



**Project no. 038644**

## **BioNorm II**

**Pre-normative research on solid biofuels for improved European standards**



### **DII.2.8**

## **Best practice guideline for rapid field methods for the determination of Cl, K and Na**

Due date of deliverable: month 36

Actual submission date: month 39

Start date of project: 1/1/2007

Duration: 36 month

Task Leader organisation name: Ofi-Austrian Research Institute for Chemistry and Technology

Revision [4]

Project co-funded by the European Commission		
Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	

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**Revisions**

<b>Version</b>	<b>Date</b>	<b>Author(s)</b>	<b>Change</b>
1	-	Ciemat	-
2	-	Dong	-
3	-	ECN	-
4	-	<i>ofi</i>	-
End	-	All teams	-

## Abstract

The development of European Standards (EN) is a precondition to expand the market for solid biofuels and a very important step to fulfil the political and environmental goals of the European Union.

The aim of the BioNorm II project is to carry out pre-normative research in the field of solid biofuels in close collaboration with the work of CEN TC 335 "Solid Biofuels". This includes the development of an overall quality assurance system for solid biofuels, their characterization and corpus of legislation.

Comparison between chlorine determination methods including sample digestion and including water soluble method demonstrated excellent recovery of chlorine, Potassium and sodium as water soluble elements in biomass samples. The standard prEN15104 describes an analytical method for determination of water soluble elements and was the base document for the experiments within this WP II Task II.2.3.

Rapid test method for field use should be easy to use and should be fast methods without special demands on laboratory equipment or highly qualified staff. The elements chlorine, Potassium and sodium are quality relevant parameter because of their direct influence on corrosion, fouling and slagging, so the developed technique should be applicable for their analysis in a wide range.

A Danish study was basis of performed tests (Danish project: PSO 5297. Biofuel Characterization 2004 – Development of methods) and allowed Dong Energy, Ciemat, ECN and ofi a fast realization of first test series. The companies used following sample preparation methods after the sampling of biomass on field:

- Small sized materials were milled in mills (laboratory and household mills e.g. coffee mill)
- Larger materials like pellets were blended in jug blenders
- Wood chips samples were shredded by laboratory mills and simple equipment like garden shredders
- Herbaceous materials (e.g. grass) were cut in smaller pieces with secateurs

More than 30 different plants/fields were sampled and used for further tests including filtering steps and the quantification method. For the determination of chlorine different test kits (titrimetric method, and test stripes methods) were tested, because they were commercial available. For Potassium and sodium fast quantification methods are scarce, so new ideas like determination of the evaporation residues as total amount of water soluble salts or flame tests were tested.

An advantage of rapid field methods is the diminished costs. In some cases the new form of determination could avoid slow and expensive laboratory analysis. This savings could help the young but growing market of solid biofuels (pellets, agricultural residues) to save costs, time and efforts. This simplification decreases market barriers and supports trade which both build the basics to provide the growth of the biofuel sector. The project keeps in mind that rapid test methods are not able to replace full chemical characterisation of solid biofuels. The capacity of fast procedures is routine analysis. All these supporting properties open the biofuel market to a much wider target group.

It was not possible to quantify chlorine, Potassium and sodium using one method for all biomass types. The practical applicability of all evaluated test methods and the proposed advantage for the biomass supply chain is seen critical by the work group.

**List of Abbreviations**

<b>Cl</b>	Chlorine
<b>cm</b>	centimeter
<b>g</b>	gram
<b>IC</b>	Ionchromatography
<b>K</b>	Potassium
<b>L</b>	liter
<b>mL</b>	milliliter
<b>mm</b>	millimeter
<b>Na</b>	Sodium
<b>SO<sub>4</sub></b>	Sulphate
<b>wt%</b>	Weight percent

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## **1 Introduction**

In this part rapid test methods for the determination of chlorine, sodium, and Potassium in solid bio-fuels will be developed for cheap outdoor use. Cl, Na and K may cause operational problems in form of corrosion, slagging, and fouling. These elements are found in widely varying concentrations in the same type of solid biofuel. The methods should be applicable for biofuels with usually high contents of these elements. The methods will utilise the high solubility of Cl, K and Na in water, a principle that is already used in the laboratory method CEN TS 15105 “Solid biofuels – Methods for determination of the water soluble content of chloride, sodium and Potassium.” Starting from this method and the experiences from Danish research projects, a method will be established that can be used for quick semi-quantitative measurements in field using a minimum of laboratory equipment.

## **2 Description of work**

The research will focus on finding the best eluent, an appropriate experimental procedure and a guideline for the minimal necessary sample preparation for different biofuels. Extraction of solid biofuels with deionised water, different diluted acids using cold and hot extraction will be tested. The samples will be extracted using different sample preparation and different particle sizes. For the quantification of chlorine, sodium and Potassium (or the sum of the alkali metals) in the resulting aqueous solutions, different methods will be tested: conductivity, test stripes and change of colour in Dräger-type test tubes (that are not commercially available at the moment) and eventually ion selective electrodes. With conductivity, only the sum of ions can be detected and therefore a correlation between the conductivity and the sum of Na and K will be investigated. Since there are no suitable quick methods available for a rough determination of Na and K in the prepared water extract, these tests will be developed (principles and/or prototypes) by the partners. The results of the field methods will be evaluated by using the existing CEN TS methods. For the best procedure, the reliability of the method will be tested with respect to the needs of the potential users.

### 3 Sample material

Within this task more than 30 different samples and more than 10 analysis methods were investigated. To guarantee the utilization of the developed method the first step was to sample biomass on field and perform the analytical tests and the sample preparation without any laboratory equipment. The second part was to test the “rapid test methods” on different samples e.g. the BioNorm I and II samples and new, on field sampled biomasses (Table 1)

**Table 1: test fuels and parameters for field tests**

	<b>Test fuels</b>	<b>Field test method</b>
<b>Series a</b>	12 field samples	chloride test Aquamerck (titrimetric determination with a titration pipette), Range 2-200 mg/l
<b>Series b</b>	7 BioNorm samples and 5 field samples	Cl: HACH Quantab Low Range 30-600 mg/l K: Visocolor Macherey-Nagel, Range 2-15 mg/l and Quantofix Macherey-Nagel, Range 200-1500 mg/l
<b>Series c</b>	Field samples Straw and woodchips	Cl: HACH Quantab Low Range 30-600 mg/l Na: flame test K: only lab-finish
<b>Series d</b>	10 BioNorm samples	Test –kits for Cl <sup>-</sup> , SO <sub>4</sub> , K <sup>+</sup> and Ion-selective electrode for Na <sup>+</sup>

The Table 2 describe the different possibilities of sample preparation.

**Table 2: sample preparation recommendation**

<b>Form of solid biofuel</b>	<b>Sample preparation</b>
Straw and straw-like materials	Cut the material into pieces of maximum length 3 cm
Grains, seeds and shells	Mill the material in a coffee mill for about 10 seconds
Pellets	Blend the pellets in a blender for 10 – 30 seconds, depending of the durability of the pellets
Chips and shavings	Run a larger portion of the material, e.g. ½ kg, through a garden shredder

### 3.1 Sampling on field and sample preparation

The objective of the sampling and sample preparation is the development of the easiest and fastest process to dissolve the highest possible amount of salts in the eluate.

The first step was to plan and figure out which tools were qualified for a simple sampling of the biomass. As cutting tool secateurs were used and for the packing strong plastic bags were applied directly in the field. Household equipment should be used for sample preparation according to the guideline. The preparation was carried out by household equipments like scissors, coffee mill, jug blender and garden shredder.

This part describes the sampling direct on field of eight different biomass samples (Series a) started in the east of Vienna. The selected region called Marchfeld, one of the most famous agricultural areas in Austria, offered a big variety of agricultural plants. The high range of biomass was used to get more detailed results and to find out if the test methods can be applied for every biomass or if the results of the various samples demonstrate differences due to the sample preparation or test methods. The material taken from eight different plants resulted in 9 samples. It seemed necessary to take two sunflower samples, because of the inhomogeneity of the sites and the subsequent differences. As sample materials the following reference plants were taken into account:

- Sample 1: Maize
- Sample 2: Beet
- Sample 3: Legume
- Sample 4: Reed
- Sample 5: Weed
- Sample 6: Sorghum
- Sample 7: Pulse
- Sample 8: Sunflower I
- Sample 9: Sunflower II

The samples were taken on-site by students by scissors and airproof packed. The packing was complicated, because the biomass was not always easy to sample and was in big peaces. Every sample material was numbered and the individual sample amount was at least 1,5 kg. The sample area was described through the geographic position, specific characterisations as growth height and canopy. The sample area was documented like in the following Figure 1.



**Figure 1: Sample “Reed”, coordinates: 48°16’N, 16°37’O**



**Figure 2: Sample Sunflower, monoculture, coordinates: 48°7’N, 16°51’O**

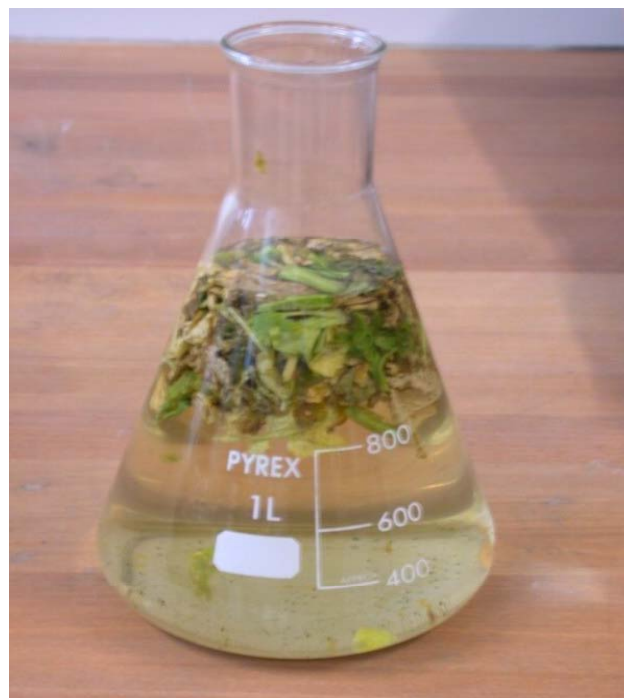
In the laboratory approximately 50 grams (g) of every sample were weighed in and cut by scissors and/or similar household equipment in small pieces of 3-5 cm.

The high inhomogeneity of some biomass samples made it necessary to divide several samples in two fractions. The first fraction (a) consists of the halms, stems etc. (see Figure 3) of the taken sample. The second fraction (b) is built by the corns or blossoms (see Figure 4).



**Figure 3+4: Sample maize (halm, stem etc.) left; and maize (corn) after cutting right**

After the sampling several tests were performed. In the first test the biomass was cut to a maximum length of 3-5 cm and mixed with a litre of distilled water in Erlenmeyer flasks (Figure 5). The eluate was shaken up and down 30 times to get a homogenous eluate. The flasks were left for 30 minutes. To homogenize the liquid before taking the sample the flasks were shaken up and down 5 times and left until the particles were settled again. The eluate was filtered after several minutes of rest period because the floating particles would else wise clog the filter. The solution of each sample was applied for the following tests. The blend was filtered with folded filters to get rid of the remaining small particles, which would constrain further analysis.



**Figure 5: Erlenmeyer flask with prepared sample 5 Legume**

For the second sample preparation method the biomass was cut to a length of 3-5 cm and was also mixed with a litre of distilled water. Afterwards the mixture was mixed with a “Braun Power Blend” jug blender (Figure 6).



**Figure 6: Preparation of the samples with the “Braun Power Blend” Jug Blender**

In this last sample preparation method the samples were prepared like in the second variant, but the mixtures were left overnight (24 hours). This variant was applied to find out if the examined concentration would rise with a higher leaching time (Figure 7).



**Figure 7: Water biomass blend left overnight in Erlenmeyer flasks**

The prepared solutions/eluates were filtered and the rapid tests for Chlorine determination were performed.

## 4 Test methods

### 4.1 Titrimetric determination

In this part of rapid test methods for the determination of chlorine the titrimetric test from Aquamerck was used. In nitric solution, chloride ions are titrated with mercury(II) nitrate solution against 1,5-dphenylcarbazone as the indicator, forming slightly dissociated mercury(II) chloride in the process. The excess mercury(II) ions react with the indicator and form a blue-violet liquid. The chloride concentration is determined from the consumption of titration solution. The chloride content rises coherent with the absorption of titration solution. The test was conducted with every biomass sample. Table 3 specifies the results of the rapid test.

**Table 3: Chloride content in mg/l observed in three different test variants of 9 biomass samples**

Sample	Chloride content [mg/l]		
	preparation method 1	preparation method 2	preparation method 3
Maize (halm)	15	20	22
Maize (corn cob)	5	15	20
Beet	10	105	105
Legume	25	77	77
Reed	57	65	70
Weed	110	110	110
Sorghum (halm)	40	57	60
Sorghum (corn)	10	10	40
Pulse	10	10	10
Sunflower (stem)	70	150	150
Sunflower (blossom)	100	100	105
Sunflower (stem)	130	130	135
Sunflower (blossom)	42	50	55

**Table 4: Comparison of the Chlorine measurement with the rapid test and the ionchromatography**

Number of sample	Sample preparation method	Ion chromatography	Rapid test
			[mg/l]
1a	1	7,6	15
1a	2	17,3	20
1a	3	15,1	22
1b	1	5,6	5
1b	2	12,3	15
1b	3	11,8	20
2a	1	5,2	10
2a	2	61,6	105
2a	3	60,3	105
3a	1	20,1	25
3a	2	55,6	77
3a	3	49,9	77
4a	1	46,5	57
4a	2	46,5	65
4a	3	46,1	150
5a	1	38,7	110
5a	2	84,9	110
5a	3	83,0	110

The results of the titrimetric tests do not correlate to the laboratory analysis using the standardised ion chromatography method. The reason could be the coloured eluate, because the trimetric method is working with a colour change which is difficult to see on turbid and coloured water.

On the other side, the sample preparation influence the chlorine content in the eluate. The sample preparation methods 2 and 3 with mixing the biomass with water in an jug blender are better than the shaking method.

In this part also one test was the determination of evaporation residues. With this method just water soluble salts can be eluated and measured and this salts should be found in the evaporation residues. The testing was realized with the prepared and filtered liquid.

The weight of the empty beakers was determined an a definition volume of the eluate was pippered in the beaker. The filled beakers were put overnight for 24 hours into the drying oven to ascertain the evaporation residue. The water evaporated and the salt crystals remained in the beaker. The next morning the left-over was determined. Therefore the new weight of the beakers was ascertained. The difference between the empty beaker and the beaker with the evaporation residue was calculated and represents the weight of the crystalline left-over itself.

Unfortunately also this method does not achieve satisfying results, because the evaporation residues were continuously higher than the sum of water soluble salts (K, Na, Cl, etc.).

**Table 5: Calculation of the evaporation residue and comparison to ionchromatography results**

Number of sample	Sample Preparation Method	Evaporation residue	Chloride content (IC)
		[mg/l]	
1a	1	237	15
1a	2	4502	20
1a	3	897	22
1b	1	14	5
1b	2	712	15
1b	3	718	20
2	1	205	10
2	2	1993	105
2	3	1821	105
3	1	291	25
3	2	1091	77
3	3	118	77

## 4.2 Sample preparation of BioNorm samples and fresh biomass

Previously to the determination of chloride, sodium and Potassium, biomass samples were submerged into water by following the PSO 5297 method “Solid biofuels- determination of the contents of chloride, sodium, Potassium and sulfate-sulfur by simple tests. Liquid extraction methods”, a Danish method created by FORCE technology [1]. The principle of the extraction was carried out according to this procedure (Series b):

- Transfer a portion of 25 g of the prepared material into a dissolution container with 1000 ml of distilled water. For materials of pure wood a portion of 100 g may be used when only chloride is to be determined.
- Shake the closed container 25 times and let the suspension stand for at least 30 minutes. With the purpose of decreasing the cost of the method, CIEMAT extraction differed a little

from PSO 5297 method. The amount of distilled or demineralised water used in the extraction was reduced from 1000 ml to 100 ml. The amount of biomass added to the dissolution container was proportionally decreased to the used volume of water; i. e. 2.5 g in 100 ml. ultrapure water was preferred in order to eliminate interferences from other elements.

### 4.3 Different rapid test methods for Chlorine, Potassium and Sodium

The chloride test from HACH (Quantab) with a range of measurement between 30 – 600 mg chloride/l was found suitable as previously was recommended by FORCE technology [1], to determine chloride contents in water extracts of solid biofuels. The reading of this test stick is given as “Quantab units” which is converted into chloride concentration in mg/l by the conversion table on the packing of the sticks.

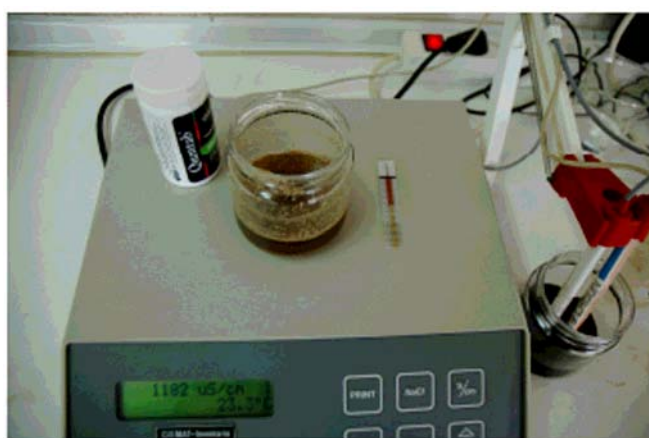


Figure 8: Test kit of chloride content: Quantab HACH

The measurement of conductivity was also carried out in the samples in order to determine the level of dissolution of the salts contained in the biomass samples. The conductivity tester was a commercial instrument.

A kit based on turbidimetric method was found suitable for determination of the content of Potassium in extracts of solid biofuels, e.g. the Visocolor Potassium test from Macherey-Nagel (Figure 9). However the range of measurement of this test kit is just 2 – 15 mg Potassium/l, therefore, it was necessary to dilute in most extracts. This kit was also recommended by FORCE technology [1].



Figure 9: Test kit of Potassium content: Visocolor MACHEREY-NAGEL

Another rapid kit based on colour change of a test stick submerged in extract solution, similarly to chloride quick method, was also found suitable for determination of the content of Potassium in extracts. This test is called Quantofix (Figure 10) from HACH, whose measurement range goes from 200 to 1500 mg/l Cl<sup>-</sup>. Therefore, the dilution of the extracts was not necessary.



**Figure 10: Test kit of Potassium content: Quantofix HACH**

A search about quick test kit for the determination of the content of sodium in field was performed, although this kit was not found. Therefore, sodium concentrations in solid biofuels were not carried out. It is important to point out that the content of sodium in the major part of biofuels is negligible compared with the Potassium content.

BioNorm I and II samples such as wood chips, wheat straw, rape straw, almond kernels and exhausted olive residue were evaluated with the purpose of knowing the accuracy and the performance of the quick tests. The particle size of the biofuels was below 1 mm because these samples were milled to pass 1 mm sieve before shipping to the laboratories participating in the projects BioNorm I and II.

In addition, the amount of material tested and biofuel particle size was evaluated in other biomass samples. The field biofuels studied were: pine chips, herbaceous samples (wheat straw and pellet of *Brassica carinata*) and agro-industrial biomass (almond kernels and exhausted olive residue). These biofuels were different of those used in BioNorm samples, excepting the agroindustrial samples, because they were Spanish biomass delivered to ofi to be studied by all laboratories involved in the projects BioNorm I and II.

With the purpose of comparing results among biofuel samples and studying the accuracy and precision of the quick tests, several tests were carried out by applying the PSO 5297 method. The precision data (results not shown) were considered acceptable. The data for chloride and Potassium as a function of the biofuel are shown in Tables 6 and 7, respectively. The quantification limit was calculated and resulted to be 0.03% with 10 g of wood chips in 100 ml of ultrapure water. No quantification of chloride was reached by using 10 g of almond kernels; consequently 20 g of almond kernels was added into the ultrapure water to reduce the quantification limit from 0.03% to 0.015% and to try the measurement of chloride. In order to determine the accuracy, the determination of chloride by means of the Technical Specification CEN/TS 15105 “Solid Biofuels - Methods for the determination of water soluble chloride (Cl) content, sodium (Na) and Potassium (K)” was carried out and the difference with PSO method was calculated (Table 6). Important differences are obtained in olive residue and seaweed. The results of chloride in PSO method are higher than in CEN/TS method. This fact can be explained by analysing the rest of the halogens contained in these samples.

Olive residue has important amounts of fluoride (0.12 wt%) and bromide (0.02 wt%) while seaweed is characterised by high bromide contents (0.14 wt%). These halogens can interfere the chloride determination, increasing the final total concentration of chloride.

**Table 6: BioNorm samples (size <1 mm). Chloride comparison between PSO 5297 and CEN/TS 15105**

	Chloride		
	PSO 5297	CEN/TS 15105	% Difference
Wood chips	< 0.03	0.012	nd
Almond kernels	0.02	0.033	36
Rape straw	0.29	0.242	-21
Cynara	1.53	1.603	5
Coconut shells	0.26	0.178	-46
Exhausted olive residue	0.37	0.183	-101
Seaweed	0.45	0.142	-218

nd: non determined

Similarly to chloride, Potassium results of the two quick tests (Visocolor and Quantofix) are compared with CEN/TS 15105 (Table 7). Quantofix test generates important differences at Potassium contents lower than 0.5 wt% as it is shown in wood chips, coconut shells and olive residue. Therefore Visocolor is better at low K concentrations, although at high Potassium concentrations it is compulsory to make dissolutions using Visocolor quick test, especially in herbaceous biofuels, consuming time (agitation and leaving to stand more than 30 minutes) due to the necessity of repeating the extraction process.

**Table 7: BioNorm samples (size <1 mm). Potassium comparison between PSO 5297 and CEN/TS 15105**

	Potassium			Potassium	
	PSO 5297*	CEN/TS 15105	% Difference*	PSO 5297**	% Difference**
Wood chips	0.10	0.076	-32	0.20	-163
Almond kernels	nd	0.380	nd	0.10	74
Rape straw	0.80	0.709	-13	0.80	-13
Cynara	0.80	1.197	33	1.60	-34
Coconut shells	0.16	0.214	25	0.80	-274
Exhausted olive residue	2.40	1.980	-21	1.60	19
Seaweed	0.12	0.316	62	0.80	-153

(\*): Visocolor                      (\*\*): Quantofix

Regarding the second objective of this subtask, several particle sizes and amounts of each selected biofuel were studied. The particle sizes were three: original particle size, biofuel ground to pass a 2 mm sieve and biofuel ground to pass a 0.5 mm sieve (dust). The amount of the biofuel depends on kind of biofuel. The higher de biofuel particle density the bigger the amount of biofuel added to the 100 ml of ultrapure water. The criterion followed was to use the maximum amount of sample in order to quantify the chloride and Potassium. Results for pine chips of chloride and Potassium (Quantofix kit) are shown in Tables 8 and 9, respectively. Taking into account the conductivity and chloride content of the dissolutions, the milling of the sample below 0.5 mm is necessary to quantify the chloride (Table 8) and to improve the extraction of salts into water. However, an increase of amount of sample from 10 to 20 g does not improve the extraction of salts too much. Conductivity should be around 900 RS/cm at 0.5 mm particle size while the obtained conductivity was only 735 RS/cm. Amount of 40 g per 100 ml was impossible of measuring as a consequence of the almost complete absorption of water into the solid sample.

**Table 8: Chloride content as a function of particle size and amount of pine chips**

Pine chips	Chloride		
	Particle size		
Amount (grams in 0.1 litre of water)	1-30 mm	< 2 mm	< 0.5 mm
<b>10 g</b>	< 0.03 % (111 microS/cm)	< 0.03 % (380 microS/cm)	< 0.03 % (462 microS/cm)
<b>20 g</b>	< 0.015 % (269 microS/cm)	< 0.015 % (656 microS/cm)	0.018 % (735 microS/cm)
<b>40 g</b>	no data	no data	no data
Cl= 0.032% according to CEN/TS 15105			

Potassium results, which were obtained using 10 and 20 g per 100 ml water, show an improvement in the recovery of Potassium when decreasing the particle size. No differences are found at 10 g per 100 ml as a function of the particle size. Probably, the sensitivity of the kit is too low to detect this variation as a consequence of the decrease of the particle size.

**Table 9: Potassium content as a function of particle size and amount of pine chips.**

Pine chips	Potassium		
	Particle size		
Amount (grams in 0.1 litre of water)	1-30 mm	< 2 mm	< 0.5 mm
<b>10 g</b>	0.20 % (111 microS/cm)	0.20 % (380 microS/cm)	0.20 % (462 microS/cm)
<b>20 g</b>	0.10 % (269 microS/cm)	0.20 % (656 microS/cm)	0.20 % (735 microS/cm)
<b>40 g</b>	no data	no data	no data
K= 0.16% according to CEN/TS 15105			

Chloride contents of herbaceous materials are shown in Tables 10 and 11. Previously to the determination, the wheat straw was manually cut in little straws around 20 mm length. The addition of 10 g or 5 g of wheat straw per 100 ml of water does not improve the conductivity with respect to 2.5 g. The addition of 10 g could present problems of lack of water in the dissolution to carry out the tests due to the absorption of the water by the solid sample, especially at lower particle sizes (below 2 mm). The milling of the herbaceous samples does not improve the salt extraction it as can be seen in Tables 10 and 11. In the case of pellets, the disintegration of the pellet in water is quick and the particles are enough low in the original pellet, subsequently, both parameters, fast disintegration and low particle sizes, allow to eliminate the milling of the pellet. Similar comments can be performed in Potassium tests with wheat straw (Table 12) and pellet of *Brassica carinata* (Table 12). Moreover, the Cl and K contents are so high that the use of 2.5 or 5 g of herbaceous material without grinding are considered optimum amounts to determine chloride and Potassium in field.

**Table 10: Chloride content as a function of particle size and amount of wheat straw**

Wheat straw	Chloride		
	Particle size		
Amount (grams in 0.1 litre of water)	1-30 mm	< 2 mm	< 0.5 mm
<b>2.5 g</b>	0.272% (916 microS/cm)	no data	no data
<b>5 g</b>	0.272% (1746 microS/cm)	0.298 % (1890 microS/cm)	0.272% (1800 microS/cm)
<b>10 g</b>	0.209% (2730 microS/cm)	no data	no data
Cl= 0.233% according to CEN/TS 15105			

It is also to be noted that the content of chloride based on CEN/TS 15105 is lower than that obtained by PSO 5297. Thus, interferences of other halogens different to chloride have occurred in brassica pellet (Table 10), similarly to BioNorm samples: olive residue and seaweed (Table 6).

**Table 11: Chloride content as a function of particle size and amount of pellet (Brassica carinata)**

Pellet <i>Brassica carinata</i>	Chloride		
	Particle size		
	6-30 mm	< 2 mm	< 0.5 mm
Amount (grams in 0.1 litre of water)			
<b>2.5 g</b>	0.452% (1279 microS/cm)	0.368 % (1316 microS/cm)	0.328% (1367 microS/cm)
<b>5 g</b>	no data	no data	no data
<b>10 g</b>	no data	no data	no data
Cl= 0.171% according to CEN/TS 15105			

**Table 12: Potassium content as a function of particle size and amount of wheat straw**

Wheat straw	Potassium		
	Particle size		
	1-30 mm	< 2 mm	< 0.5 mm
Amount (grams in 0.1 litre of water)			
<b>2.5 g</b>	1.40 % (916 microS/cm)	no data	no data
<b>5 g</b>	1.40 % (1746 microS/cm)	1.40 % (1890 microS/cm)	1.40 % (1800 microS/cm)
<b>10 g</b>	1.00 % (2730 microS/cm)	no data	no data
K= 1.18% according to CEN/TS 15105			

**Table 13: Potassium content as a function of particle size and amount of pellet (Brassica carinata)**

Pellet <i>Brassica carinata</i>	Potassium		
	Particle size		
	6-30 mm	< 2 mm	< 0.5 mm
Amount (grams in 0.1 litre of water)			
<b>2.5 g</b>	1.60 % (1279 microS/cm)	1.60 % (1316 microS/cm)	1.60 % (1367 microS/cm)
<b>5 g</b>	no data	no data	no data
<b>10 g</b>	no data	no data	no data
Cl= 1.38% according to CEN/TS 15105			

Results of chloride in agro-industrial biomass such as almond kernels and olive residue are shown in Tables 14 and 15, respectively. Important variations in conductivity were observed among particle sizes. Almond kernels and olive residue are hard materials, probably not very porous materials and the water can not penetrate easily inside the material. Therefore, the milling of almond shells and olive residue is necessary to extract the salts into the water.

The Potassium contents shown in Table 16 and Table 17 for almond kernel and olive residue, respectively, corroborate the conductivity and chloride comments of the previous paragraph. The accuracy between K results of the quick test (Quantofix kit) and the EN/TS 15105 is considered acceptable taking into account the relative low sensitivity of these quick kits.

**Table 14: Chloride content as a function of particle size and amount of almond kernels.**

Almond kernels	Chloride		
	Particle size		
	1-30 mm	< 2 mm	< 0.5 mm
Amount (grams in 0.1 litre of water)			
<b>10 g</b>	no data	no data	no data
<b>20 g</b>	< 0.015 % (299 microS/cm)	< 0.015 % (1100 microS/cm)	0.021 % (1200 microS/cm)
<b>40 g</b>	no data	no data	no data
Cl= 0.033% according to CEN/TS 15105			

**Table 15: Chloride content as a function of particle size and amount of exhausted olive residue.**

Exhausted olive residue	Chloride	
	Particle size	
	0.1-3 mm	< 1 mm
Amount (grams in 0.1 litre of water)		
<b>2.5 g</b>	0.26 % (666 microS/cm)	0.37 % (1479 microS/cm)
<b>5 g</b>	no data	no data
<b>10 g</b>	no data	no data
Cl= 0.183% according to CEN/TS 15105		

**Table 16: Potassium content as a function of particle size and amount of almond kernels.**

Almond kernels	Potassium		
	Particle size		
	1-30 mm	< 2 mm	< 0.5 mm
Amount (grams in 0.1 litre of water)			
<b>10 g</b>	no data	no data	no data
<b>20 g</b>	0.10 % (299 microS/cm)	0.20 % (1100 microS/cm)	0.20 % (1200 microS/cm)
<b>40 g</b>	no data	no data	no data
K= 0.38% according to CEN/TS 15105			

**Table 17: Potassium content as a function of particle size and amount of exhausted olive residue.**

Exhausted olive residue	Potassium	
	Particle size	
	0.1-3 mm	< 1 mm
Amount (grams in 0.1 litre of water)		
<b>2.5 g</b>	0.80 % (666 microS/cm)	1.60 % (1479 microS/cm)
<b>5 g</b>	no data	no data
<b>10 g</b>	no data	no data
K= 1.98% according to CEN/TS 15105		

#### 4.4 Chlorine determination using grinded samples and acetic acid

Within this test series straw and woodchips samples were analysed. The straw was cut to a maximum length of 3 cm by scissors. In the first test 25 g of the cut material was mixed with 1000 mL demineralised water. In the second test acetic acid was applied in place of the water.

The woodchips were cut in a “Retsch SM 2000” cutting mill with 20 mm sieve. 100 g of the prepared material was like in the test with straw mixed at first with 1000 mL demineralised water and 1000 mL acetic acid.

All 4 solutions were filled in plastic buckets and tight fitting lids (2,5 L). The buckets were shaken up and down 25 times and left for 30 minutes. Then the samples were shaken up and down 5 times and left for the fuel materials to settle. The extracts were poured into plastic bags. The surface layers of the straw were held back with a spoon while the extracts of the woodchips were filtered through a tea strainer.

For the determination of chloride in the eluates the “HACH Quantab Low Range 30-6000 mg/L Cl<sup>-</sup>” test kits were applied in Series c. In this method the test sticks were inserted in the extracts. The reactions were finished when the yellow bands on the sticks turned dark. The Quantab units marked on the sticks were converted to mg/L Chlorine by a table.

The results of Series c are summarized in Figure 11, 12 and 13.

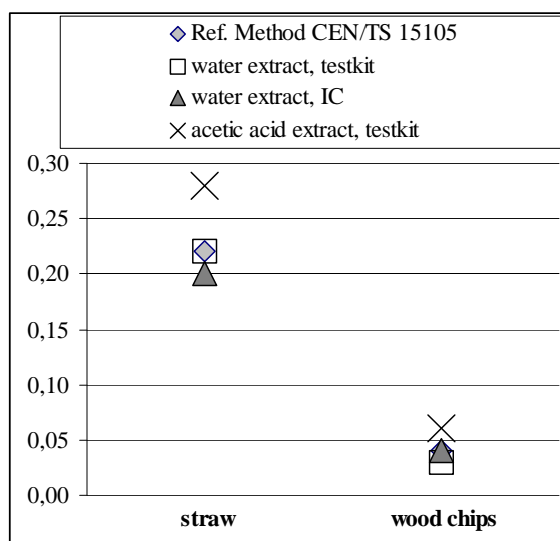


Figure 11: Cl determination using field- and reference methods

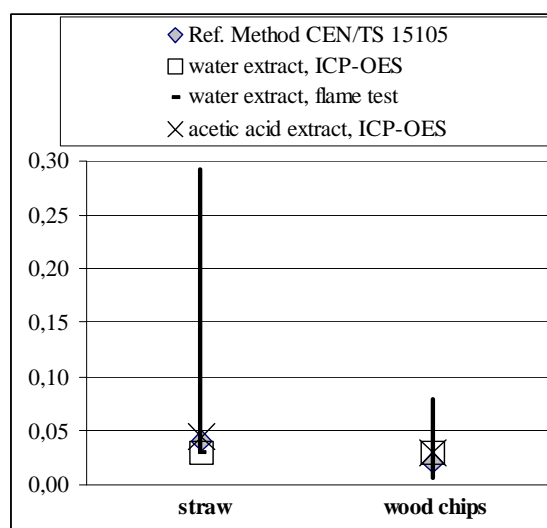
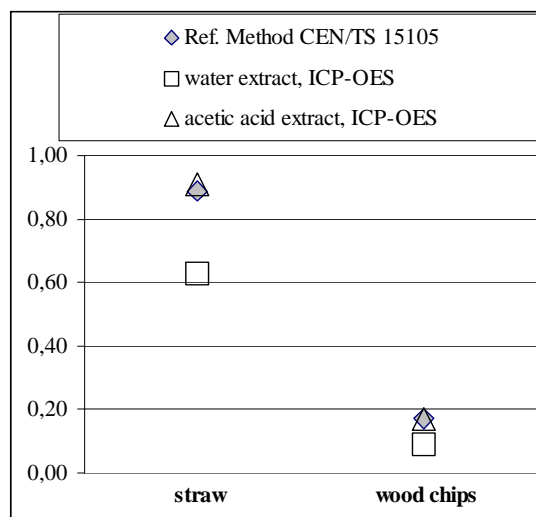


Figure 12: Na determination using field- and reference methods



**Figure 13: Potassium determination using field-preparation and lab-finish and reference methods**

Concerning the extraction, the field method delivers results that comply quite well with the reference method for all three elements. For chlorine, the quantification with the test kit supplies acceptable results.

#### 4.5 Flame test

In this method the determination of sodium in extracts is realized through a wire with an “eye”, which is inserted into the flame. The wire was held in the flame until the yellow colour disappeared. The wire is dipped into an extract or in this case a standard sodium solution to reach comparable results. The wire is re-inserted in the flame and the colour of the flame shows the concentration of sodium:

Now yellow colour: Concentration < 10 mg/L

Vague yellow colour: Concentration 10 – 75 mg/L Na

Intense yellow colour: Concentration > 75mg/L Na

#### 4.6 Quick test kits

For this test Series d all samples prepared for BioNorm I and II for method development to cover a wide range of concentrations, see Table 18. Thus, sample preparation (cutting, grinding) was not evaluated. 1 g sample was mixed with 100 ml deionised water, similar to CEN TS 15105, but the slurry was only shaken, not stirred and no heating was applied.

The quick test kits were applied according the instructions. For Series d only results for Na and K could be obtained. The concentrations of Cl and SO<sub>4</sub> were below lowest measurement range and could not be evaluated. Especially the colours of the biofuel eluates disturbed the readings.

**Table 18: results of quick test kits determination**

Sample	Na	Naref	K	Kref
Bark	10	120	25000	2100
Rapestraw	10	660	< 250	9000
Fir without bark	50	5	< 250	310
Orujilo (1:100)	530	170	25000	24000
Orujilo (5:100)	260	170	14000	24000
Seaweed	4900	12000	< 250	10300
Coconut shells	2200	1950	< 250	3500
Almond kernels	350	50	< 250	4000
Palm pit kernels	80	90	< 250	1200
Cyanara	8800	12000	9000-14000	13000
Straw	1200	70	5000-9000	11000



**Figure 14: equipment used in series d**

## 5 Conclusion

Herbaceous materials and pellets are easily mixed and disintegrated into the water and, consequently it is not necessary to grind them before analysing. Contrarily, materials such as wood chips, fruit kernels and other agro-industrial biofuels need a grinding before being analysed. This can happen before the leaching tests, but can also be performed within the sample preparation step by mixing a water – biomass mixture.

Biomass with high contents of other halogens such as fluoride and bromide, e. g. exhausted olive residue and seaweed, can cause interferences in the determination of the chloride content.

Quantofix method is a method to determine Potassium faster than Visocolor method, although inaccurate at low contents of Potassium (< 0.5%). The titrimetric method from “Aquamerck” is not an appropriate method for Chlorine determination of biomass eluates, because of the intensive colour of the eluates.

For chlorine, the quantification with the test kit supplies acceptable results, the flame test for the determination of Sodium is not sufficient.

New tested method like the evaporation residues as an indicator for the total water soluble salt was not satisfying.

PSO 5297 method is a very suitable method to determine soluble chlorine and alkali metals. Higher contents than 10 g per 0.1 litre of water could be necessary in order to decrease the limit of quantification for chloride (0.03%).

Currently it seems, that it is not possible to use one rapid test method for all solid biofuels and for all possible element concentrations. It is recommended to validate a procedure for one kind of biofuel and the corresponding experimental procedure (sample preparation, sample amount, test kits, etc.).

## 6 References

- [1] Westborg S. PSO 5297 method “solid biofuels- determination of the contents of chloride, sodium, Potassium and sulfate-sulfur by simple tests. Liquid extraction methods”. FORCE Technology, 2004: Version 13-03-2008.