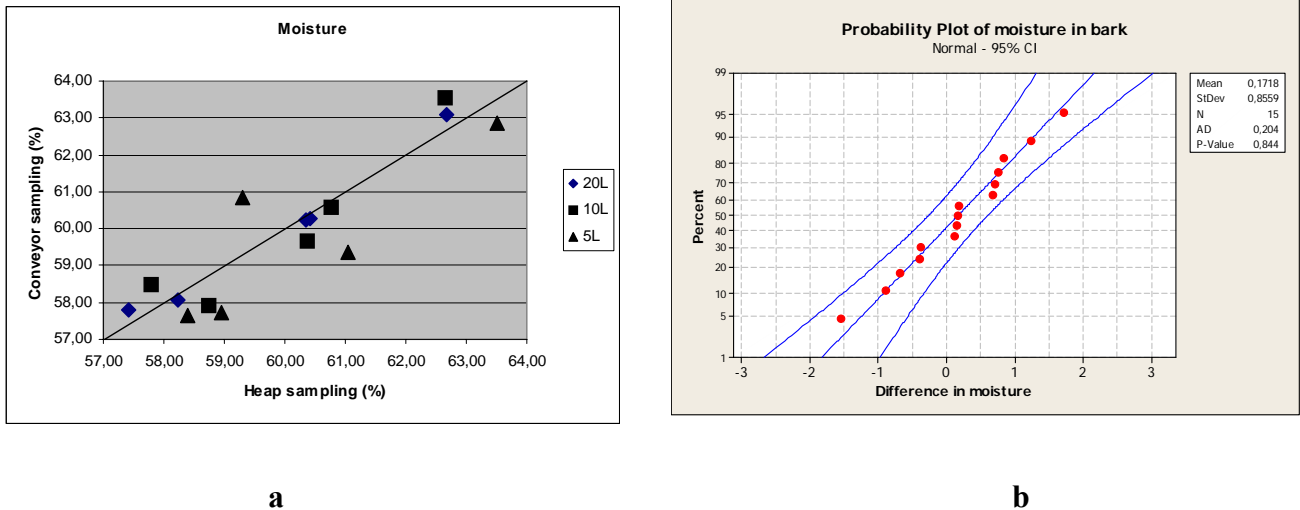


Figure 2.1.1 Bias testing between heap and conveyor sampling. a) Plot of conveyor sampling results versus heap sampling results for moisture content in bark. b) Probability plot of the difference between heap and conveyor sampling of moisture content in bark.

2.2 Evaluation of variances

2.2.1 Analysis of variance (ANOVA) of batches, increments and sub-sample tests

Basic information on the variability between bathes, increments and sub-sample tests due to sampling was provided by Analysis of Variances (ANOVA). An example of ANOVA for the moisture content in bark is given in Table 2.2.1.1 for the 10L increment.

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 batch, \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 batches B, the number of increments S and the number of sub-sample test T for the calculation of Sum of Squares (SoS) for the batches, the increments and the sub-sample tests according to the formulas given in table 2.2.1.1.

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

From the MS-values the individual variances σ_B^2 , σ_S^2 , σ_T^2 and the corresponding standard deviations s_B , s_S , s_T for the batches, the increments and the sub-sample tests were calculated from the formulas

$$MS_B = ST \sigma_B^2 + T \sigma_S^2 + \sigma_T^2$$

$$MS_S = T \sigma_S^2 + \sigma_T^2$$

$$MS_T = \sigma_T^2$$

Table 2.2.1.1 Analysis of variance (ANOVA) of moisture content in bark for the 10L increment size. a) heap sampling b) conveyor sampling. y_{bst} are the individual results of the sub-samples A and B, \hat{y}_{bs} is the average value of each increment, \hat{y}_b is the average value of each batch and \hat{y} is the grand average of all sub-samples. B is the number of batches, S is the number of increments and T is the number of sub-samples tested on each increment. SoS is the sum of squares, DoF is the degrees of freedom and MS is the mean squares.

a)

Sample No	Mark code Material and date	Heep or Conveyer and Point	Volume	y_{bst}		\hat{y}_b	\hat{y}_{bs}
				Sub-sample A %	Sub-sample B %		
				(1)	(2)		
202	B-080129	H 1:1	10 L	65,83	66,68		66,25
205	B-080129	H 1:2	10 L	64,96	66,11		65,54
208	B-080129	H 1:3	10 L	60,19	59,06		59,62
211	B-080129	H 1:4	10 L	59,10	59,28	62,65	59,19
226	B-080130	H 2:1	10 L	58,26	57,64		57,95
229	B-080130	H 2:2	10 L	57,75	57,56		57,65
232	B-080130	H 2:3	10 L	59,23	59,89		59,56
235	B-080130	H 2:4	10 L	60,28	59,26	58,73	59,77
250	B-080131	H 3:1	10 L	57,20	55,24		56,22
253	B-080131	H 3:2	10 L	57,97	57,73		57,85
256	B-080131	H 3:3	10 L	58,77	60,80		59,79
259	B-080131	H 3:4	10 L	57,24	57,37	57,79	57,30
274	B-080204	H 4:1	10 L	61,79	60,93		61,36
277	B-080204	H 4:2	10 L	60,48	62,04		61,26
280	B-080204	H 4:3	10 L	59,93	58,98		59,45
283	B-080204	H 4:4	10 L	59,54	59,26	60,37	59,40
298	B-080205	H 5:1	10 L	61,46	60,87		61,17
301	B-080205	H 5:2	10 L	62,93	62,30		62,62
304	B-080205	H 5:3	10 L	58,18	58,47		58,32
307	B-080205	H 5:4	10 L	61,13	60,74	60,76	60,93
$\hat{y} =$				60,06			

	SoS	DoF	MS		
Batches	$ST\sum(\hat{y}_b - \hat{y})^2 = 113,70$	$B-1 = 4$	28,43	$\sigma_B^2 = 2,46$	$s_B = 1,57$
Samples	$T\sum\sum(\hat{y}_{bs} - \hat{y}_b)^2 = 131,64$	$B(S-1) = 15$	8,78	$\sigma_S^2 = 4,16$	$s_S = 2,04$
Test	$\sum\sum\sum(y_{bst} - \hat{y}_{bs})^2 = 9,18$	$BS(T-1) = 20$	0,46	$\sigma_T^2 = 0,46$	$s_T = 0,68$

b)

Sample No	Mark code Material and date	Heep or Conveyer and Point	Volume	y_{bst}		\hat{y}_b	\hat{y}_{bs}
				Sub-sample A %	Sub-sample B %		
				(1)	(2)		
214	B-080129	C 1:1	10 L	67,92	67,97		67,94
217	B-080129	C 1:2	10 L	63,83	64,98		64,41
220	B-080129	C 1:3	10 L	61,36	62,02		61,69
223	B-080129	C 1:4	10 L	60,16	60,17	63,55	60,17
238	B-080130	C 2:1	10 L	58,28	58,78		58,53
241	B-080130	C 2:2	10 L	58,55	59,08		58,82
244	B-080130	C 2:3	10 L	58,68	58,13		58,41
247	B-080130	C 2:4	10 L	56,56	55,17	57,90	55,87
262	B-080131	C 3:1	10 L	62,19	58,11		60,15
265	B-080131	C 3:2	10 L	55,87	57,13		56,50
268	B-080131	C 3:3	10 L	58,44	58,90		58,67
271	B-080131	C 3:4	10 L	59,29	57,91	58,48	58,60
286	B-080204	C 4:1	10 L	60,67	60,14		60,40
289	B-080204	C 4:2	10 L	61,81	61,98		61,90
292	B-080204	C 4:3	10 L	57,22	56,77		56,99
295	B-080204	C 4:4	10 L	59,62	59,05	59,66	59,34
310	B-080205	C 5:1	10 L	61,18	61,13		61,15
313	B-080205	C 5:2	10 L	62,11	63,15		62,63
316	B-080205	C 5:3	10 L	60,41	61,31		60,86
319	B-080205	C 5:4	10 L	57,09	58,29	60,58	57,69
				$\hat{y} =$	60,04		

	SoS	DoF	MS		
Batches	$ST\sum(\hat{y}_b - \hat{y})^2 = 158,18$	B-1 = 4	39,55	$\sigma_B^2 = 3,73$	$s_B = 1,93$
Samples	$T\sum(\hat{y}_{bs} - \hat{y}_b)^2 = 146,14$	B(S-1) = 15	9,74	$\sigma_S^2 = 4,51$	$s_S = 2,12$
Test	$\sum\sum(y_{bst} - \hat{y}_{bs})^2 = 14,55$	BS(T-1) = 20	0,73	$\sigma_T^2 = 0,73$	$s_T = 0,85$

2.2.2 Significance tests of variances between increment sizes and sampling methods

Significance tests of differences in variances between increment sizes were performed on Mean Square-values since these have well defined Degrees of Freedom. In table 2.2.2.1 the MS-values for the determination of moisture content in bark are summarized. The differences in MS between the increment sizes were tested for their significance by using the F-distribution with $\alpha = 0.05$ (see table 2.2.2.2). As can be seen in table 2.2.2.2 the only significant difference between increment sizes was obtained for the increment sizes 20L and 5L for the sub-sample test variance. This difference, however, was not significant with $\alpha = 0.01$. If no significant difference is found between increment sizes within a sampling method an average of the variance may be calculated. This is carried out in table 2.2.2.3 for the batches and the increments for the two sampling methods and the differences between the methods are then tested for their significance as before. No significant difference was found.

For the sub-sample test variances the significance test of the difference between sampling methods was performed for the individual increment sizes. A significant difference in MS between the sampling methods was found for the 20L increment size. This difference, however, was not significant with $\alpha = 0.01$.

Table 2.2.2.1 Summary of the mean square values for the three increment sizes and the two sampling methods for the analyses of moisture in bark. MS_B , MS_S and MS_T are the mean squares of the batches, increments and sub-sample tests, respectively.

	20L	10L	5L
Heap	$MS_B = 34,4$	$MS_B = 28,4$	$MS_B = 34,7$
	$MS_S = 9,61$	$MS_S = 8,78$	$MS_S = 12,17$
	$MS_T = 0,293$	$MS_T = 0,459$	$MS_T = 0,773$
Con-veyor	$MS_B = 36,4$	$MS_B = 39,5$	$MS_B = 39,2$
	$MS_S = 10,55$	$MS_S = 9,74$	$MS_S = 11,87$
	$MS_T = 0,680$	$MS_T = 0,728$	$MS_T = 1,148$

Table 2.2.2.2 Significance tests of the mean squares (F-distribution) between the increments for the batches, increments and sub-sample tests, respectively for the two sampling methods.

		F (20L vs 10L)	F (20L vs 5L)	F (10L vs 5L)	F_{crit}
Heap	Batches	1,21	1,01	1,22	6,39
	Increments	1,09	1,27	1,39	2,40
	Sub-sample Tests	1,57	2,64	1,68	2,12
Con-veyor	Batches	1,09	1,08	1,01	6,39
	Increments	1,08	1,12	1,22	2,40
	Sub-sample Tests	1,07	1,69	1,58	2,12

Table 2.2.2.3 Significance tests of the mean squares (F-distribution) between the sampling methods for the batches, increments and sub-sample tests, respectively. $H_{average}$ and $C_{average}$ are the average values of the mean square for the three increment sizes for the heap and the conveyor sampling method, respectively.

	20L	10L	5L	$H_{average}$	$C_{average}$	F_{crit}
Batches	1,18			32,50	38,35	2,69
Increments	1,05			10,18	10,72	1,65
Sub-sample Tests	2,32	1,58	1,49			2,12

2.2.3 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.

2.2.4 Calculation of number of increments and sub-sample tests.

To evaluate the appropriate number of increments and sub-sample tests for a certain accepted sampling error, e , the pooled variances for the increments and the sub-sample tests, $\sigma^2_{\text{pooled,S}}$ and $\sigma^2_{\text{pooled,T}}$, were used in the equation

$$e = t^* (\sqrt{(\sigma^2_{\text{pooled,S}}/S + \sigma^2_{\text{pooled,T}}/T)}) / \hat{y} * 100$$

where e is the relative sampling confidence interval; S is the number of increments, T is the sub-sample tests, t is the Student's value for $\alpha = 0.05$ and \hat{y} is the grand average. The graph e vs S was then used for the evaluation of the relative sampling error as a function of increment numbers for certain values of sub-sample tests (see figure 2.2.4.1). However, the calculations of the number of increments and sub-sample tests are preliminary, since a thorough discussion within the WP I group how to interpret the statistical results is necessary.

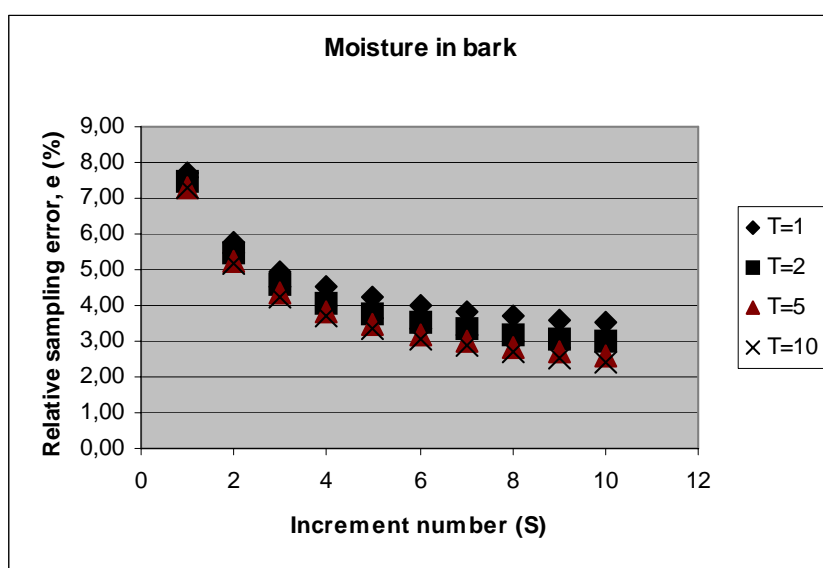


Figure 2.2.4.1 Relative sampling confidence interval (e) as a function of increment numbers (S) for certain values of sub-sample tests (T).

3 Results

3.1 Olive residue

3.1.1 Bias

No bias between the sampling methods was found except for the 2L-increments of Aluminium and Magnesium, where the heap sampling showed higher values than the conveyor sampling (see figure 3.1.1.1). The t-values were 3.3 and 3.7 for Al and Mg, respectively.

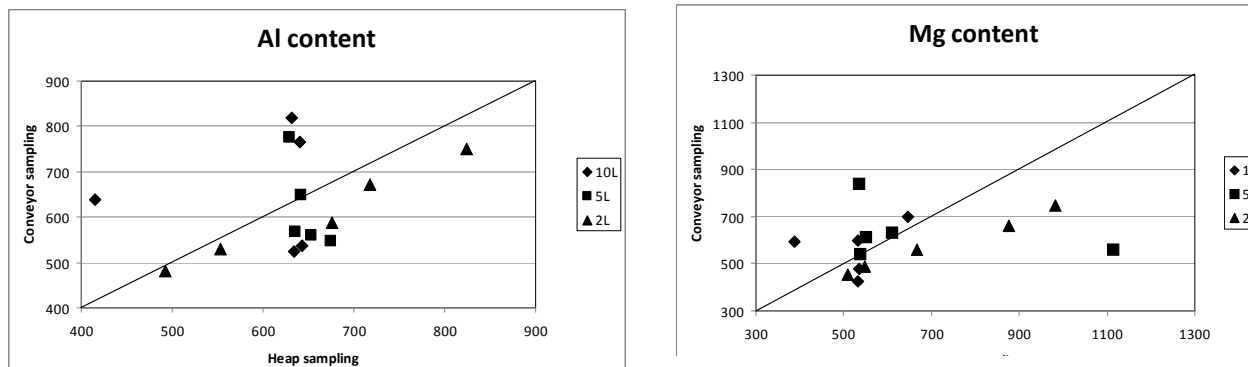


Figure 3.1.1.1 Test of bias between sampling methods for aluminium and magnesium in olive residue by potting conveyor sampling vs. heap sampling.

3.1.2 Analysis of Variance

Moisture: A significant difference in variance of the tests was found between the sample sizes. However, the sampling methods showed opposite behaviour. In addition, significant differences in test variances were found between the sampling methods for the 10L and 5L increments, but in different directions.

In figure 3.1.2.1 the relative sampling error as a function of increment number is shown for moisture.

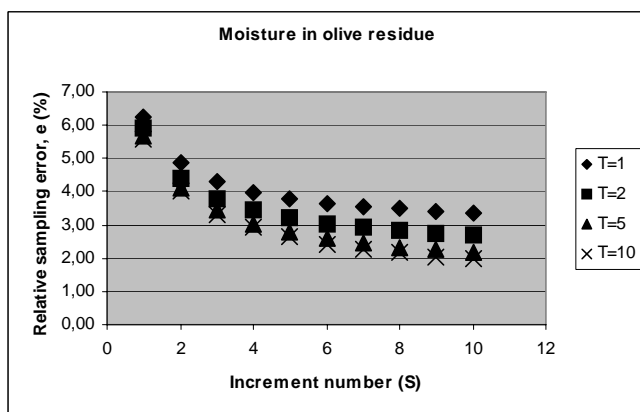


Figure 3.1.2.1 Relative sampling error of moisture in olive residue as a function of increment number for various numbers of sub-sample tests.

Ash: Significant differences between variances were found for both sample sizes and sampling methods, but without any clear trend. In figure 3.1.2.2 the relative sampling error as

a function of increment number is shown for ash. Since the variability of ash in olive residue is high, a large number of increments are needed to obtain a reasonable confidence interval. The figure also shows that the number of sub-sample tests has a large impact on the sampling error. The relative repeatability standard deviation for ash content was 3.0 %.

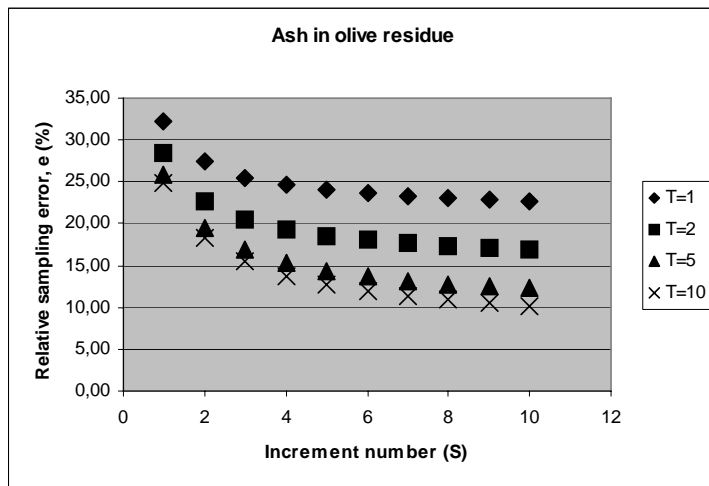


Figure 3.1.2.2 Relative sampling error of ash in olive residue as a function of increment number for various numbers of sub-sample tests.

Aluminium: Significant differences between variances were found for both sample sizes and sampling methods, but without any clear trend. In figure 3.1.2.3 the sampling error as a function of increment number is shown for aluminium. Since the variability of aluminium in olive residue is high a large number of increments are needed to obtain a reasonable confidence interval. The figure also shows that the number of sub-sample tests has a large impact on the sampling error. The relative repeatability standard deviation for aluminium content was 10.6 %.

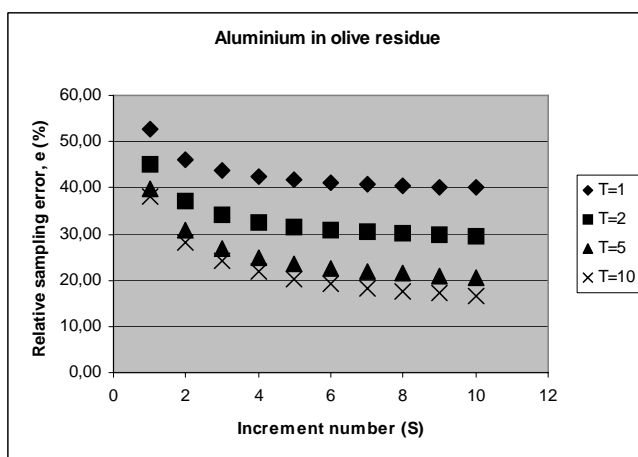


Figure 3.1.2.3 Relative sampling error of aluminium in olive residue as a function of increment number for various numbers of sub-sample tests.

Calcium: Significant differences were found between the 2L increment compared to the larger increments. In addition, the conveyor sampling method showed lower variance compared to the heap sampling

Figure 3.1.2.4 shows the relative sampling error as a function of increment number for calcium. The figure shows that the increment number has little effect on the sampling error since the variance of the sub-sample test is much larger than the increment variance. The relative repeatability standard deviation for calcium content was 12.8 %.

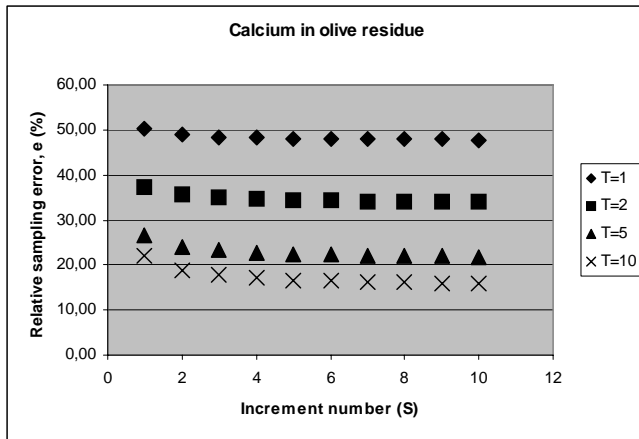


Figure 3.1.2.4 Relative sampling error of calcium in olive residue as a function of increment number for various numbers of sub-sample tests.

Magnesium: Significant differences between variances were found for both sample sizes and sampling methods, with a smaller variability for the conveyor sampling. In figure 3.1.2.5 the sampling error as a function of increment number is shown for magnesium. Due to the large variability of the sub-sample tests for magnesium, little effect of the increment number on sampling error was shown. The relative repeatability standard deviation for magnesium content was 5,9 %.

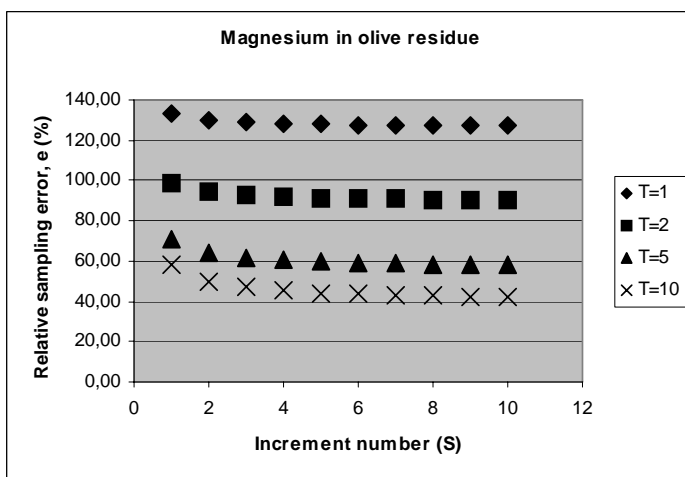


Figure 3.1.2.5 Relative sampling error of magnesium in olive residue as a function of increment number for various numbers of sub-sample tests.

Sodium: Only small differences in variance between the increment sizes and the sampling methods were found for sodium. In figure 3.1.2.6 the sampling error as a function of increment number is shown for sodium. As shown, both the increment number and the number of sub-sample tests effect the sampling error. The relative repeatability standard deviation for sodium content was 2.5 %.

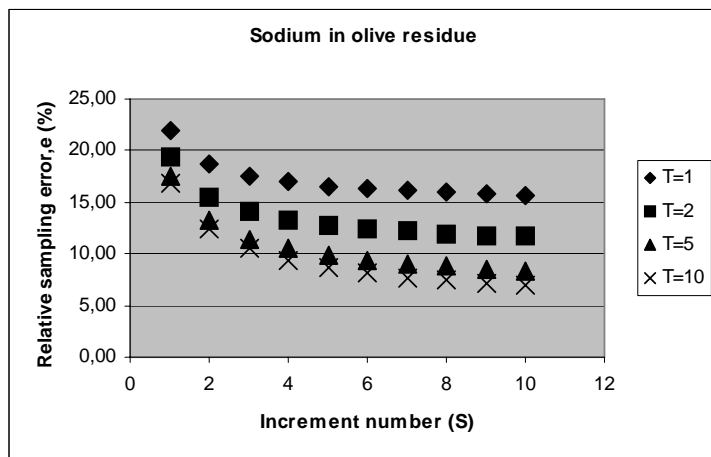


Figure 3.1.2.6 Relative sampling error of sodium in olive residue as a function of increment number for various numbers of sub-sample tests.

Phosphorous: Only small differences in variance were found for phosphorous. In figure 3.1.2.7 the sampling error as a function of increment number is shown for phosphorous. Both the increment number and the number of sub-sample tests have effect on the sampling error. The relative repeatability standard deviation for phosphorous content was 5.3 %.

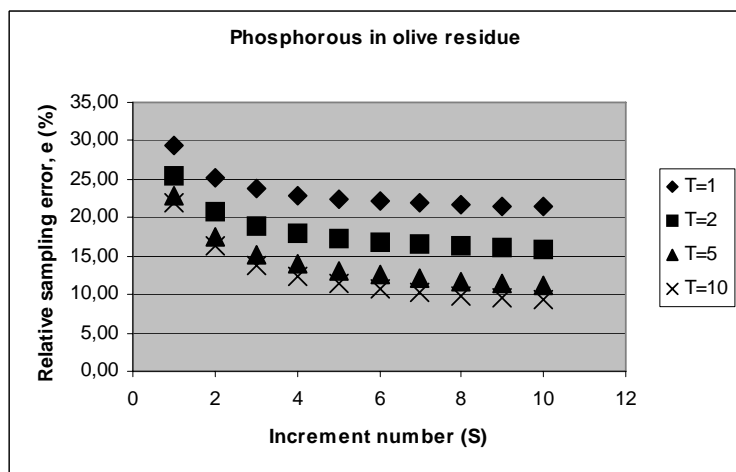


Figure 3.1.2.7 Relative sampling error of phosphorous in olive residue as a function of increment number for various numbers of sub-sample tests.

Silicon: Significant differences between variances were found for both sample sizes and sampling methods, but without any clear trend. In figure 3.1.2.8 the sampling error as a function of increment number is shown for silicon. Since the variability of silicon in olive residue is high a large number of increments are needed to obtain a reasonable confidence interval. Also the number of sub-samples has considerable effect on the sampling error. The relative repeatability standard deviation for silicon content was 14.6 %.

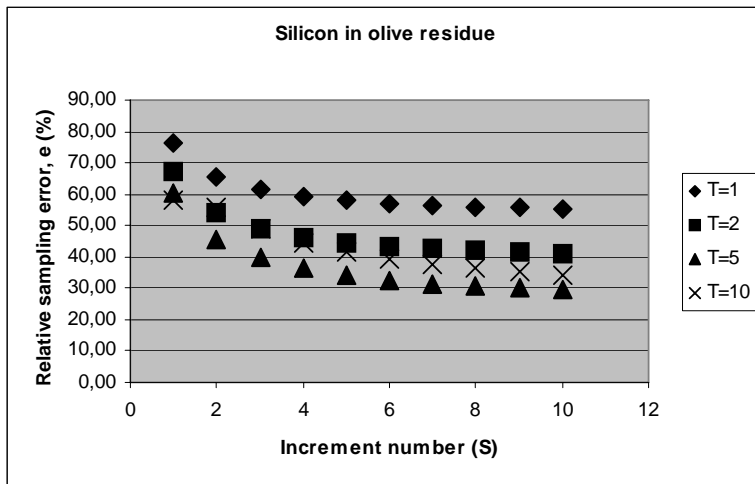


Figure 3.1.2.8 Relative sampling error of silicon in olive residue as a function of increment number for various numbers of sub-sample tests.

Potassium: Only small differences in variance were found for potassium. In figure 3.1.2.9 the sampling error as a function of increment number is shown for potassium. The effect of increment number and number of sub-sample tests on the sampling error was of the same order. The relative repeatability standard deviation for potassium content was 2.7 %.

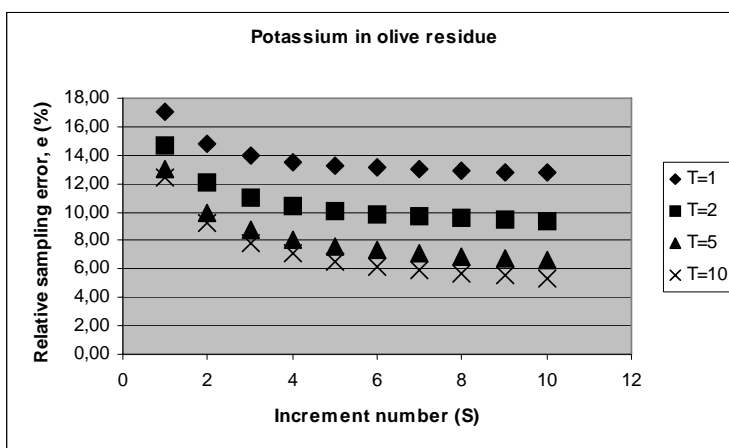


Figure 3.1.2.9 Relative sampling error of potassium in olive residue as a function of increment number for various numbers of sub-sample tests.

Nitrogen: Only the difference in increment variance between the 10L increment compared to the other two was found significant. No difference between the sampling methods was found. In figure 3.1.2.9 the sampling error as a function of increment number is shown for potassium. The effect of the number of sub-sample tests on the sampling error is larger than the increment number due to its larger variance. The relative repeatability standard deviation for nitrogen content was 4,6 %.

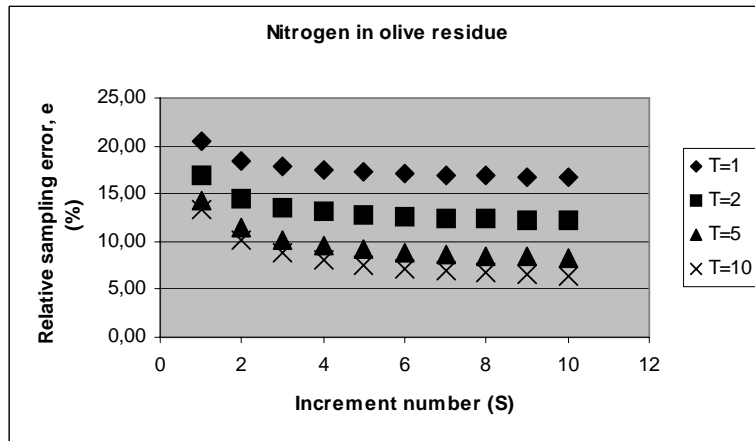


Figure 3.1.2.9 Relative sampling error of nitrogen in olive residue as a function of increment number for various numbers of sub-sample tests.

3.2 Grape residue

3.2.1 Bias

A bias between the sample methods was found for the 2L increment of potassium, where the conveyor sampling gave higher potassium content than the heap sampling (see figure 3.2.1.1). The t-value was 5.78. In all other cases no difference between the sampling methods was found.

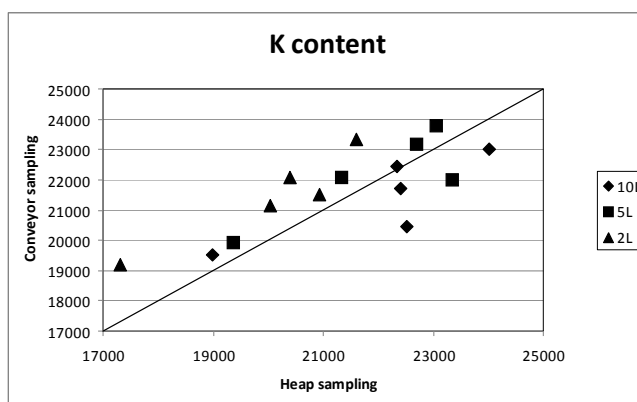


Figure 3.2.1.1 Test of bias between sampling methods for potassium in grape residue by plotting conveyor sampling vs. heap sampling.

3.2.2 Analysis of Variance

Moisture: The 2L increment for the conveyor sampling showed a significant lower variance compared to both the other increment sizes and the heap sampling.

In figure 3.2.2.1 the sampling error as a function of increment number is shown for moisture. The number of sub-sample tests has the dominating effect on the sampling error and due to the low variability a small confidence interval is obtained.

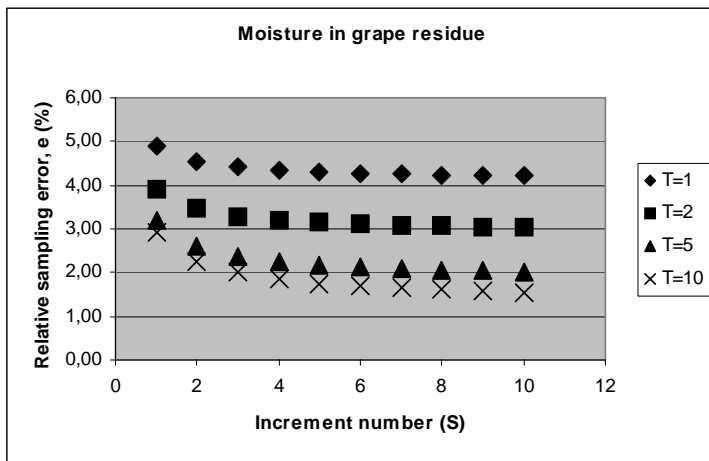


Figure 3.2.2.1 Relative sampling error of moisture in grape residue as a function of increment number for various numbers of sub-sample tests.

Ash: Significant differences in variance between the various increment sizes were found for both sampling methods. Figure 3.2.2.2 shows the sampling error as a function of increment number for ash. Due to the large variability of ash content in grape residue a rather large confidence interval is obtained. The relative repeatability standard deviation for ash content was 3.3%.

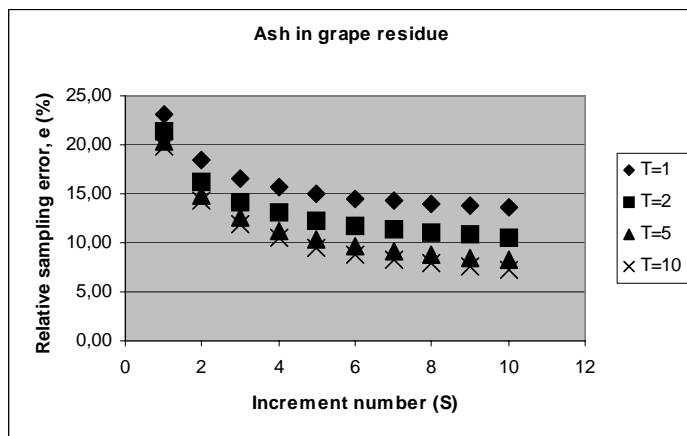


Figure 3.2.2.2 Relative sampling error of ash in grape residue as a function of increment number for various numbers of sub-sample tests.

Aluminium: Significant differences in variance in the sub-sample tests between the increment sizes were found for both sampling methods. Figure 3.2.2.3 shows the sampling error as a function of increment number for aluminium. A large variability of the aluminium content and a large repeatability standard deviation causes a large confidence interval. The relative repeatability standard deviation for aluminium was 17.4 %.

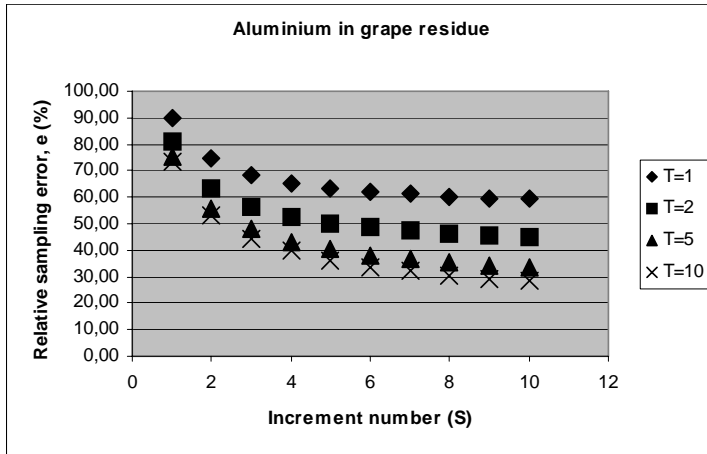


Figure 3.2.2.3 Relative sampling error of aluminium in grape residue as a function of increment number for various numbers of sub-sample tests.

Calcium: Significant differences in variance were found between increment sizes and sampling methods, but no clear trend was noticed. Figure 3.2.2.4 shows the sampling error as a function of increment number for calcium. A very large variability of calcium in grape residue is the reason for the large sampling error. The relative repeatability standard deviation for calcium was as small as 1.6 %.

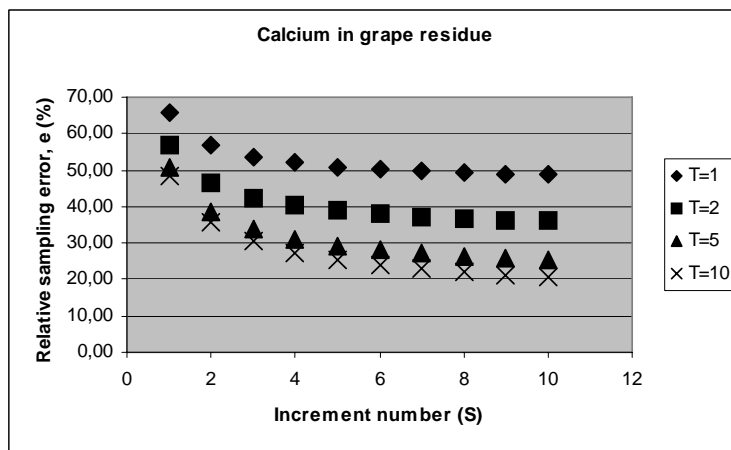


Figure 3.2.2.4 Relative sampling error of calcium in grape residue as a function of increment number for various numbers of sub-sample tests.

Magnesium: The same pattern as for the former elements with significant differences in variance between increment sizes and sampling methods was also shown for magnesium. Figure 3.2.2.5 shows the sampling error as a function of increment number for magnesium. A rather small variability of magnesium gives a reasonable confidence interval. The relative repeatability standard deviation for calcium was 3.4 %.

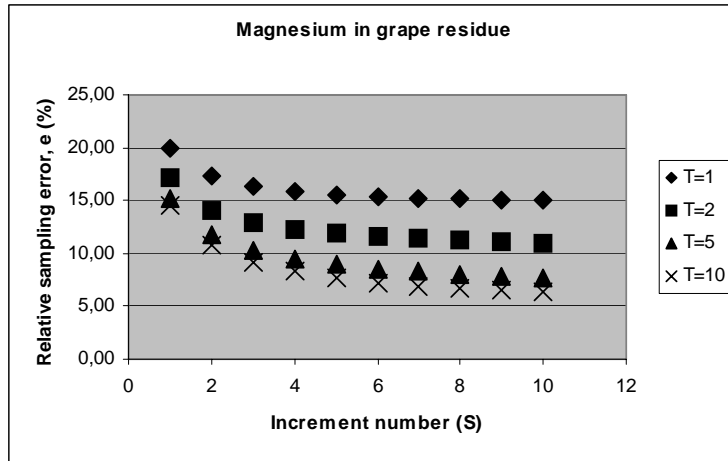


Figure 3.2.2.5 Relative sampling error of magnesium in grape residue as a function of increment number for various numbers of sub-sample tests.

Sodium: The pattern for sodium is the same as for calcium and magnesium. Figure 3.2.2.6 shows the sampling error as a function of increment number for sodium. A large relative variability gives rise to a large confidence interval. The number of sub-sample tests has little impact on the sampling error. The relative repeatability standard deviation for sodium was 5.8 %.

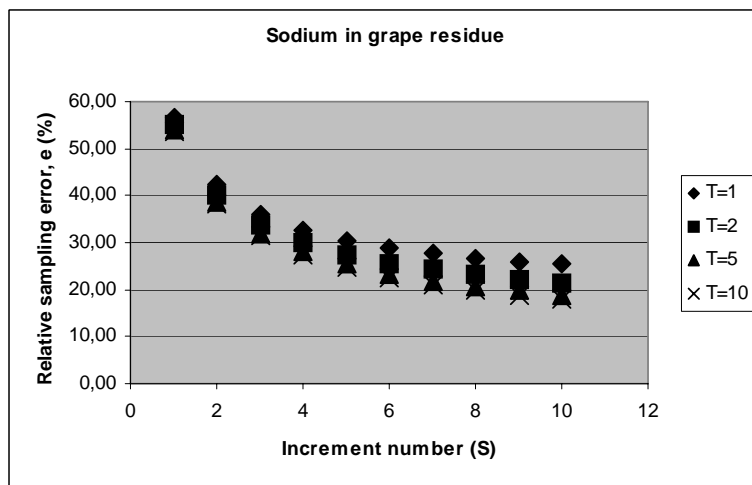


Figure 3.2.2.6 Relative sampling error of sodium in grape residue as a function of increment number for various numbers of sub-sample tests.

Phosphorous: Only a few significant differences were found for phosphorous. Figure 3.2.2.7 shows the sampling error as a function of increment number for phosphorous. The increment number and the number of sub-sample tests have similar effects on the sampling error. The relative repeatability standard deviation for phosphorous was 2.7 %.

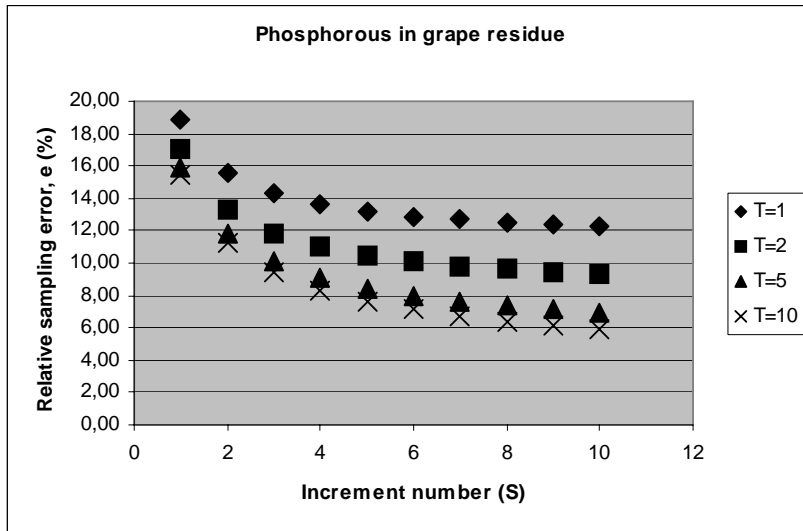


Figure 3.2.2.7 Relative sampling error of phosphorous in grape residue as a function of increment number for various numbers of sub-sample tests.

Silicon: Large significant differences in variance were found between both the increment sizes and the sampling methods. Figure 3.2.2.8 shows the sampling error as a function of increment number for silicon. The large variability of silicon in grape residue and the large repeatability standard deviation are the cause of the large confidence interval. The figure also shows that the number of sub-sample tests has the dominating effect on the sampling error. The relative repeatability standard deviation for silicon was as large as 18.0 %.

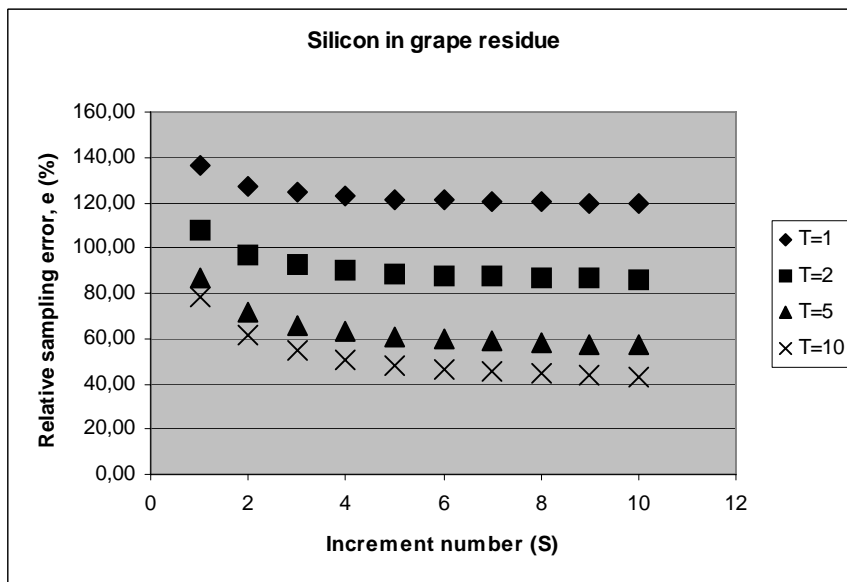


Figure 3.2.2.8 Relative sampling error of silicon in grape residue as a function of increment number for various numbers of sub-sample tests.

Potassium: Almost no significant difference in variance was found for potassium. In figure 3.2.2.9 the sampling error as a function of increment number is shown for potassium. A reasonable sampling error was obtained due to moderate variance. The relative repeatability standard deviation for potassium was 2.4 %.

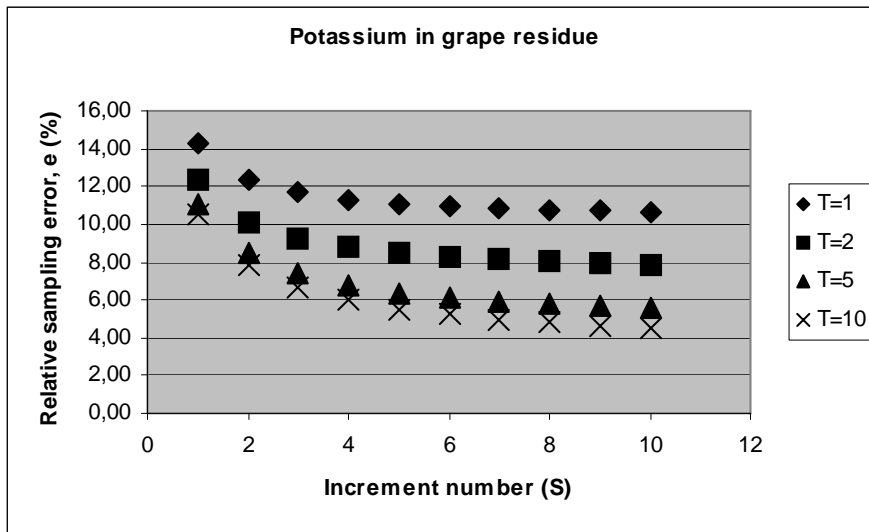


Figure 3.2.2.9 Relative sampling error of potassium in grape residue as a function of increment number for various numbers of sub-sample tests.

Nitrogen: As for potassium small differences in variance were found for nitrogen. In figure 3.2.2.10 the sampling error as a function of increment number is shown for nitrogen. A rather small confidence interval was obtained due to low variability of nitrogen in grape residue and a small repeatability standard deviation for the analytical method. The relative repeatability standard deviation for nitrogen was 1.6 %.

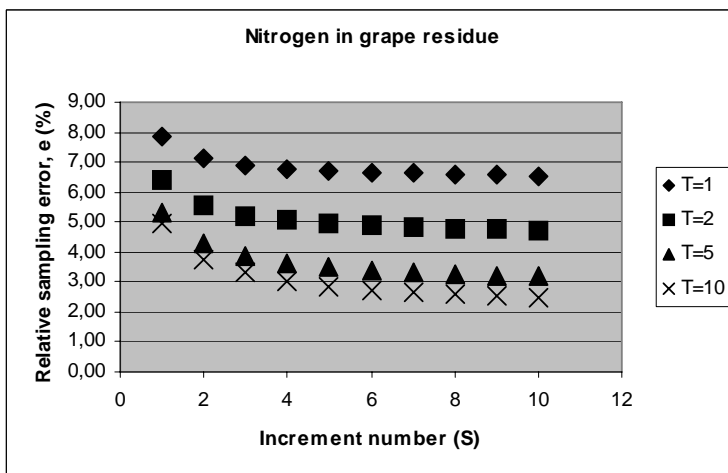


Figure 3.2.2.10 Relative sampling error of nitrogen in grape residue as a function of increment number for various numbers of sub-sample tests.

3.3 Wood chips

3.3.1 Bias

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 3.3.1.1). 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.

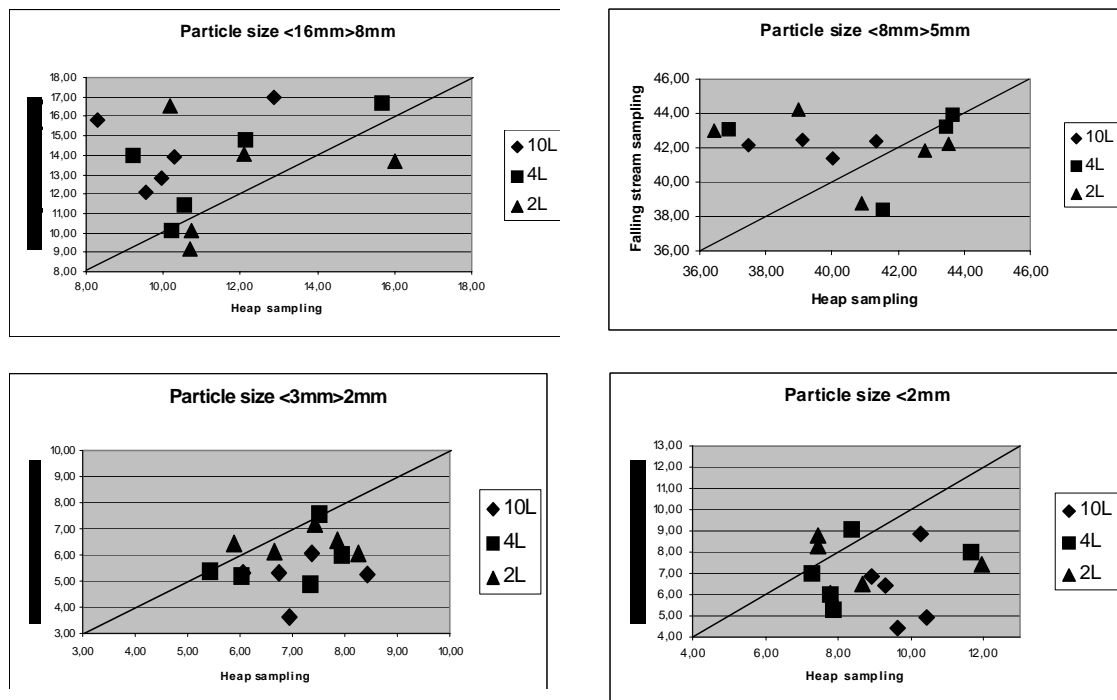


Figure 3.3.1.1 Test of bias between sampling methods for particle size in wood chips by plotting conveyor sampling vs. heap sampling.

3.3.2 Analysis of Variance

No pronounced trend for the difference in variance for moisture and particle size distribution was found in wood chips, even if a slightly higher variance in the conveyor sampling can be observed. In figure 3.3.2.1 the sampling error as a function of increment number is shown for moisture content, ash content and the five particle sizes. In all cases only the increment number has any effect on the sampling error. A rather high confidence interval was obtained for the ash content due to high variability in wood chips. The relative repeatability standard deviation for nitrogen was 1.9 %.

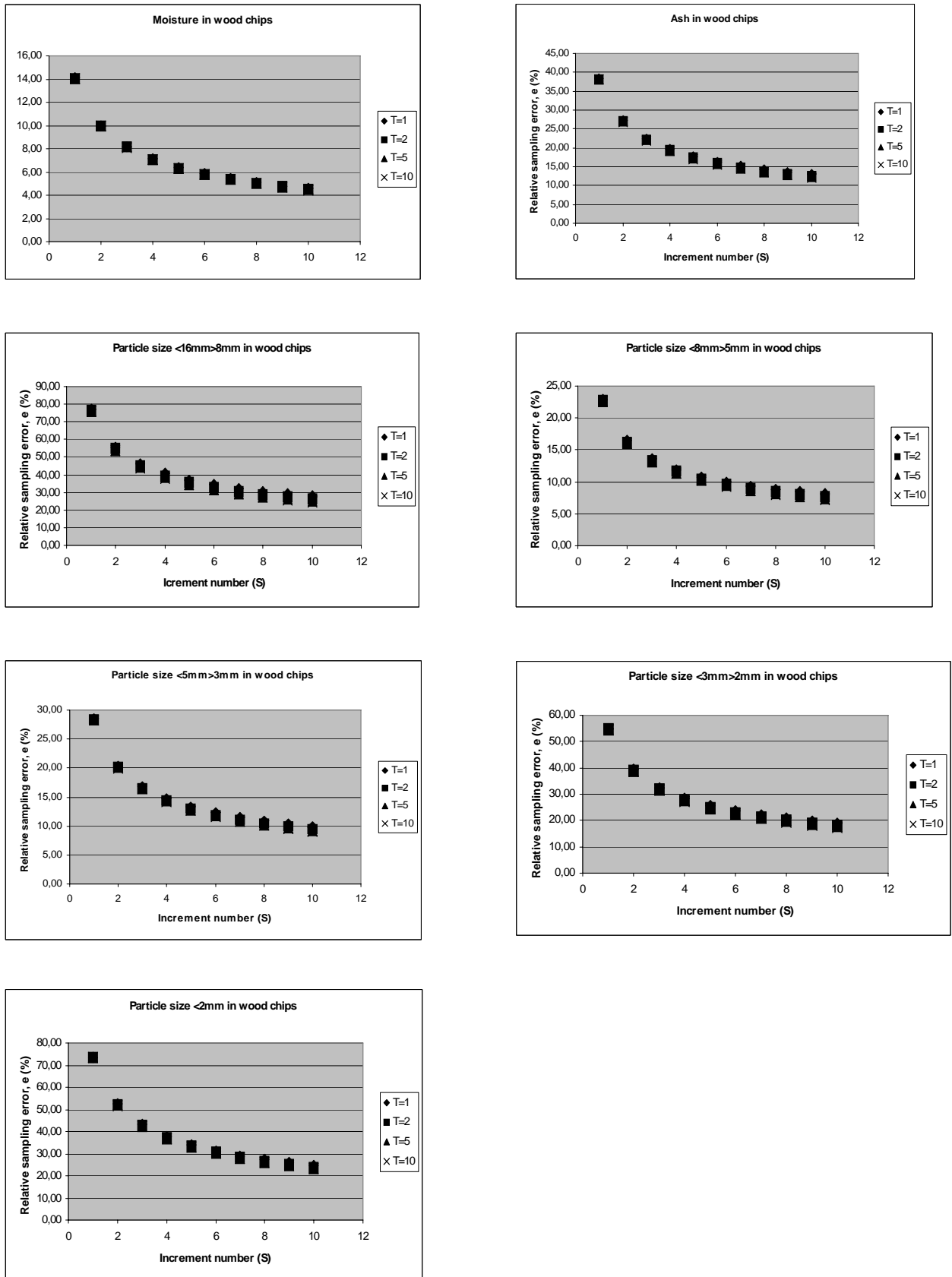


Figure 3.3.2.1 Relative sampling error of moisture content, ash content and five different particle sizes in wood chips as a function of increment number for various numbers of sub-sample tests.

3.4 Bark

3.4.1 Bias

No bias between the sampling methods was observed for the bark material.

3.4.2 Analysis of Variance

No significant difference in variance was found for moisture content and calorific value in bark, while a significant higher test and increment variation of ash content was observed for the conveyor sampling.

In figure 3.4.2.1 the sampling as a function of increment number is shown for moisture content, calorific value and ash content. For moisture content only the increment number affect the sampling error significantly, while also the number of sub-sample tests influence the confidence interval for ash content and gross calorific value. An extremely low sampling error below 1% was obtained for gross calorific value. The relative repeatability standard deviations for were 0.33 % and 0.08 % for ash content and calorific value, respectively.

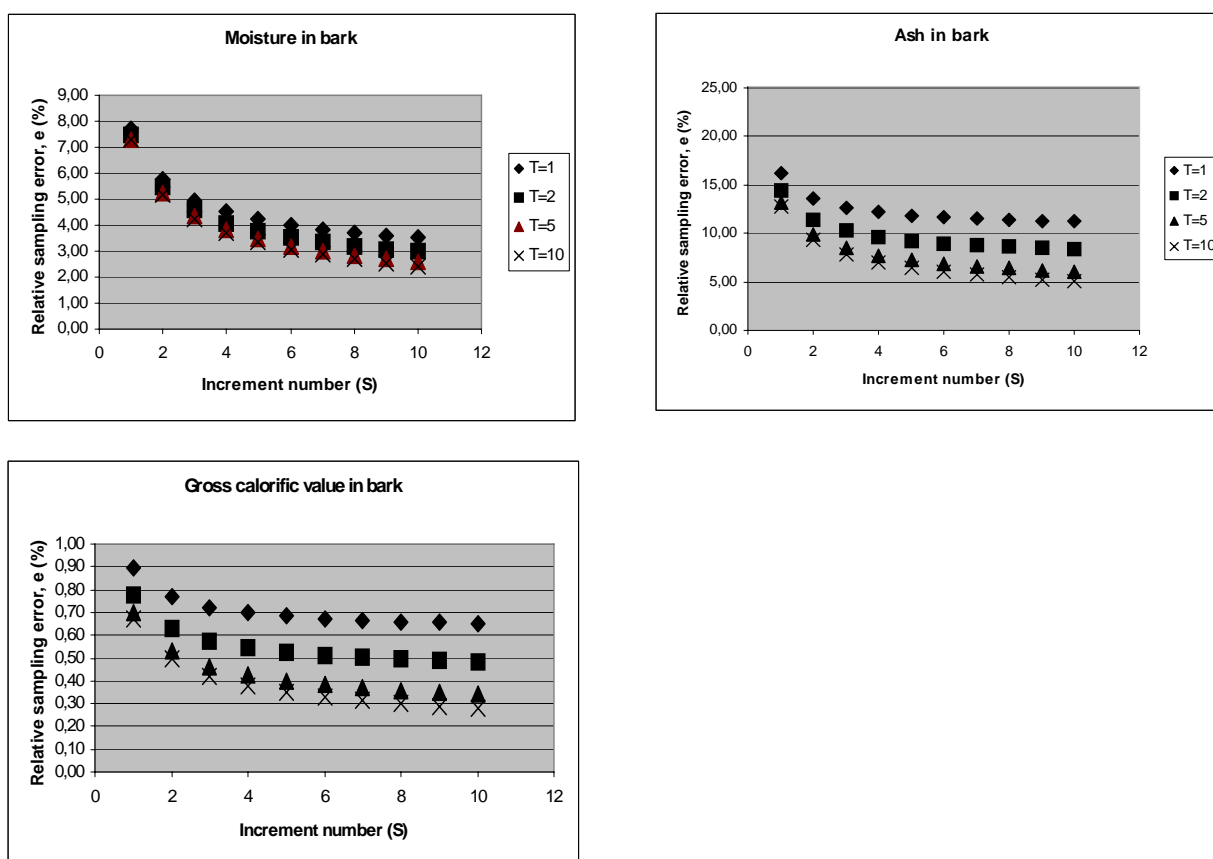


Figure 3.4.2.1 Relative sampling error of moisture content, ash content and gross calorific value in wood chips as a function of increment number for various numbers of sub-sample tests.

3.5 Pellets (6mm)

3.5.1 Bias

No significant bias between the sampling methods was observed for the pellets material.

3.5.2 Analysis of Variance

Moisture: Significant differences in variance were found between both increment sizes and sampling methods. However, no pronounced trend was observed. Figure 3.5.2.1 shows the sampling error as a function of increment number for moisture content. A low confidence interval was obtained due to low variability in pellets. The increment number and the number of sub-sample tests affected the sampling error of the same order.

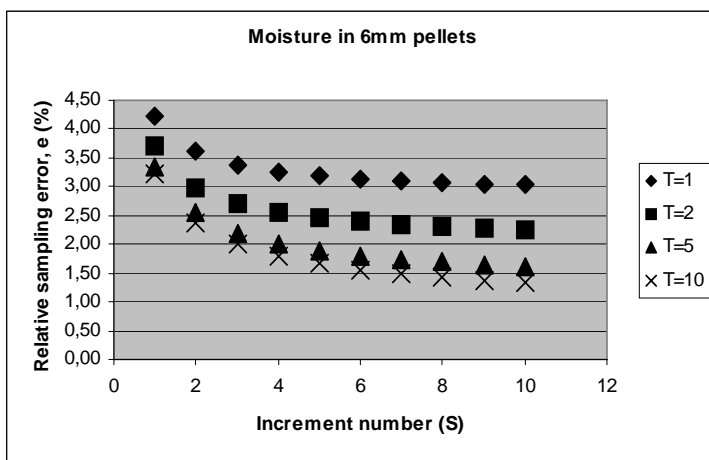


Figure 3.5.2.1 Relative sampling error of moisture content in 6mm pellets as a function of increment number for various numbers of sub-sample tests.

Ash: No significant difference in variance was observed for ash content in 6mm pellets. Figure 3.5.2.2 shows the sampling error as a function of increment number for ash content.

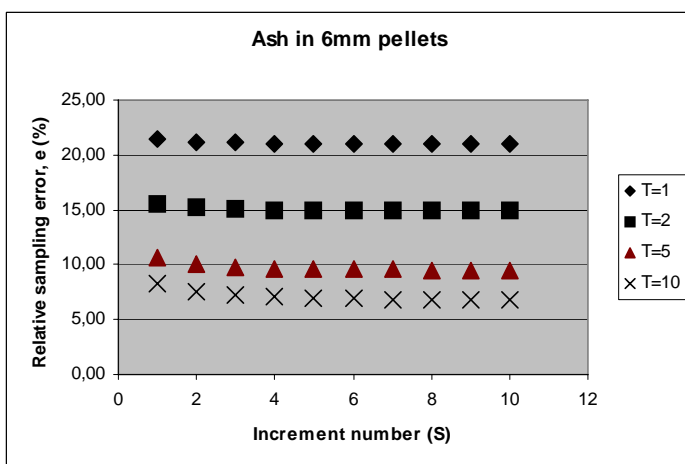


Figure 3.5.2.2 Relative sampling error of ash content in 6mm pellets as a function of increment number for various numbers of sub-sample tests.

As shown in figure 3.5.2.2 only the number of sub-sample tests affects the sampling error. A rather high confidence level was obtained mostly due to the high relative repeatability standard deviation for ash content of 14.4 %.

Mechanical durability: A significant difference in variance was found between increment sizes for the conveyor sampling method, where the smallest increment size showed the smallest variance. No difference between sampling methods was observed.

Figure 3.5.2.3 shows the extremely small sampling error a function of increment number for mechanical durability.

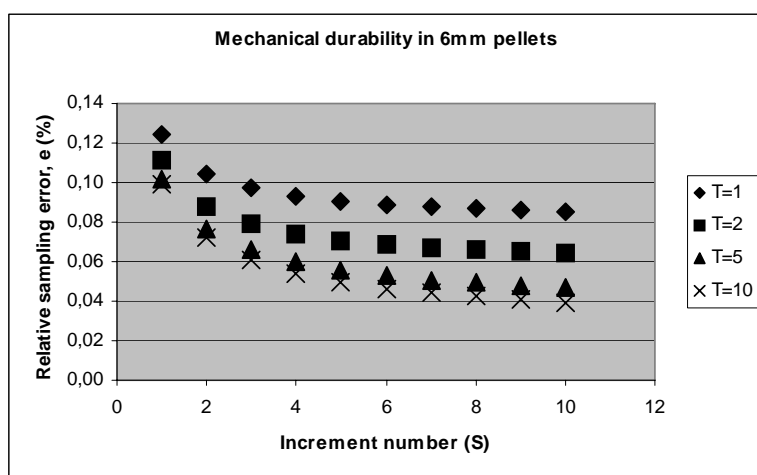


Figure 3.5.2.3 Relative sampling error of mechanical durability in 6mm pellets as a function of increment number for various numbers of sub-sample tests.

4. Conclusions

For bark, wood chips and 6mm pellets easy interpretable results for most analytical parameters have been obtained with small differences in variance and an observed bias between the sampling methods only for the particle size distribution.

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. An explanation to this might be the high degree heterogeneity of these materials. In most cases, however, no bias was observed between the sampling methods.

Part II. Sample reduction

1. Introduction

Part II contains tables and graphs displaying the results of the analysis of the data obtained in the sample reduction experiments carried out by Partner 2 (CTI), Partner 3 (UNIVPM) and Partner 4 (SLU).

These results are presented so that:

- The originators of the test results can check the accuracy of suspicious values;
- The partners in WPI can make an assessment of the results.

In each sample reduction experiment, a sample of biofuel was reduced to 16 sub-samples by the application of one of the methods of sample reduction. Results are presented in the following ways.

- Tables of averages, standard deviations, coefficients of variation, confidence interval of the averages, repeatability standard deviation of the test methods and relative repeatability standard deviation of the test methods.
- Graphs displaying the individual test results on the 16 sub-samples together with lines representing one and two standard deviations, respectively.

The averages and standard deviations are calculated using the formulas given in paragraph 2.2. In work of the type presented here it is common to find a small proportion of outliers or suspicious results in the data. Therefore outliers, detected by using the Dixons outlier test (Dixon 1953), were rejected before the calculation of the average and the standard deviation.

The CoV expresses a standard deviation as a percentage of the corresponding average.

2. Statistical methods

2.1. Symbols and abbreviations

The abbreviations used in the graphs are listed in Table 2.1.1.

Table 2.1.1 Key to abbreviations used in the graphs

Abbreviation	Description
C&Q	Coning and quartering
RB	Riffle box
LP	Long pile
\bar{x}	Average
s	Standard deviation
CoV	Coefficient of variation
Conf.int.	Confidence interval
F	F-distribution
s_r	Repeatability standard deviation of the test method
$s_{r, rel}$	Relative repeatability standard deviation of the test method

2.2. Statistical calculations

The average, \bar{x} and the standard deviation, s of the test results on the 16 sub-samples are calculated as:

$$\bar{x} = \frac{\sum x_i}{n}, \quad \text{and}$$

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}, \quad \text{where } x_i \text{ is the individual test results and } n \text{ is the number of sub-}$$

samples. Outliers according to Dixon (Dixon 1953) were eliminated before the calculation of \bar{x} and s .

Given the average \bar{x} and standard deviation s of the test results on 16 sub-samples, the coefficient of variation (CoV) is calculated as:

$$CoV = 100 \times \frac{s}{\bar{x}} \quad \%$$

This formula is used with the results of moisture, ash and chloride determinations. With determinations of particle size distribution, a modified formula (CoV') is used:

$$CoV' = 100 \times \frac{s}{\sqrt{\bar{x}(100 - \bar{x})}} \quad \%$$

This is because the results of particle size determinations must fall between 0% and 100%.

The confidence interval is used to decide whether the average for the various sample reduction methods differ significantly and is calculated as:

$$\text{Conf.int.} = \bar{x} \pm t \frac{s}{\sqrt{n}}$$

where t is the Student's t-factor for $\alpha = 0.05$.

The F-distribution is used to decide whether there is a significant difference in variance between the various sample reduction methods. F is calculated from the following formula:

$$F = \frac{s_1^2}{s_2^2}, \text{ where } s_1^2 > s_2^2.$$

If F is larger than the F_{crit} -value obtained from a table of percentage points of the F-distribution for $\alpha = 0.05$, the variance s_1^2 is significantly larger than s_2^2 .

The repeatability standard deviation, s_r of the test methods were determined either by measuring 5 replicates of the general analysis sample from one sub-sample, or from the analysis of variance (ANOVA) of duplicate determinations of the general analysis sample from the 16 sub-samples respectively. s_r is used to decide whether the variability of the sample reduction is significantly larger than for the test methods. $s_{r, \text{rel}}$ expresses the repeatability standard deviation as a percentage of the corresponding average.

3. Main conclusions

- None of the methods of sample reduction used in the experiments gave disastrous results, so no method can be ruled out from use in practice on the basis of these experiments.
- It is possible to make mistakes and obtain poor quality results with all the methods. Thus it is important that technicians should regularly and routinely check the repeatability that they achieve with whatever sample reduction methods they use.
- Table 3.1.1 gives the “preferred” methods (i.e. those that gave the least variation between sub-samples) in each of the experiments. As was noticed, however, no method of sample reduction was significantly better than the others in every case and in most cases no significant difference in variability between the sample reduction methods was found (for details, see discussion for the specific material). This means that the choice of sample reduction method in most cases is decided from a practical point of view, i.e. time consumption, number and size of sub-samples, etc. It should be pointed out, however, that the long pile method is very time consuming and might affect i.e. moisture content, while the riffle box is fast and convenient and it has also the advantage to collect all of the sub-sample which reduces the risk of losing fine particles during the reduction step.
- Determination of moisture was included in these experiments because of the importance of moisture in biofuels, and because moisture is an example of a property that is not liberated (i.e. every particle can be expected to contain a similar proportion of moisture). However in some cases it has been observed that the moisture content in the materials alters noticeably during the reduction process. Hence it is clearly important that reduction should be avoided with samples that are taken for moisture determination and a sample size should be chosen so that reduction is not necessary for such samples.

Table 3.1.1 Preferred methods for sample reduction

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

4. Discussion – Olive residue

From Table 4.1, no one method of sample reduction gave a significant smaller between sub-sample standard deviation than the others for all three of the test methods.

- Moisture – Long pile and Coning & Quartering are significantly better than Riffle box.
- Ash – Riffle box is significantly better than Long pile.
- Potassium – Coning & Quartering is significantly better than Riffle box.
- Nitrogen – Riffle box is significantly better than Long pile.

Thus for determination of the studied parameters the choice of sample reduction method in most cases is decided from a practical point of view, i.e. time, number and size of sub-samples, etc. For moisture, as stated before, sample reduction should be avoided due to alteration of moisture during the reduction step and a sample size should be chosen so that reduction is not necessary for such samples.

From Table 4.1, ash and nitrogen determinations gave the highest CoVs and moisture determinations the lowest CoVs.

The confidence intervals (Table 4.1) indicate that a significant difference in average between at least two of the sample reduction methods is obtained for all parameters but ash content. This is probably a consequence of the high degree of heterogeneity of the olive material.

The repeatability standard deviation (Table 4.1) is rather high for all parameters, which also indicate a high degree of heterogeneity of the olive residue and that it is difficult to homogenize the sub-sample before the analysis. By using a mill with a 0,2mm sieve and a thorough homogenisation before the analysis, the repeatability standard deviation of the ash content analysis was decreased by a factor of 5-10.

Figures 4.1 – 4.3 show the individual analyses results where outliers according to Dixon are represented by unfilled symbols.

Table 4.1 Sample reduction of olive residue.

	Moisture content			Ash content		
	C&Q	LP	RB	C&Q	LP	RB
\bar{x}	5,35	10,70	4,91	9,46	10,21	10,53
s	0,042	0,032	0,076	3,226	3,847	2,392
CoV	0,79	0,30	1,55	34,1	37,7	22,7
Conf.int.	±0,042	±0,017	±0,094	±1,71	±2,04	±1,27
s_r				0,94	1,67	2,48
$s_{r, rel}$				10,0	16,3	23,5
	F=1,79 C&Q vs. LP $F_{crit, 0,05} = 2,46$ F=3,27 RB vs. C&Q $F_{crit, 0,05} = 2,58$ F=5,84 RB vs. LP $F_{crit, 0,05} = 2,46$			F=1,82 C&Q vs. RB $F_{crit, 0,05} = 2,40$ F=1,42 LP vs. C&Q $F_{crit, 0,05} = 2,40$ F=2,59 LP vs. RB $F_{crit, 0,05} = 2,40$		

	Potassium content			Nitrogen content		
	C&Q	LP	RB	C&Q	LP	RB
\bar{x}	5254	7973	6573	1,28	1,55	0,83
s	915	1269	1827	0,509	0,592	0,337
CoV	17	16	28	39,7	38,3	40,4
Conf.int.	±485	±672	±968	±0,27	±0,31	±0,18
s_r	728	815	1174	0,23	0,21	0,26
$s_{r, rel}$	13,9	10,2	17,9	18,1	13,5	30,8
	F=1,92 LP vs. C&Q $F_{crit, 0,05} = 2,40$ F=2,07 RB vs. LP $F_{crit, 0,05} = 2,40$ F=3,98 RB vs. C&Q $F_{crit, 0,05} = 2,40$			F=2,29 C&Q vs. RB $F_{crit, 0,05} = 2,40$ F=1,35 LP vs. C&Q $F_{crit, 0,05} = 2,40$ F=3,10 LP vs. RB $F_{crit, 0,05} = 2,40$		

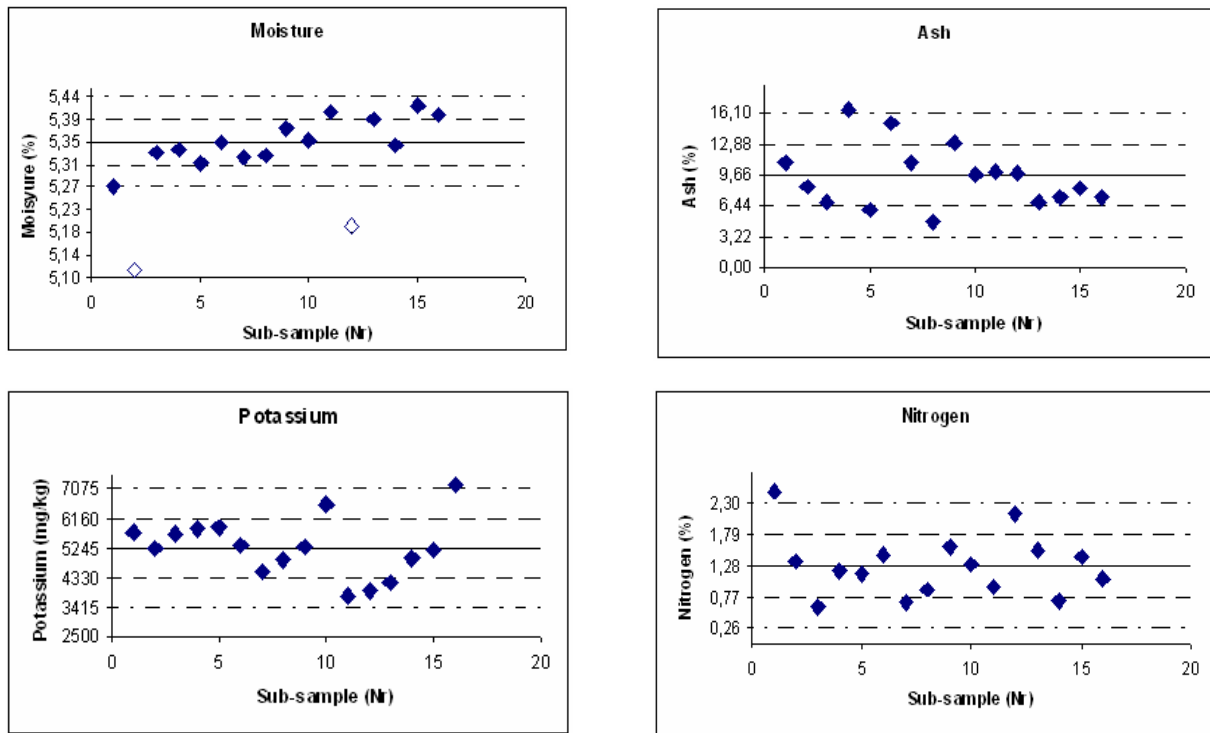


Figure 4.1 Sample reduction of wo by using coning & quartering. Test results, averages and between sub-sample standard deviations. (— = average, - - - = one standard deviation, - · - · = two standard deviations). Unfilled symbols are outliers according to Dixon.

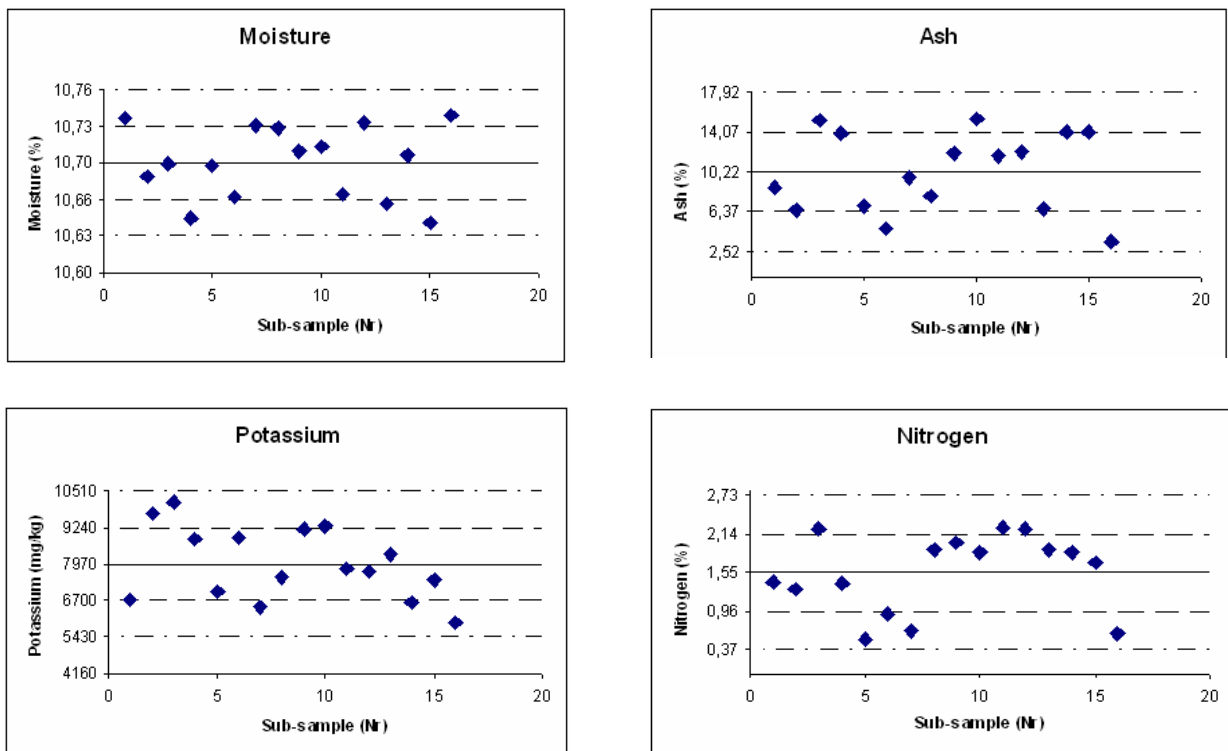


Figure 4.2 Sample reduction of olive residue by using long pile. Test results, averages and between sub-sample standard deviations. (— = averages, - - - = one standard deviation, - · - · = two standard deviations).

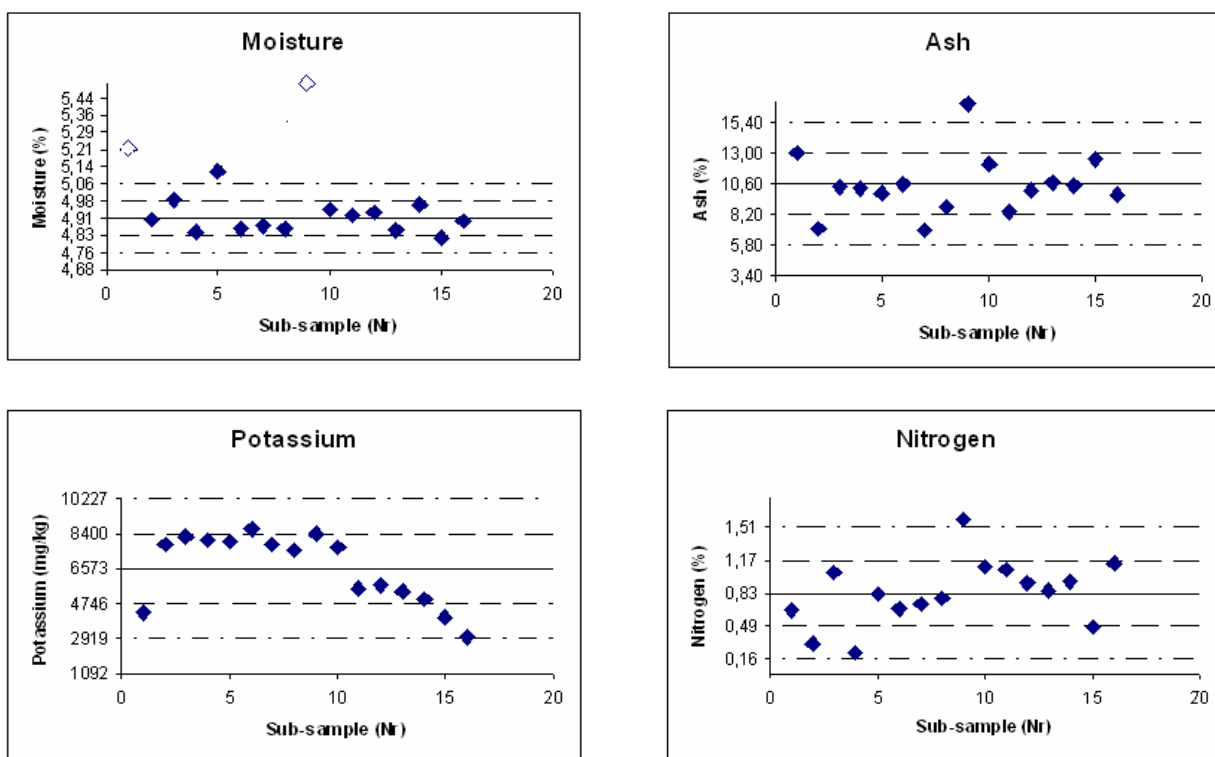


Figure 4.3 Sample reduction of olive residue by riffle box. Test results, averages and between sub-sample standard deviations. (_____ = average, - - - - = one standard deviation, = two standard deviations). Unfilled symbols are outliers according to Dixon.

5. Discussion – Grape residue

From Table 5.1, no one method of sample reduction gave a significant smaller between sub-sample standard deviation than the others for all three of the test methods.

- Moisture – Long pile and Riffle box are significantly better than Coning & Quartering.
- Ash – No significant difference in variability between the methods
- Potassium – Long pile is significantly better than Riffle box
- Nitrogen – Riffle box and Long pile are significantly better than Coning & Quartering.

However, Coning & Quartering was the only method that did show a significant higher between sub-sample standard deviation compared to the other two and should be avoided unless other reasons dominate. For moisture, as stated before, sample reduction should be avoided due to alteration of moisture during the reduction step and a sample size should be chosen so that reduction is not necessary for such samples.

From Table 5.1, moisture determinations gave the lowest CoVs while the other parameters showed a similar CoV.

The confidence intervals (Table 5.1) indicate that a significant difference in average between at least two of the sample reduction methods is obtained for all parameters. This is probably a consequence of the high degree of heterogeneity of the grape material.

As for olive residue the repeatability standard deviation (Table 5.1) for grape residue is rather high and varying in most cases, which also may indicate a high degree of heterogeneity of the grape residue and that it is difficult to homogenize the sub-sample before the analysis.

Figures 5.1 – 5.3 show the individual analyses results where outliers according to Dixon are represented by unfilled symbols.

Table 5.1. Sample reduction of grape residue.

	Moisture content (%)			Ash content (%)		
	C&Q	LP	RB	C&Q	LP	RB
\bar{x}	62,4	56,9	56,6	6,60	7,02	7,98
s	1,40	0,70	0,62	0,536	0,640	0,799
CoV	2,3	1,2	1,1	8,1	9,1	10,0
Conf.int.	$\pm 0,74$	$\pm 0,37$	$\pm 0,33$	$\pm 0,28$	$\pm 0,34$	$\pm 0,42$
s_r				0,47	0,42	1,29
$S_{r, rel}$				6,8	6,2	19,3
	F=1,28 LP vs. RB $F_{crit, 0,05} = 2,40$			F=1,42 LP vs. C&Q $F_{crit, 0,05} = 2,40$		
	F=4,07 C&Q vs. LP $F_{crit, 0,05} = 2,40$			F=1,56 RB vs. LP $F_{crit, 0,05} = 2,40$		
	F=5,21 C&Q vs. RB $F_{crit, 0,05} = 2,40$			F=2,22 RB vs. C&Q $F_{crit, 0,05} = 2,40$		

	Potassium content (mg/kg)			Nitrogen content (%)		
	C&Q	LP	RB	C&Q	LP	RB
\bar{x}	15727	23414	20251	2,36	2,70	2,56
s	2694	1888	2964	0,315	0,147	0,178
CoV	17,1	8,1	14,6	13,3	5,4	6,9
Conf.int.	± 1428	± 1001	± 1571	$\pm 0,167$	$\pm 0,079$	$\pm 0,094$
s_r	1630	576	999	0,19	0,45	0,15
$S_{r, rel}$	11,6	2,6	5,4	8,8	15,0	7,2
	F=2,03 C&Q vs. LP $F_{crit, 0,05} = 2,40$			F=1,47 RB vs. LP $F_{crit, 0,05} = 2,51$		
	F=1,21 RB vs. C&Q $F_{crit, 0,05} = 2,40$			F=3,13 C&Q vs. RB $F_{crit, 0,05} = 2,53$		
	F=2,46 RB vs. LP $F_{crit, 0,05} = 2,40$			F=4,59 C&Q vs. LP $F_{crit, 0,05} = 2,46$		

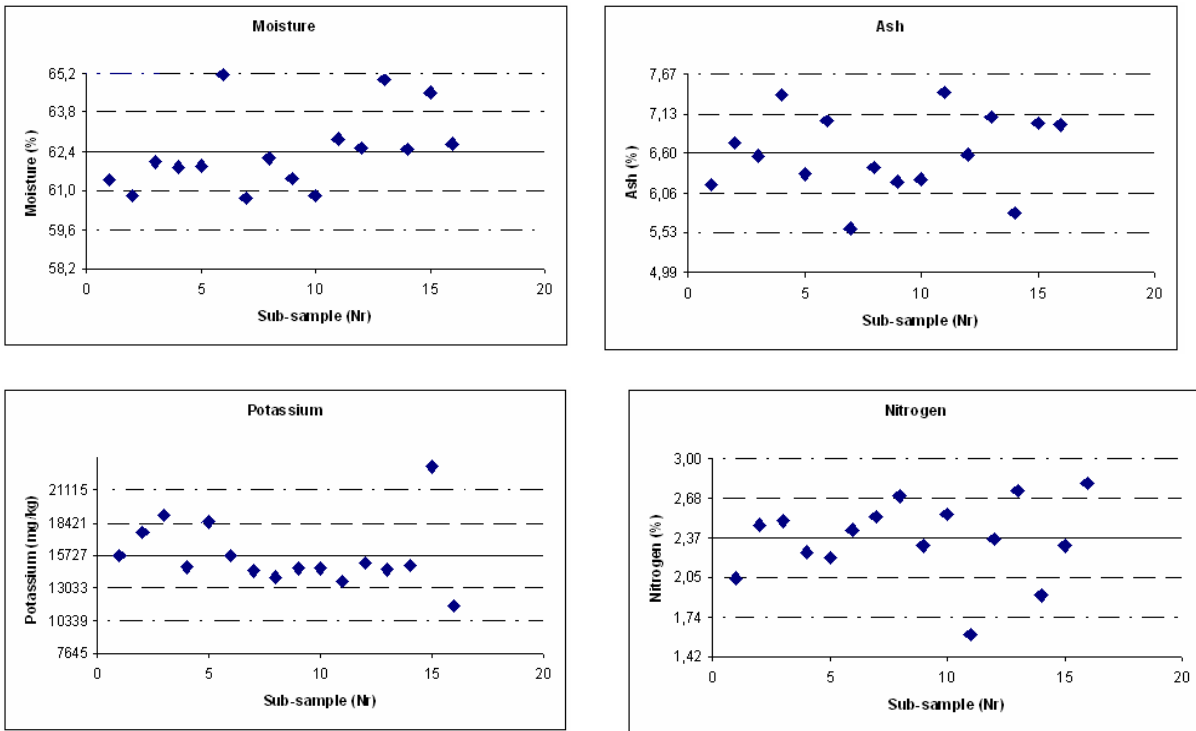


Figure 5.1. Sample reduction of grape residue by using coning & quartering. Test results, averages and between sub-sample standard deviations. (—— = average, - - - = one standard deviation, - . - . = two standard deviations).

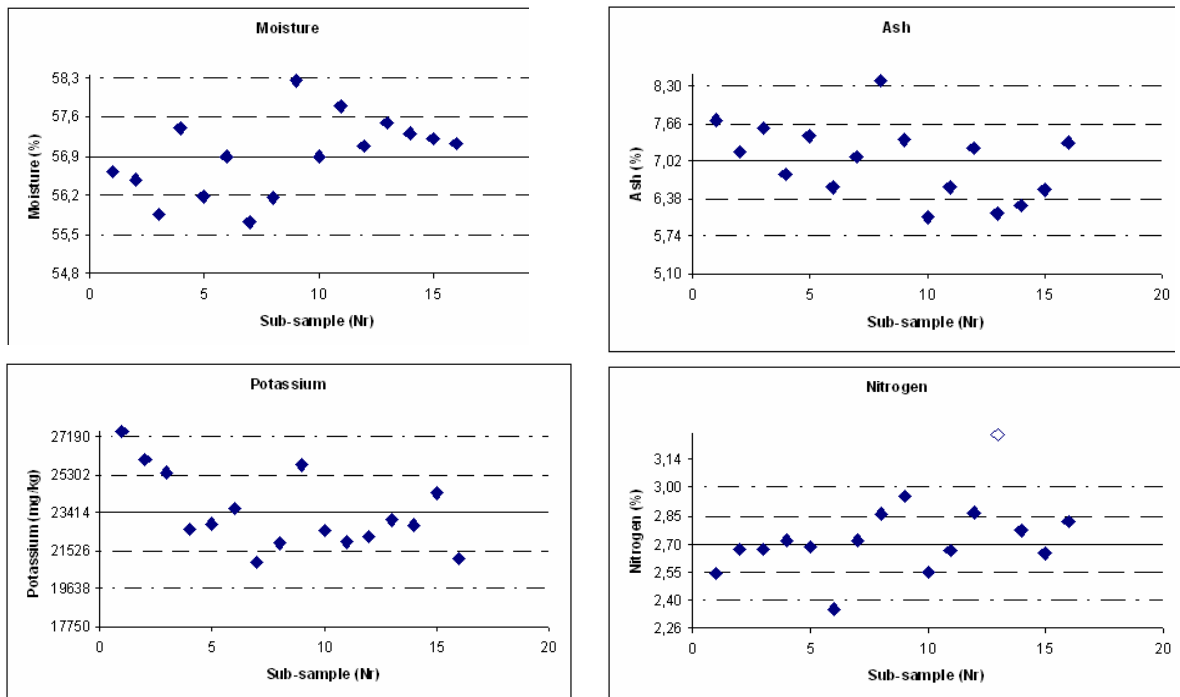


Figure 5.2. Sample reduction of grape residue by using long pile. Test results, averages and between sub-sample standard deviations. (—— = averages, - - - = one standard deviation, - . - . = two standard deviations). Unfilled symbols are outliers according to Dixon.

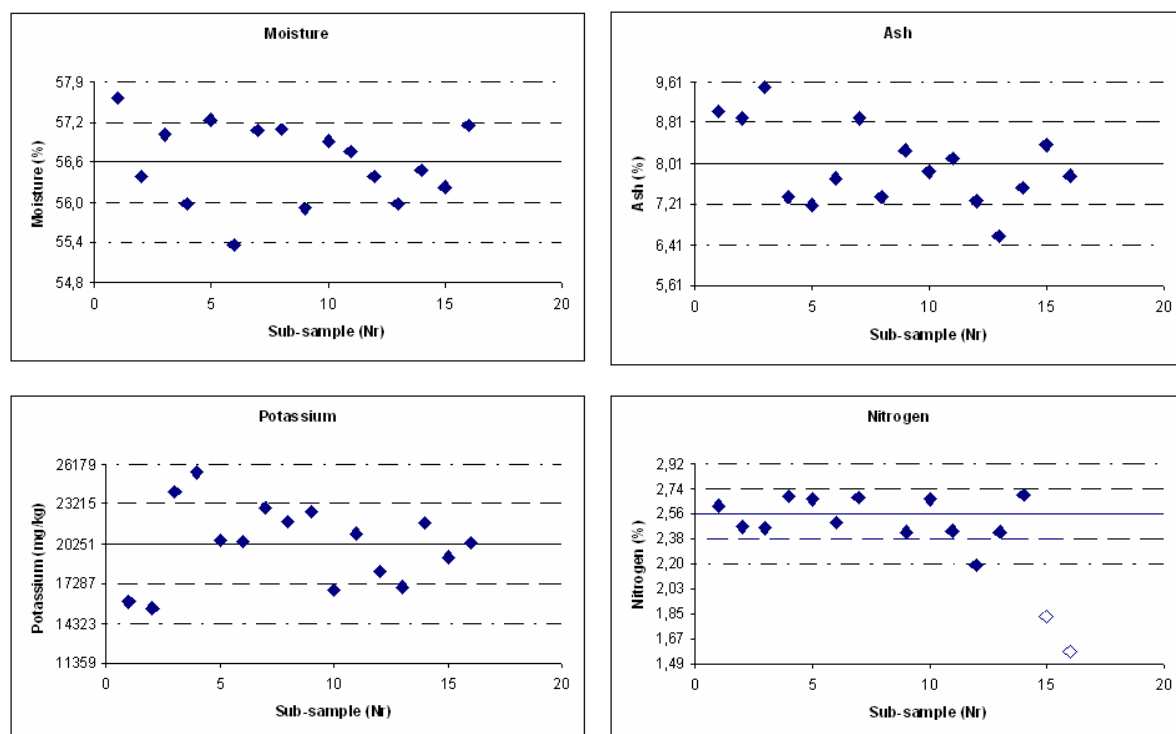


Figure 5.3. Sample reduction of grape residue by riffle box. Test results, averages and between sub-sample standard deviations. (— = average, - - - = one standard deviation, - · - = two standard deviations). Unfilled symbols are outliers according to Dixon.

6. Discussion - bark

From Table 6.1, no significant difference in between sub-sample standard deviation was found for the sample reduction methods.

Thus for determination of the studied parameters the choice of sample reduction method in most cases is decided from a practical point of view, i.e. time, number and size of sub-samples, etc. For moisture, as stated before, sample reduction should be avoided due to alteration of moisture during the reduction step and a sample size should be chosen so that reduction is not necessary for such samples.

From Table 6.1, ash determination gave the highest CoV compared to the other methods which was expected.

The confidence intervals (Table 6.1) indicate that a significant difference in average between at least two of the sample reduction methods is obtained for all parameters. This is probably a consequence of the fact that the sample reduction experiments were carried out on two different sub-lots.

The repeatability standard deviation (Table 6.1) is low, which indicate a high degree of homogeneity within the sub-samples.

Figures 6.1 – 6.2 show the individual analyses results.

Table 6.1. Sample reduction of bark.

	Moisture content (%)		Ash content (%)		Calorific value (MJ/kg)	
	C&Q	LP	C&Q	LP	C&Q	LP
\bar{x}	54,2	56,2	6,53	7,60	20,00	19,77
s	0,311	0,333	0,409	0,367	0,090	0,074
CoV	0,57	0,59	6,3	4,8	0,45	0,37
Conf.int.	0,165	0,177	0,217	0,194	0,048	0,039
s_r			0,041	0,021	0,017	0,020
$S_{r,rel}$			0,6	0,3	0,1	0,1
	F=1,15 $F_{crit, 0,05} = 2,40$		F=1,24 $F_{crit, 0,05} = 2,40$		F=1,49 $F_{crit, 0,05} = 2,40$	

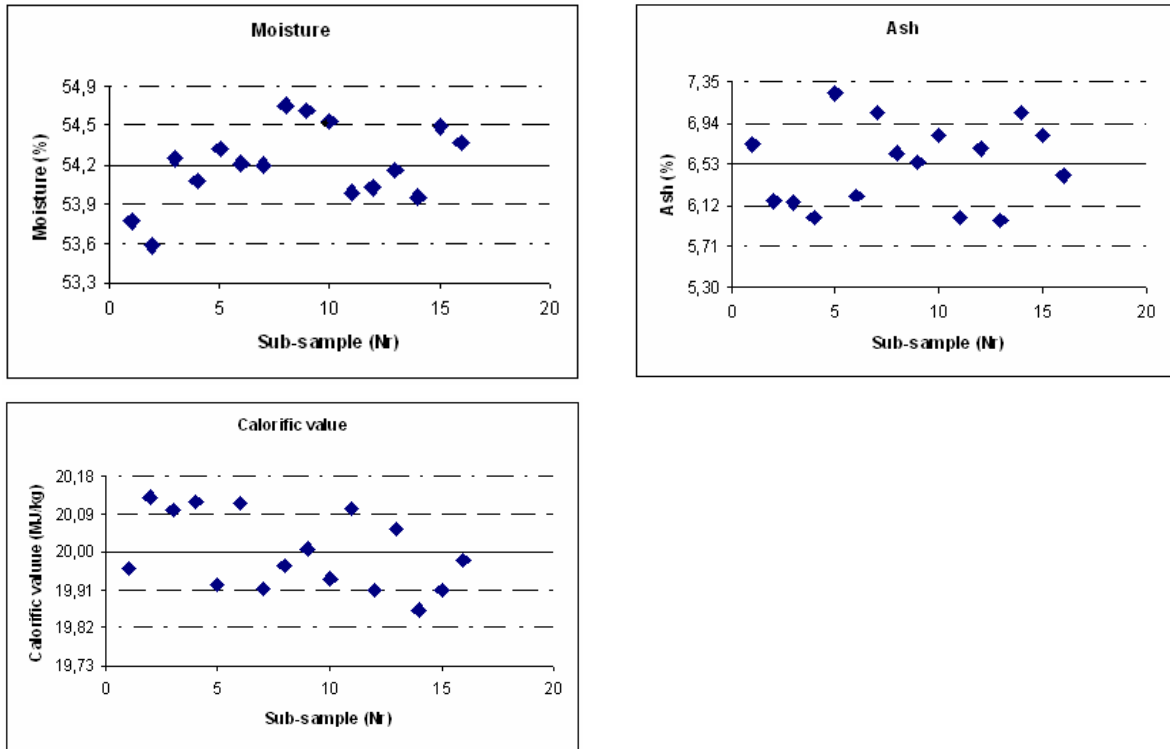


Fig _____ & quartering. Test results, averages and between sub-sample standard deviations. (— = average, - - - - = one standard deviation, - · - · = two standard deviations).

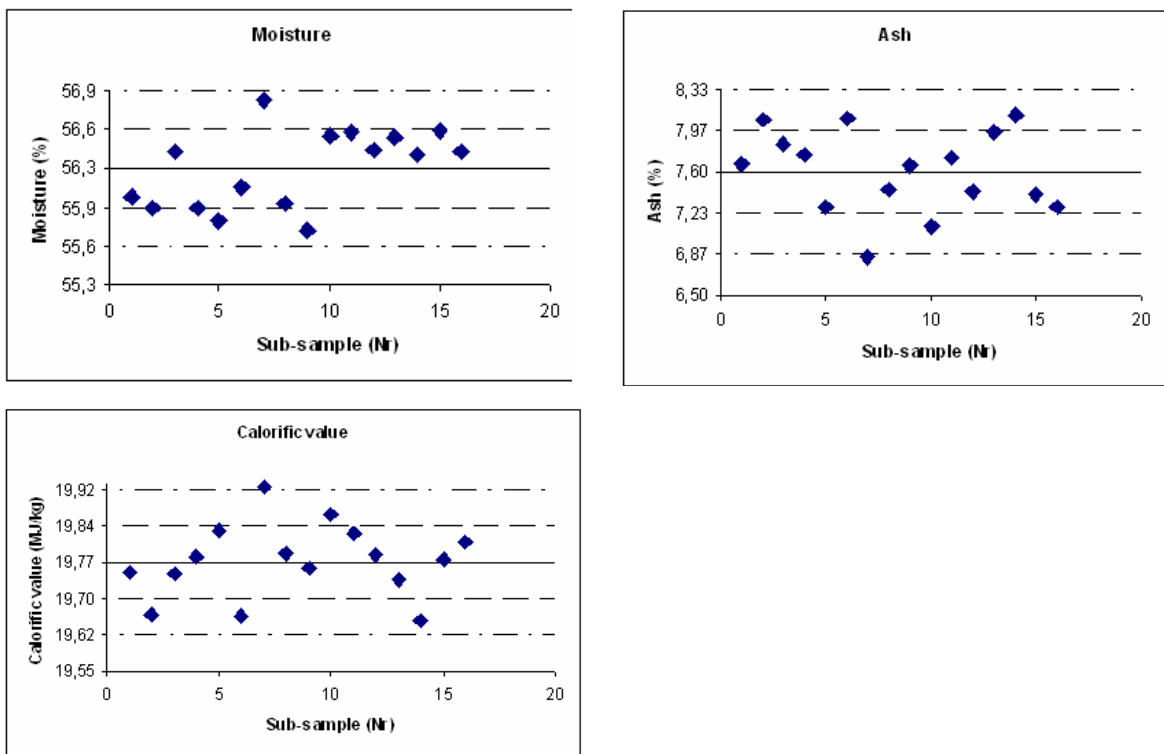


Figure 6.2. Sample reduction of bark by using long pile. Test results, averages and between sub-sample standard deviations. (— = averages, - - - - = one standard deviation, - · - · = two standard deviations).

7. Discussion – pellets (8 mm)

From Table 7.1, no significant difference in between sub-sample standard deviation was found for the sample reduction methods. Thus for determination of the studied parameters the choice of sample reduction method in most cases is decided from a practical point of view, i.e. time, number and size of sub-samples, etc.

From Table 7.1, the CoV for the ash determination was of the same order as the relative repeatability standard deviation which is a consequence of the low ash content in pellets and indicates that the obtained sub-sample standard deviation is equal or less than the standard deviation of the analytical method.

The confidence intervals (Table 7.1) indicate that a significant difference in average between at least two of the sample reduction methods is obtained for the ash content. This is probably not caused by the reduction methods but rather by the fact that three different pellets sacks were used for the sample reduction methods, respectively.

The repeatability standard deviation (Table 7.1) is rather high for the ash content, which is caused by the low ash content of the pellets material compared to the standard deviation of the analytical method.

Figures 7.1 – 7.3 show the individual analyses results where outliers according to Dixon are represented by unfilled symbols.

Table 7.1. Sample reduction of pellets (8 mm).

	Ash content (%)			Mechanical durability (%)		
	C&Q	LP	RB	C&Q	LP	RB
\bar{x}	0,361	0,344	0,342	96,7	96,8	96,9
s	0,0186	0,0234	0,0151	0,12	0,09	0,13
CoV	5,2	6,8	4,4	0,06	0,05	0,13
Conf.int.	0,0099	0,0124	0,0080	0,15	0,09	0,07
s_r	0,034	0,019	0,029			
$S_{r,rel}$	9,5	5,4	8,5			
	F=1,51 C&Q vs. RB $F_{crit, 0,05} = 2,40$			F=1,72 C&Q vs. LP $F_{crit, 0,05} = 2,48$		
	F=1,59 LP vs. C&Q $F_{crit, 0,05} = 2,40$			F=1,12 RB vs. C&Q $F_{crit, 0,05} = 2,46$		
	F=2,40 LP vs. RB $F_{crit, 0,05} = 2,40$			F=1,93 RB vs. LP $F_{crit, 0,05} = 2,46$		

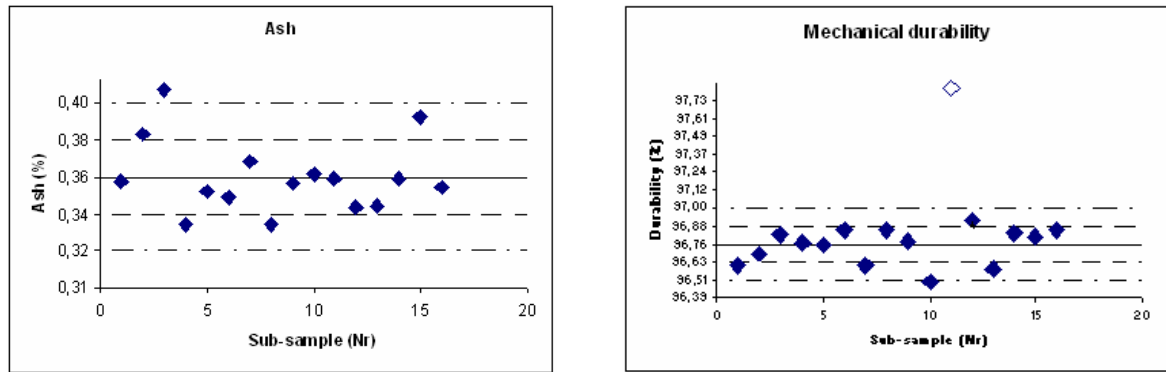


Figure 7.1. Sample reduction of pellets (8 mm) by using coning & quartering. Test results, averages and between sub-sample standard deviations. (— = average, - - - = one standard deviation, - · - · = two standard deviations). Unfilled symbols are outliers according to Dixon (ref).

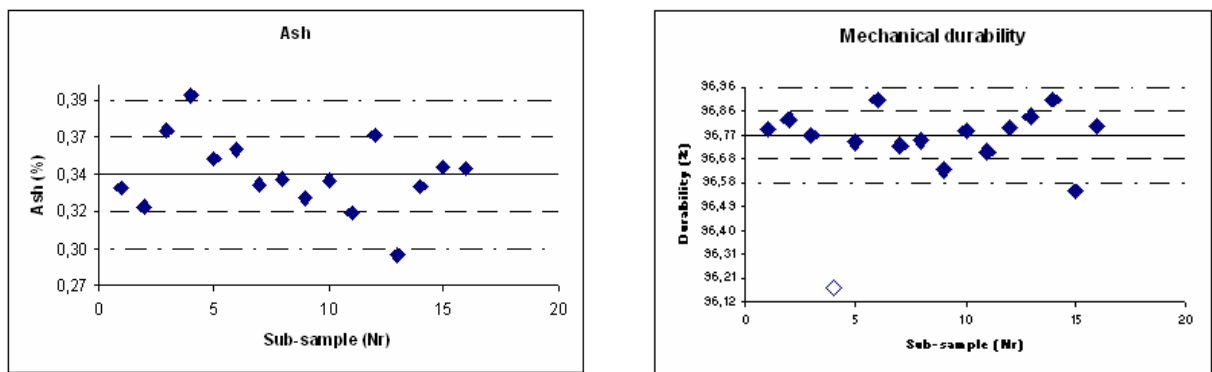


Figure 7.2. Sample reduction of pellets (8 mm) by using long pile. Test results, averages and between sub-sample standard deviations. (— = averages, - - - = one standard deviation, - · - · = two standard deviations). Unfilled symbols are outliers according to Dixon.

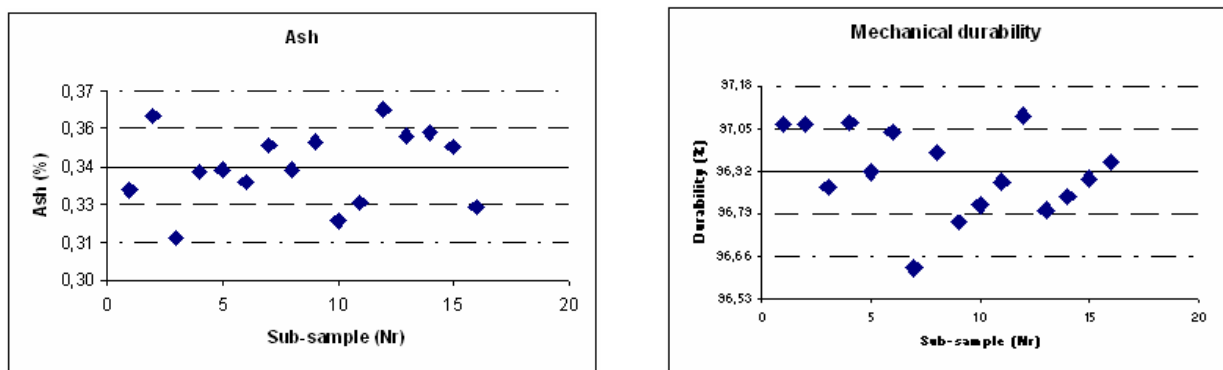


Figure 7.3. Sample reduction of pellets (8 mm) by riffle box. Test results, averages and between sub-sample standard deviations. (— = averages, - - - = one standard deviation, - · - · = two standard deviations).

8 Discussion – pellets (6 mm)

A significant lower between sub-sample standard deviation was found for the riffle box compared to the other methods for the ash content determination (Table 8.1). For mechanical durability long pile and riffle box showed lower standard deviation compared to coning & quartering. Since the riffle box is a too rough method when analyzing mechanical durability, however, the long pile method is recommended for this method.

From Table 8.1, the CoV for the ash determination was of the same order as the relative repeatability standard deviation which is a consequence of the low ash content in pellets together with a high inhomogeneity of the material and indicates that the obtained sub-sample standard deviation is equal or less than the standard deviation of the analytical method.

The confidence intervals (Table 8.1) indicate that a significant difference in average between at least two of the sample reduction methods is obtained for both parameters. This is probably not caused by the reduction methods but rather by the fact that three different pellets sacks were used for the sample reduction methods, respectively.

The relative repeatability standard deviation (Table 8.1) is rather high for the ash content, which is probably caused by the inherent heterogeneity and the low ash content of the pellets material compared to the standard deviation of the analytical method.

Figures 8.1 – 8.3 show the individual analyses results where outliers according to Dixon are represented by unfilled symbols.

Table 8.1. Sample reduction of pellets (6 mm).

	Ash content (%)			Mechanical durability (%)		
	C&Q	LP	RB	C&Q	LP	RB
\bar{x}	0,613	0,540	0,470	96,4	96,4	96,6
s	0,1337	0,1940	0,0803	0,29	0,16	0,12
CoV	21,8	35,9	17,1	0,30	0,16	0,12
Conf.int.	0,0709	0,1028	0,0426	0,15	0,08	0,07
s_r	0,102	0,126	0,077			
$s_{r,rel}$	23,5	24,8	16,8			
	F= 2,77 C&Q vs. RB $F_{crit,0,05} = 2,40$			F= 1,84 LP vs. RB $F_{crit,0,05} = 2,53$		
	F= 2,11 LP vs. C&Q $F_{crit,0,05} = 2,40$			F= 3,35 C&Q vs. LP $F_{crit,0,05} = 2,40$		
	F= 5,83 LP vs. RB $F_{crit,0,05} = 2,40$			F= 6,17 C&Q vs. RB $F_{crit,0,05} = 2,53$		

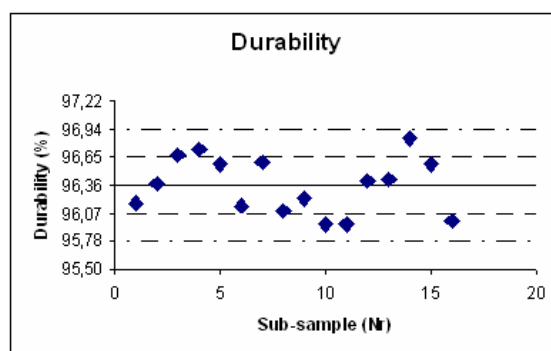
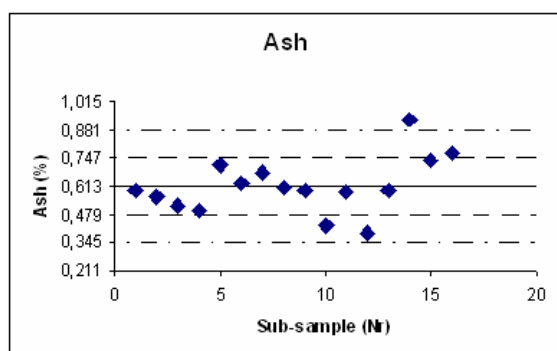


Figure 8.1. Sample reduction of pellets (6 mm) by using coning & quartering. Test results, averages and between sub-sample standard deviations. (— = average, - - - = one standard deviation, - · - · = two standard deviations).

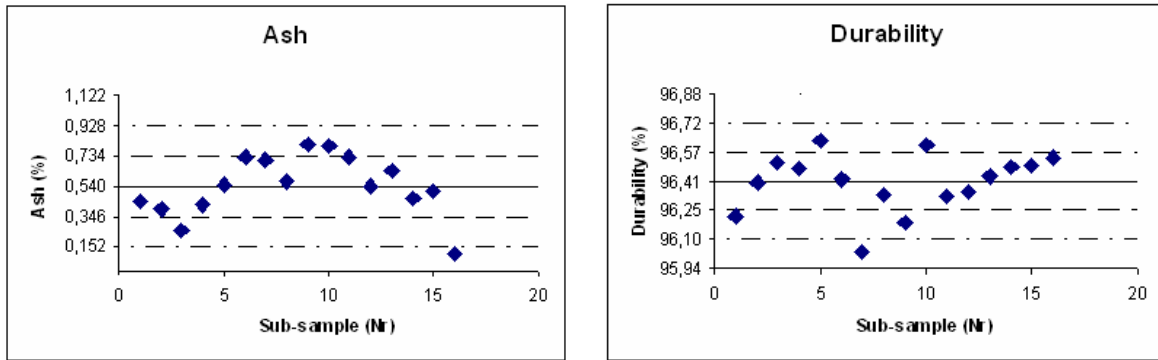


Figure 8.2. Sample reduction of pellets (6 mm) by using long pile. Test results, averages and between sub-sample standard deviations. (— = averages, - - - = one standard deviation, - · - · = two standard deviations).

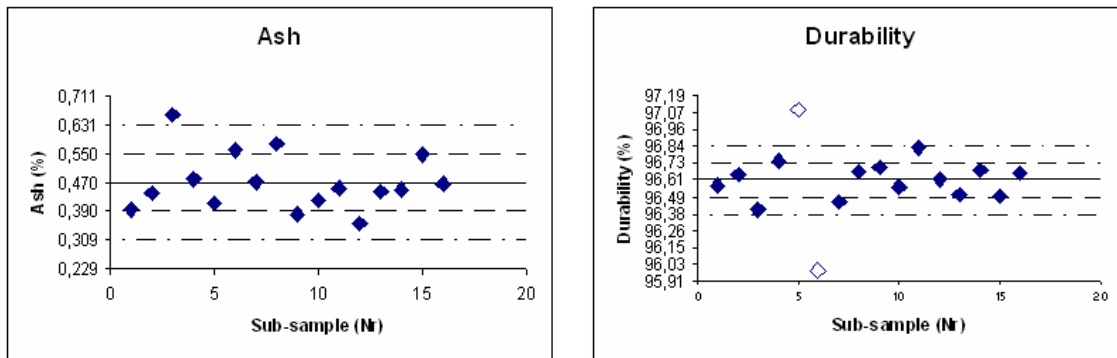


Figure 8.3. Sample reduction of pellets (6 mm) by riffle box. Test results, averages and between sub-sample standard deviations. (— = averages, - - - = one standard deviation, - · - · = two standard deviations). Unfilled symbols are outliers according to Dixon.

9 Discussion – Wood chips

From Table 9.1, no one method of sample reduction gave a significant smaller between sub-sample standard deviation than the others for all three of the test methods.

- Moisture –No significant difference in standard deviation was found between the sample reduction methods
- Ash – The long pile and riffle box methods have a significant lower standard deviation compared to the coning & quartering method.
- Particle size <16mm>8mm, , <5mm>3mm – No significant difference in standard deviation between the methods
- Particle size <8mm>5mm – Riffle box has a significant lower between sub-sample standard deviation compared to coning & quartering. No significant difference was found between the long pile and the coning & quartering method, or between the long pile and the riffle box method.
- Particle size <3mm>2mm – Riffle box has a significant lower between sub-sample standard deviation compared to the other methods
- Particle size <2mm – Riffle box has a significant lower sub-sample standard deviation compared to the long pile method. No significant difference was found between the riffle box and the coning & quartering method, or between the long pile and the coning & quartering method.

Thus for determination of the studied parameters the choice of sample reduction method in most cases is decided from a practical point of view, i.e. time, number and size of sub-samples, etc. For moisture, as stated before, sample reduction should be avoided due to alteration of moisture during the reduction step and a sample size should be chosen so that reduction is not necessary for such samples.

From Table 9.1, moisture determinations had the lowest CoVs of 0,3 % while the other parameters showed CoVs between 2 - 6 %.

The confidence intervals (Table 9.1) indicate that a significant difference in average between the sample reduction methods is obtained for all parameters. This is probably a consequence of the heterogeneity of the wood chip material.

Figures 9.1 –9.3 show the individual analyses results where outliers according to Dixon are represented by unfilled symbols.

Table 9.1. Sample reduction of wood chips.

	Moisture content			Ash content		
	C&Q	LP	RB	C&Q	LP	RB
\bar{x}	48,40	49,51	50,38	0,588	0,765	0,743
s	0,14	0,17	0,11	0,033	0,020	0,018
CoV	0,30	0,34	0,23	5,5	2,6	2,4
Conf.int.	$\pm 0,077$	$\pm 0,090$	$\pm 0,060$	$\pm 0,025$	$\pm 0,011$	$\pm 0,010$
	F=1,39 LP vs. C&Q		F _{crit, 0,05} =2,40	F= 1,23 LP vs. RB		F _{crit, 0,05} =2,46
	F= 1,61 C&Q vs. RB		F _{crit, 0,05} =2,46	F= 3,24 C&Q vs. RB		F _{crit, 0,05} =2,42
	F=2,23 LP vs. RB		F _{crit, 0,05} =2,46	F= 2,64 C&Q vs. LP		F _{crit, 0,05} =2,55

	Particle size <16mm>8mm			Particle size <8mm>5mm		
	C&Q	LP	RB	C&Q	LP	RB
\bar{x}	13,72	14,03	12,33	35,59	36,05	34,3
s	0,93	1,10	0,88	0,78	0,57	0,38
CoV	2,72	3,17	2,66	1,62	1,18	1,18
Conf.int.	$\pm 0,50$	$\pm 0,58$	$\pm 0,46$	$\pm 0,41$	$\pm 0,30$	$\pm 0,30$
	F=1,38 LP vs. C&Q		F _{crit, 0,05} =2,40	F=4,28 C&Q vs. RB		F _{crit, 0,05} =2,40
	F=1,58 LP vs. RB		F _{crit, 0,05} =2,40	F=1,86 C&Q vs. LP		F _{crit, 0,05} =2,40
	F=1,14 C&Q vs. RB		F _{crit, 0,05} =2,40	F=2,30 LP vs. RB		F _{crit, 0,05} =2,40

	Particle size <5mm>3mm			Particle size <3mm>2mm		
	C&Q	LP	RB	C&Q	LP	RB
\bar{x}	32,48	31,29	33,14	8,02	7,83	8,35
s	0,89	0,75	0,74	0,45	0,46	0,26
CoV	1,90	1,61	1,56	1,66	1,71	0,95
Conf.int.	$\pm 0,47$	$\pm 0,39$	$\pm 0,39$	$\pm 0,24$	$\pm 0,24$	$\pm 0,14$
	F=1,43 C&Q vs. LP		F _{crit, 0,05} =2,40	F=2,94 C&Q vs. RB		F _{crit, 0,05} =2,40
	F=1,02 LP vs. RB		F _{crit, 0,05} =2,40	F=1,04 LP vs. C&Q		F _{crit, 0,05} =2,40
	F=1,46 C&Q vs. RB		F _{crit, 0,05} =2,40	F=3,06 LP vs. RB		F _{crit, 0,05} =2,40

	Particle size <2mm		
	C&Q	LP	RB
\bar{x}	9,67	10,17	10,98
s	0,39	0,55	0,35
CoV	1,32	1,83	1,12
Conf.int.	$\pm 0,21$	$\pm 0,29$	$\pm 0,19$
	F=2,01 LP vs. C&Q		F _{crit, 0,05} =2,46
	F=2,51 LP vs. RB		F _{crit, 0,05} =2,40
	F=1,25 C&Q vs. RB		F _{crit, 0,05} =2,48

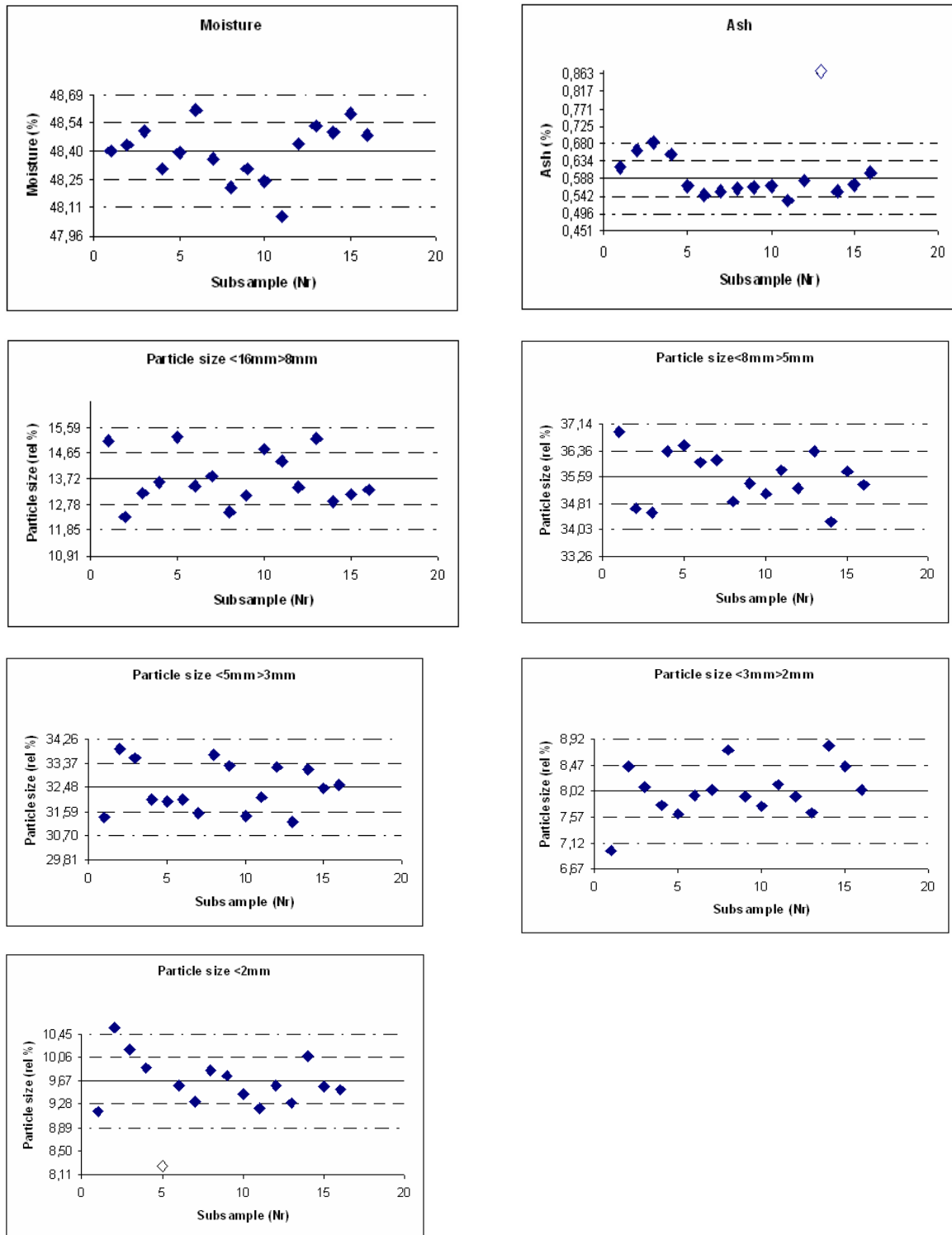


Figure 9.1. Sample reduction of wood chips by using coning & quartering. Test results, averages and between sub-sample standard deviations. (—— = average, - - - - = one standard deviation, - · - · = two standard deviations). Unfilled symbols are outliers according to Dixon.

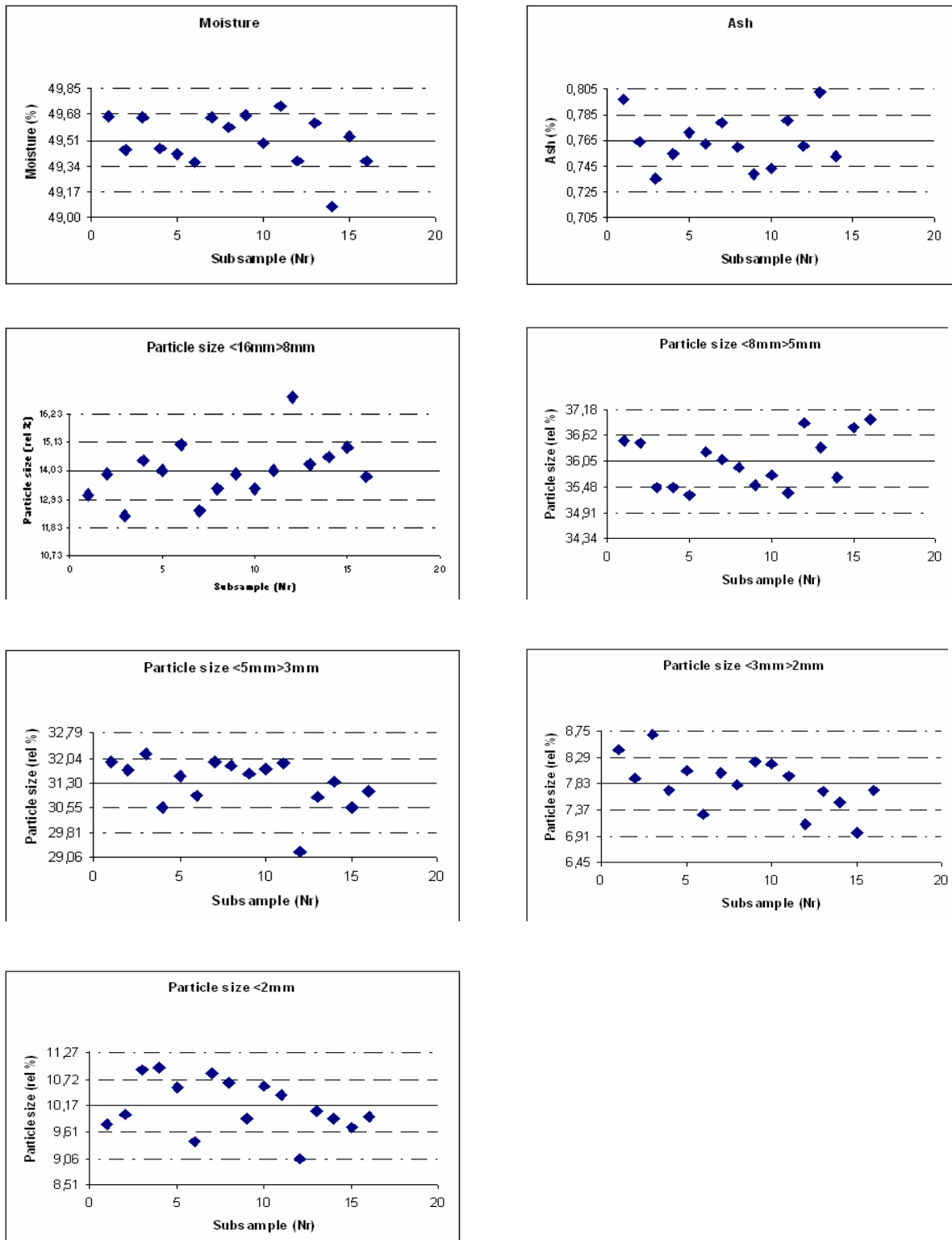


Figure 9.2. Sample reduction of wood chips by using long pile. Test results, averages and between sub-sample standard deviations. (— = averages, - - - - = one standard deviation, - . - . = two standard deviations).

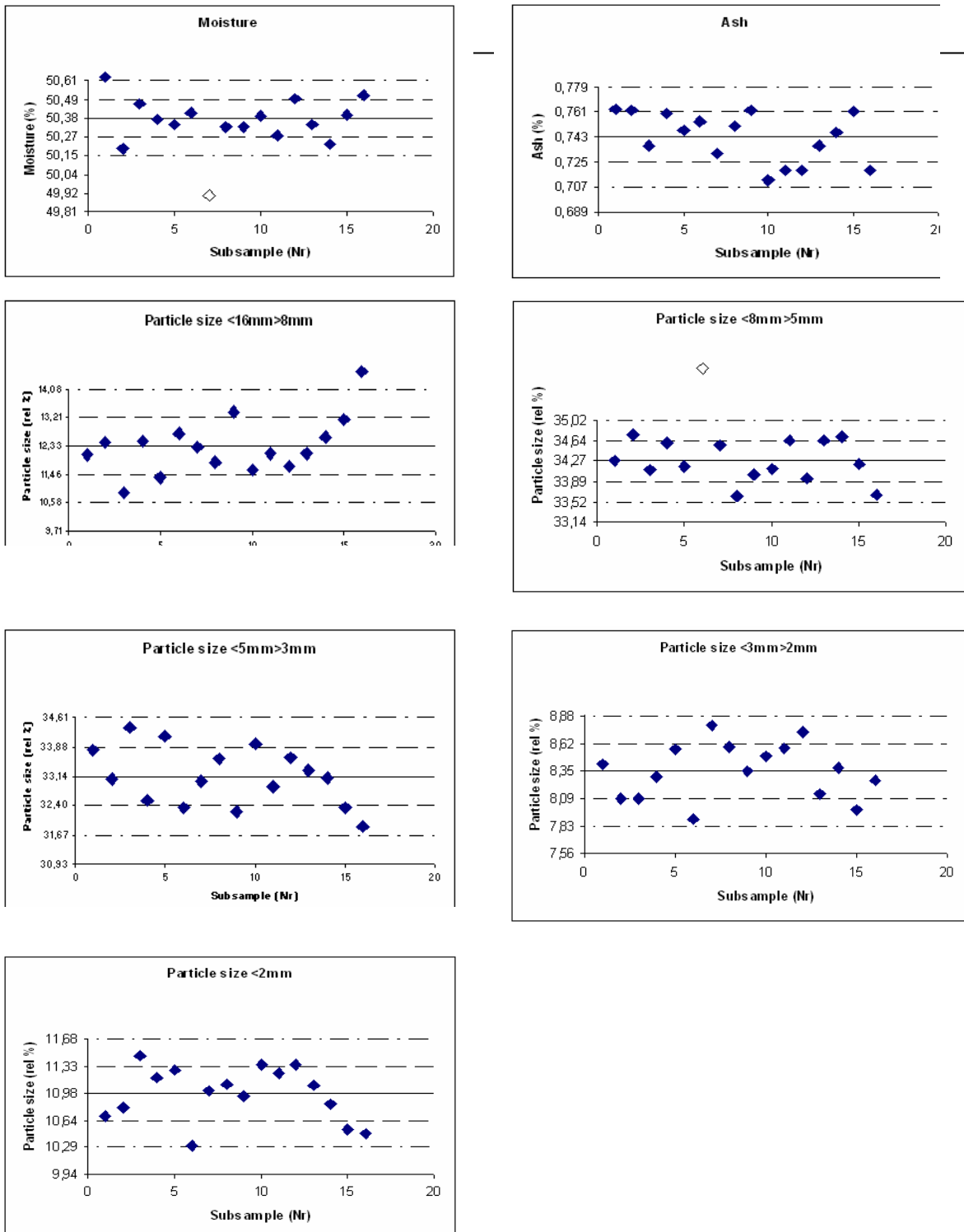


Figure 9.3. Sample reduction of wood chips by riffle box. Test results, averages and between sub-sample standard deviations. (— = average, - - - = one standard deviation, - · - · = two standard deviations). Unfilled symbols are outliers according to Dixon.

10. References

Dixon W. J. 1953. Processing data for outliers *Biometrics* 9, 74-89.