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Improved and extended best practice guideline for the determination of Sulphur and halogens

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Involved Participants

The following institutions have been involved in the generation of this deliverable:

| | |
|---|--|
|  | <p>VTT Box 1000 (Biologinkuja 3-5,), 02044 VTT, Finland, www.vtt.fi</p> <p>Jussi Ranta</p> |
|  | <p>Ofi-Austrian Research Institute for Chemistry and Technology Franz Grill Straße 5, A-1030 Wien, Austria, www.ofi.at</p> <p>Martin Englisch, Magdalena Wojcik</p> |
|  | <p>Centro de Investigaciones Energeticas, Medioambientales y Tecnológicas (Ciemat) Departamento de Energías Renovables, Avda. Complutense, 22, E-28040 Madrid, Spain, www.ciemat.es</p> <p>Miguel Fernandez</p> |
|  | <p>Energy Research Centre of the Netherlands ECN Westerduinweg 3, 1755 ZG Petten, Netherlands, www.ecn.nl</p> <p>Frits Bakker</p> |
|  | <p>DONG Energy Enstedværkets laboratorium, Flensborgvej 185, DK-6200 Aabenraa, Denmark, www.dongenergy.com</p> <p>Edith Tomsen</p> |
|  | <p>SP Swedish National Testing and Research Institute Box 857, SE-501 15 Borås, Sweden, www.sp.se</p> <p>Conny Haraldson</p> |

Revisions

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|---------|------|------------|--------|
| 1 | - | Ciemat | - |
| 2 | | SP | - |
| 3 | | <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.

In WP II Task II.2. the existing and validated method for the determination of Sulphur and Chlorine, most frequently applying an oxygen bomb combustion was tested on the limitations by the determination of high content of Chlorine and Sulphur. Furthermore, the determination of other halogens like bromine, iodine, and fluorine was of minor interest during the first BioNorm project because of low contents of these elements in chemically untreated, natural biomass. So the applicability of the method for Br, I and F was not investigated. In the solid biofuel market, biomass with high contents of halogens, except Chlorine, is very rare. For low quality raw materials and contaminated fuels (e.g. chemical treated biomass) the determination of these elements may be of certain importance. For bromine, iodine and fluorine determination spiked mushroom sample and "home made" polluted cellulose sample were used.

By modification of combustion parameter e.g. different combustion gas pressure (10-30 bar), different combustion gas mixtures (using also argon), different receiving solutions, SEM (scanning electron microscopy) analysis of filter residues etc. and performing high number of tests, the existing problems of the methods could be solved and the limitations could be described accurately. Problems for the determination of biomass with high Chlorine contents can be caused by trapping Chlorine in slag agglomerates. This can happen if the biomass has an high ash content and the combustion temperature is very high (e.g. high sample amount or high oxygen pressure increase the temperature).

The workgroup finally concluded that the methods are in principal suitable for bromine, iodine and fluorine determination but there is currently no necessity to extend the method to halogens other than Chlorine.

List of Abbreviations

| | |
|---------|---|
| Br | Bromine |
| Cl | Chlorine |
| C.V. | Coefficient of variation |
| F | Fluorine |
| IC | Ionchromatography |
| ICPMS | inductively coupled plasma mass spectrometry |
| IRMM | Institute for Reference Materials and Measurements |
| NIST | National Institute for Standards and Technology |
| REM/EDX | SEM-EDX |
| R.S.D. | Relative Standard Deviation |
| S | Sulphur |
| SEM-EDX | scanning electron microscopy energy dispersive X-ray spectroscopy |
| UW | Ultrapure water |

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1 Introduction

The work for the improvement and extended best practice guideline for the determination of Sulphur and halogens was performed in several sub tasks.

Improvement of the reference methods for total Cl and total S

The method CEN TS 15289 "Solid Biofuels – Determination of total content of Sulphur and Chlorine" works fairly well for most biofuels with moderate contents of these elements. Especially the determination of the total Cl content was found to be problematic in the recently finished BioNorm project. During the first intercomparison test the results differed by approx. 40 % between the highest and lowest results when using the method proposed to be the Technical Specification. The determined concentrations were in most cases found to be lower than the water leachable concentration. It is of course not possible that the water leachable fraction is higher than the total content. After modifying the method and using a stricter protocol for the lab practise the situation improved but the results for total Chlorine were on average still lower compared with the water leachable fraction.

The fact that the experienced laboratories received (initially) quite different results with what was considered to be insignificant modifications in combination with the lower results compared with the water leachable fraction indicates that the current best method is either not robust enough or some crucial parameters are still unidentified.

Furthermore, Chlorine determination has shown to be a serious problem for a Swedish combustion utility when Swedish labs have found high concentrations of Chlorine in samples where Belgium laboratories have found acceptable Chlorine concentrations. Audits in the involved laboratories performed by SP (Swedish National Testing and Research Institute) did not show any obvious errors in the procedures used. This further strengthens the hypothesis that the proposed standard is not sufficiently robust but the result can be significantly influenced by minor differences in the operating procedure. Differences in materials in the equipment used for the sample decomposition are another possible cause for the discrepancies in the results. However, for power plants and other industrial applications it is very important to know exactly the concentration of elements, especially of Chlorine, to achieve a correct mass balance.

The central goal of the proposed research is the identification of parameters influencing the complete liberation of Chlorine and Sulphur during the combustion step with respect to the method and the used equipment. The research will focus on experimental details of the bomb digestion only a few to be mentioned here: (i) influence of combustion aids, diluting the fuel or acting as combustion temperature enhancers (ii) construction materials inside the bomb especially interaction of the stainless steel parts of the combustion bomb and the quartz glass crucibles. Surfaces of these parts will be investigated (iii) influence of blank values and possible delays of the ions into later digestions. A further important question are possible losses by discharge in aerosols during venting of the bomb or by chemical compounds not analysed e.g. chlorate. For all these potential pathways, series of experiments will be carried out that will be used to finally improve the above mentioned Technical Specification before it becomes a European Standard (EN) because the current method is still not satisfying.

Difference between bomb digestion and the water soluble Chlorine

It was found in the recently finished BioNorm project, that for some samples (especially for samples with high ash and high Chlorine content) bomb digestion delivers significantly lower Chlorine concentrations as an elution with water. It was speculated that some of the Chlorine (and also of the Sulphur) is bound to the combustion residues, somehow comparable to the behaviour of biomass in real combustion processes. The proposed research will help to understand the process in the bomb combustion and the parameters influencing the immobilisation of Cl and S. The goal is to under-

stand trapping processes of Sulphur and Chlorine in combustion residues in the laboratory combustion procedure. This knowledge may be of fundamental importance if correlations can be found and may offer potentials for a better understanding of combustion bed kinetics.

Fluorine, Bromine and Iodine

Usually bromine and iodine are of minor importance in biofuels. However, in some biofuels such as seaweed iodine is present and may become relevant in future. Bromine can be found in waste wood that may contaminate "clean" biomass in form of e.g. brominated flame retardants. To be able to clearly identify contaminated biofuels, a method for the determination of all halogenides is necessary. There is very little experience regarding the determination of these elements in a biofuel matrix. It is unclear, if the current methods, especially bomb combustion, are suitable to determine bromine and iodine. Within this project, the available methods will be tested, using biofuels and solid recovered (bio)fuels containing bromine and iodine. It should be noticed that biofuels and solid recovered fuels (especially waste wood) are usually analysed in the same laboratories and since there is a significant overlap with respect to the involved researchers the results can also be used for improvements of standards prepared by TC 343 WG5 "Solid recovered fuels, chemical analysis". A liaison with TC 292 is also planned.

2 Description of work

Improvement of the reference methods for total Cl and total S

The research will focus on experimental details of the bomb digestion e.g. combustion aid, construction material inside the bomb and the influence of blank values. For all items listed below, a work plan and the experimental details will be discussed in the first work group meeting:

- In order to find where Chlorine is lost samples will be spiked with chemicals and with samples marked by isotopes (mainly partner ECN).
- To investigate the losses in aerosols, the combustion gases will be let through an impactor, the trapped fractions will be chemically analysed (e.g. by REM/EDX), work will be mainly done by partner Ciemat and VTT.
- In order to get a reliable reference value for S, the isotope dilution technique used at meteorological institutes preparing reference materials e.g. IRMM (Institute for Reference Materials and Measurements, Belgium) or NIST (National Institute for Standards and Technology, USA) will be used; work will be mainly done by partner SP. The principle behind this is that a known amount of a well-characterised isotope spike is added to the sample before the sample decomposition. To determine the Sulphur content, the isotopic ratio of the Sulphur isotopes is determined using a mass spectrometer; this ratio together with data about the composition and mass of the spike added makes it possible to calculate the amount of Sulphur in the sample with high accuracy. Reference materials prepared and characterised in this manner will be used for the further improvement of the combustion method.
- Influence of combustion aids, diluting the fuel or acting as combustion temperature enhancers will be investigated mainly by partner ofi
- The interaction of Sulphur and Chlorine with the construction materials inside the bomb especially interaction of the stainless steel parts of the combustion bomb and the quartz glass crucibles will be investigated mainly by partner Dong.
- Influence of blank values and possible delays of the ions into later digestions and losses by chemical compounds not analysed e.g. chlorate will be investigated by all partners.

Difference between bomb digestion and water soluble Chlorine

To verify the available results, the two methods will be applied analysing additional samples prepared in Task II.2.1. With the addition of inorganic components such as lime stone or sand, the mechanism of Chlorine and Sulphur fixation will be investigated. Systematic series of experiments will be carried out using these mineral additives with compositions similar to biomass ashes. A work plan and the experimental details will be discussed in the first work group meeting. A significant amount of time will necessarily be spent on statistically assured results for selected samples e.g. cyanara were all partners will have to contribute experimental results.

fluorine, bromine and iodine

The work will include the preparation of at least two samples containing bromine and iodine (seaweed and wood with flame retardants) and a reference sample with known concentration of halogenides prepared by using biomass powder, fluoro-benzoic acid, chloro-benzoic acid, bromo-benzoic acid, and iodo-benzoic acid; the samples will be prepared by ofi. Existing methods especially the bomb digestion and the acid digestion in closed vessels, combined with IC and ICP-MS, will be tested and evaluated by all partners. For the bomb digestion, additives to the receiving solution will be investigated e.g. alkaline solutions to neutralise the acids formed in the bomb (mainly by partner VTT). The influence of hydrogen peroxide (added to the absorption solution before combustion to improve the oxidation of Sulphur) which may oxidate iodine into iodate leading to an underestimate of iodine content and the addition of ascorbic acid to improve the bromine and iodine conversion will be investigated, mainly by partner ECN. A best practice guideline will be delivered.

For the whole task II.2. all partners (ofi, VTT, Ciemat, ECN, Dong, SP) will work in close cooperation. It should be noted that it is not possible at the moment to define every set of experiments since the first series of experiments will show the further requirements. Countries involved in WG5 of CEN TC 335 are completely represented by these partners since they are all members within this working group. Even the chairman of WG5 participates Methods for moisture determination

3 Improvement of the reference methods for total Cl and total S

The study of losses in aerosols from the exhausted vent of the bomb was carried out testing two samples characterised by different ash, Chlorine and Sulphur contents. Analyses were carried out on seaweed and Spanish Cyanara (*Cynara cardunculus*) BioNorm I and II samples, which had been sent to all the laboratories that participated on the round robins.

The procedure was set as follows: 1-g of sample was pressed to produce a compact unbreakable pellet. The pellet was introduced in a combustion bomb and burnt in an IKA C-5000 calorimeter. Once the combustion has been finished, the combustion bomb was removed from the calorimeter, and placed it into an IKA C5030 venting station. After that, the valve of the bomb was opened and the combustion gases were swept away to a washing bottle containing ultrapure water. To perform these experiments, a filter made of mixed cellulose esters (Millipore SMWP, 5 Rm particle size) was placed in two positions, as indicated in figure 1.

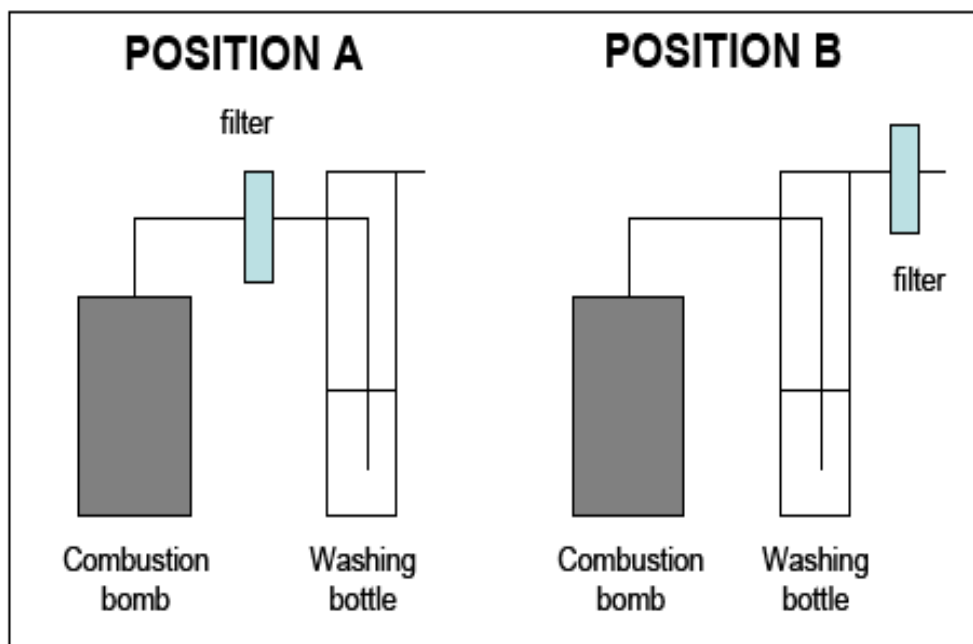


Figure 1: Position of the filter.

Thus, the exhaust vent was filtrated, and the filter was subsequently weighed and analysed by means of energy-dispersive X-ray spectroscopy – scanning electron microscopy (SEM-EDX). In addition, Chlorine and Sulphur contents from the washings of the bomb (with ultrapure water) and from the solution contained in the washing bottle were determined by ion chromatography.

The equipment used was a modular Methrom ion chromatograph operated by the Methrom IC Net 2.1 software, and consisting in several units: IC 733 separation centre, IC 732 detector and 709 IC pump. 20-RI sample were injected into the chromatograph and the ions were separated by means of a MethromSep A SUPP 5 chromatographic column (4 mm ID x 100 mm length), with a column packing of polyvinyl alcohol with quaternary ammonium groups (particle size 5 Rm). The mobile phase was a solution containing 3.2 mM of sodium carbonate and 1.0 mM of sodium bicarbonate at a standard flow of 0.7 ml min⁻¹. Ash content and total content of Chlorine and Sulphur were performed according to theirs corresponding CEN technical specifications [1,4].

In the second part of this subtask, the addition of different mineral additives and receiving solutions were studied using a homemade sample of cellulose highly polluted with F, Cl, Br, S, and I, and using the hemp and tobacco BioNorm samples prepared by ofi (Austria). The polluted cellulose sample was prepared as described in CEN technical specification 14582 for waste [2], and was created to be used as an appropriate control mixture. Moisture content in the analytical samples was determined according to CEN technical specification 14774-3 [3] at the same time as the chemical analysis, so that an appropriate correction of the concentration from wet basis to dry basis was calculated.

Also a extended test series with different combustion parameters changing the Oxygen pressure, the gas mixture or the combustion additives was performed on different biomass samples from BioNorm I and I samples.

Halogen and Sulphur contents were determined according to the CEN technical specification 15289 [4]. Sample pellets were prepared to be burnt later in a calorimeter as it was previously explained. Combustion gases were slowly passed through a washing bottle containing 50 ml of absorption solution by means of a venting valve connected to the combustion bomb. After this process, the inside

of the bomb, particularly its walls, electrodes, crucible, and cover were carefully washed with the 50 ml solution recovered from the previous gas scrubbing. The washing of the calorimeter bomb was repeated with another 50 ml of fresh solution. Finally, both portions of the solution were combined in a flask (100 ml) and finally analyzed by ion chromatography. The equipment used was described above, although a longer chromatographic column (Methrom A SUPP 5 – 250, 4 mm ID x 250 mm length) was used to improve the resolution of the peaks.

4 RESULTS AND DISCUSSION **Influence of the oxygen concentration in the Bomb and different combustion aids**

For the study of the influence of the oxygen concentration in the bomb on the determination of Chlorine and Sulphur, the sample Cyanara (and partly Orujillo) were used. Cyanara has more than 1% Chlorine and also high content of Sulphur, so small differences on this elements content should be easily detected. As gas mixtures different oxygen concentration (from 10% to 30%) and gases (Oxygen and Oxygen-Argon-mixtures) was tested. Except on this changes the determination of Chlorine and Sulphur was performed according to CEN TS 15289.

For this tests about 1g pressed sample into a 13mm pellet were digested in a PARR 1262 calorimeter with Cl-resistant bomb. As receiving solution 1 ml of ultrapure water was used and after the digestion the residues were transferred into an 100ml flask and analysed using an Dionex IC.

The following tables summarize the results from this part of the task II.2.

Table 1 Chlorine content of Cyanara and Orujillo after combustion under special conditions.

| Oxygenkonc. | Pressure | Cynara | | | Orujillo | | |
|-------------|-----------|--------|------|----|----------|-------|---|
| | | mean | s | n | mean | s | n |
| 100% | 30+35 bar | 1,62 | 0,08 | 44 | 0,195 | 0,004 | 8 |
| 100% | 10 bar | 1,71 | 0,05 | 8 | - | - | - |
| 50% | 30+35 bar | 1,60 | 0,05 | 7 | - | - | - |
| 33% | 35 bar | 1,81 | 0,09 | 12 | 0,205 | 0,002 | 6 |

Table 2 Sulphur content of Cyanara and Orujillo after combustion under special conditions.

| Oxygenkonc. | Pressure | Cynara | | | Orujillo | | |
|-------------|-----------|--------|-------|----|----------|-------|---|
| | | mean | s | n | mean | s | n |
| 100% | 30+35 bar | 0,178 | 0,007 | 38 | 0,120 | 0,005 | 8 |
| 100% | 10 bar | 0,197 | 0,007 | 9 | - | - | - |
| 50% | 30+35 bar | 0,182 | 0,004 | 7 | - | - | - |
| 33% | 35 bar | 0,200 | 0,010 | 12 | 0,127 | 0,002 | 6 |

The modification of the combustion gas and pressure is relevant for samples containing high concentration of Chlorine and Sulphur but not for the vast majority of solid biomass fuels like hog fuel or wood chips. From these results it can be concluded that lower oxygen concentrations will lead to higher recoveries (see figure 2). This could be explained with the assumption that lower oxygen pressure results in lower combustion temperatures and less sintering or melting of the combustion residues trapping some of the elements.

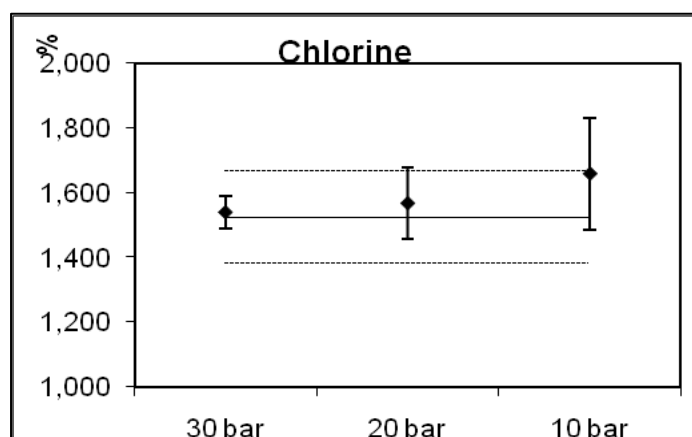


Figure 2: Chlorine content of Cyanara sample under different pressure conditions

An other possibility to change the temperature during the combustion is the application of combustion aids.

For the verification of the combustion aid influence, different aid were used. Usually are for solid biofuels polyethylen-bags a good substance to increase the temperature during the combustion and help to optimise the combustion step, but also not so usual aids like different capsules were tested. For this part two samples (Cyanara and rape straw) with different content of Chlorine were taken and amounts between 0,5g and 1 g of loos powder were digested. After the digestion step the determination of Chlorine and Sulphur are performed using ionchromatography.

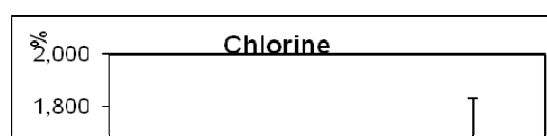
The following table 3 compare results of Chlorine and Sulphur of two biofule samples after combustion with and without the most common combustion aid polyethylene bag.

Table 3 Chlorine and Sulphur content of rapestraw and Cyanara after combustion with and without combustion aids polyethylene bag (mean values from 10-time determination)

| | Chlorine content | Sulphur content |
|---|-------------------------|------------------------|
| | [wt% d.b.] | [wt% d.b.] |
| Rapestraw with combustion aid | 0,268 | 0,186 |
| Rapestraw without combustion aid | 0,264 | 0,183 |
| Cyanara with combustion aid | 1,449 | 0,163 |
| Cyanara without combustion aid | 1,444 | 0,160 |

The application of combustion aids does not increase the Chlorine and Sulphur content significant, but the handling of loos powder sample is better using bags, because it is not necessary to press the material into pellets before combustion. The test series show that there are no reasons to exclude the application of combustion aids from the standard.

The possibility using combustion aids or different test condition was included to the standard as a note, but it was not necessary to change the tested standardised method described in the draft pr EN 15289/ CEN TC 15289.



4.2 LOSSES IN RELEASED GASES AFTER COMBUSTION

The gas phase after combustion was investigated in order to assess the losses during the pressure release after bomb combustion.

Previously, the ash content, as well as Chlorine and Sulphur contents for biomass samples included in this study (Cyanara and seaweed) were determined, and the results are presented in table 4.

Table 4 Ash, Chlorine and Sulphur content for the studied biomass samples.

| | Ash content (wt%, d.b.) | Chlorine content (wt%, d.b.) | Sulphur content (wt%, d.b.) |
|----------------|-----------------------------------|--|---------------------------------------|
| Cyanara | 10,7 | 1,65 | 0,17 |
| Seaweed | 34,4 | 0,37 | 2,31 |

After that, the amount of Cl and S recovered in the receiving solution placed in the bubbler and in the solution used for the washings of the bomb were determined by ion chromatography.

Table 5 shows the recovery results for both elements.

Table 5 Chlorine and Sulphur recoveries.

| Sample | Filter position | Chlorine recovery [%] | | Sulphur recovery [%] | |
|----------------|------------------------|------------------------------|----------------|-----------------------------|----------------|
| | | Bomb | Bubbler | Bomb | Bubbler |
| Cyanara | Position A | 99,985 | 0,015 | 99,976 | 0,024 |
| | Position B | 99,933 | 0,067 | 99,88 | 0,12 |
| Seaweed | Position A | 99,611 | 0,389 | 99,994 | 0,006 |
| | Position B | 99,888 | 0,112 | 99,936 | 0,064 |

Recoveries on table 5 were calculated without quantifying the Chlorine and Sulphur contained in the filter. As it is shown in the table, the percentage of both elements recovered in the washing bottle of the venting station (bubbler) is negligible compared to the percentage recovered in the bombs (>99.6%). Thus, the dissolution of Cl and S compounds in the aqueous phase of the bomb is quantitative. Furthermore, the bomb shall be carefully washed in order to recover both Chlorine and Sulphur, which remain in the inner parts of the bomb. In addition, the filter placed in positions A and B (see figure 1) was weighed and further characterised by identifying Sulphur and other major elements using SEM-EDX. On the filters, only some traces of deposit, that were dragged from the bomb while passing the gas stream (aerosols), were found. Particles come from the exhaust vent of the bomb. Filter weights, as well as relative weights, calculated with respect to the ash weight of the biomass burnt in the bomb are shown in table 6. Therefore, particle recoveries on filters can be considered negligible.

Table 6 Particle recoveries on filters

| Sample | Filter position | Filter recovery | |
|----------------|------------------------|------------------------|---------------------------|
| | | weight [g] | % relative weight* |
| Cyanara | Position A | 0,0006 | 0,0041 |
| | Position B | 0,0006 | 0,0042 |
| Seaweed | Position A | 0,0005 | 0,0009 |
| | Position B | 0,0004 | 0,0006 |

(*):it is calculated with respect to the ash weight of the biomass burnt in the bomb.

SEM micrographs of filters placed in different positions (A and B, see figure 1) for both samples are depicted in figure . It was found that the detected particles on the filter are characterized by a poor density. More particles were detected in the filters when analysing seaweed (7 particles for seaweed, 5 particles for Cyanara). Besides, the size of particles was higher in seaweed than in Cyanara, finding 20-30 Rm for Cyanara and 80-150 Rm for seaweed when the filter is placed between the calorimeter bomb and the washing bottle.

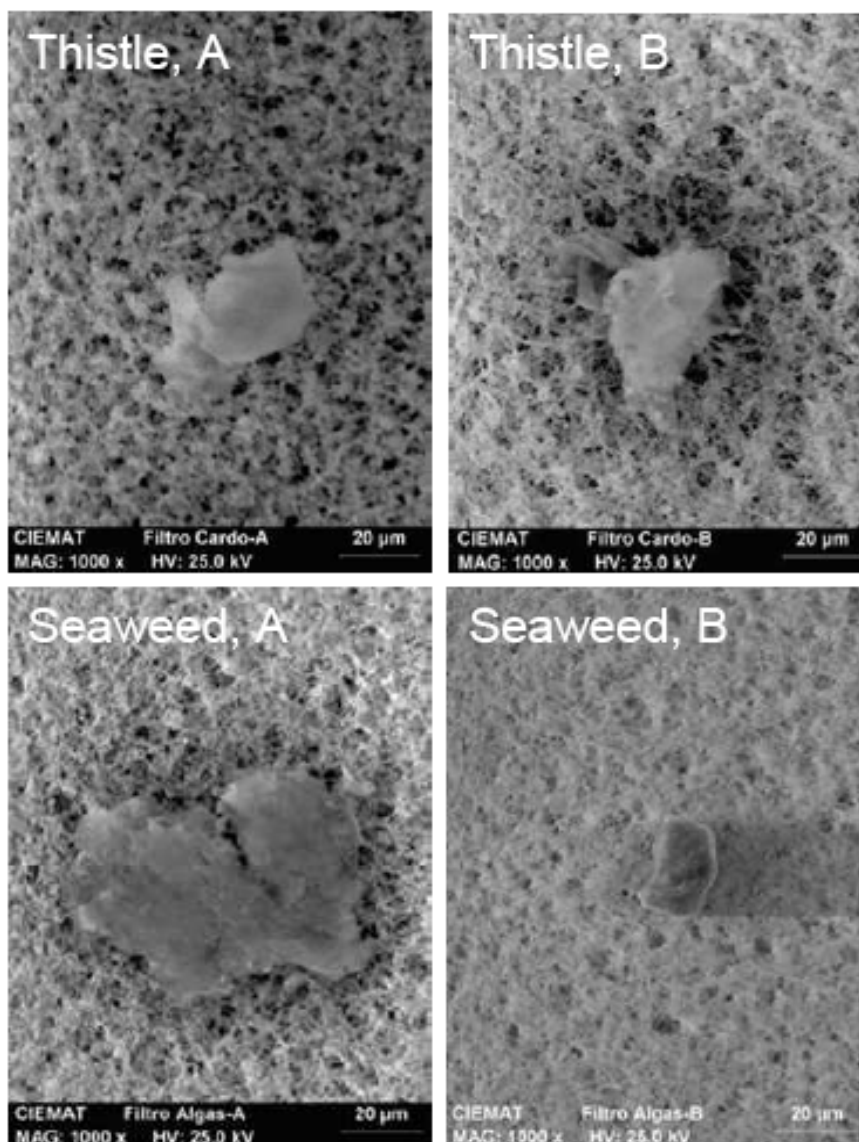


Figure 3 SEM micrographs of filters.

Major and trace elements presented in the particles found on filters were also identified by SEM-EDX, and the results are summarized in figures 4, 5 (for the Cyanara sample) and 6,7 (for seaweed). The elements found in the blank (a new filter) were carbon and oxygen. EDX analysis of the deposits revealed the presence of mainly Na, Al, Si, Cl, Ca, S, P, Mg and K.

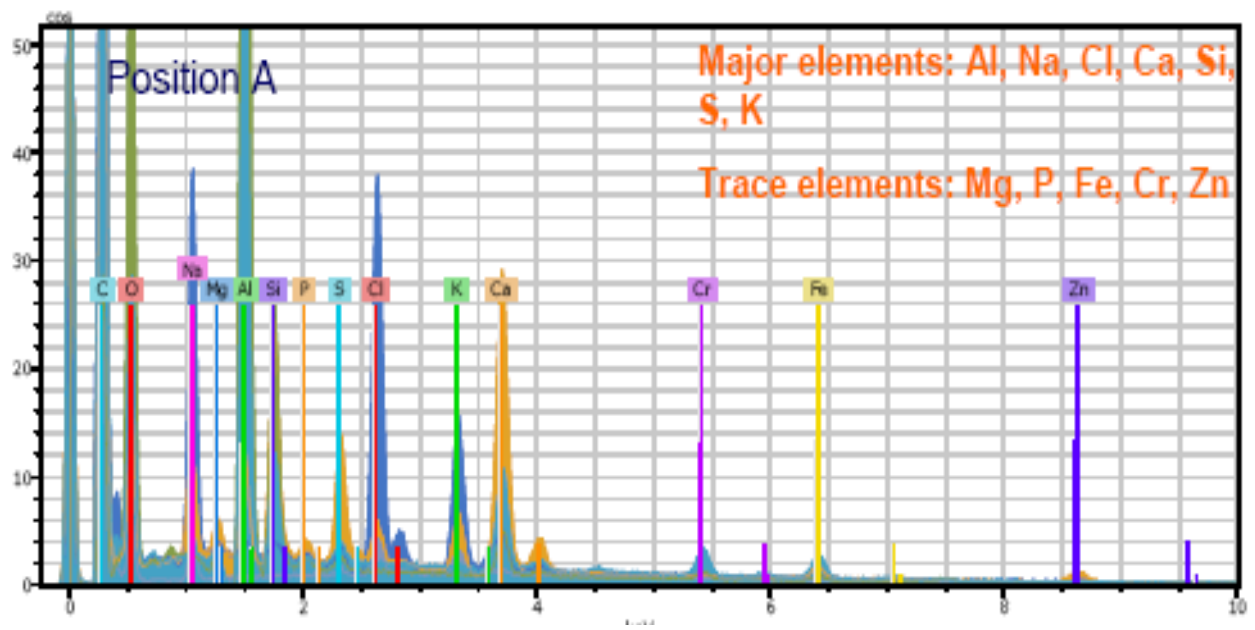


Figure 4: Elements identified in the filter particles for Cyanara

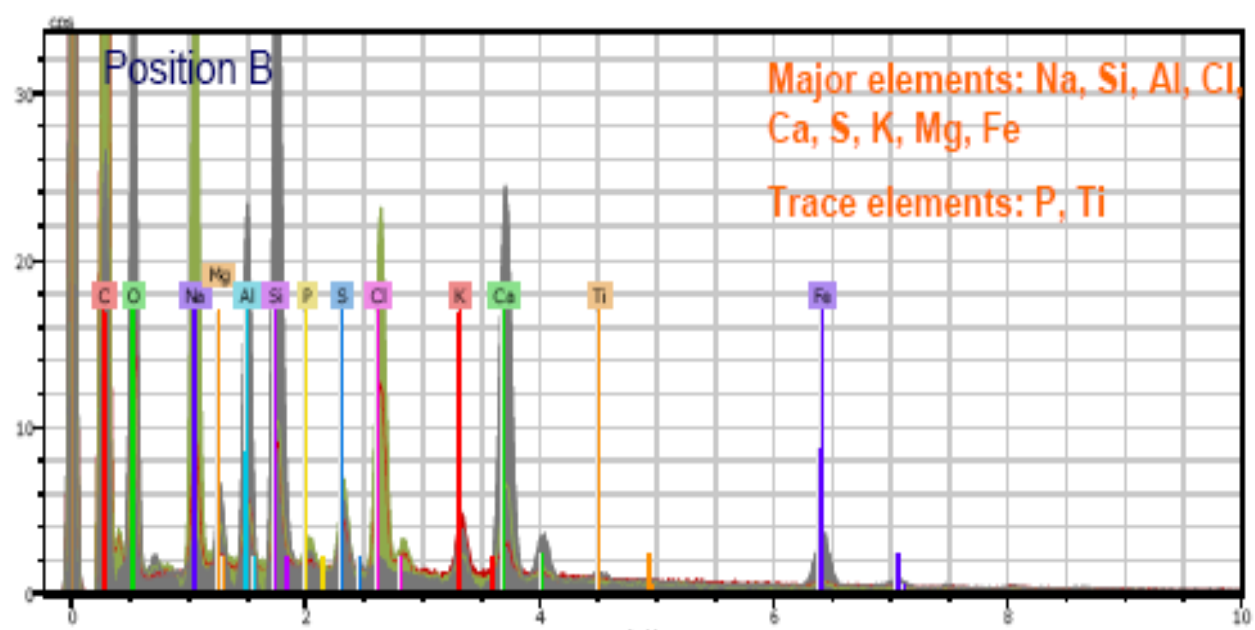


Figure 5: Elements identified in the filter particles for Cyanara

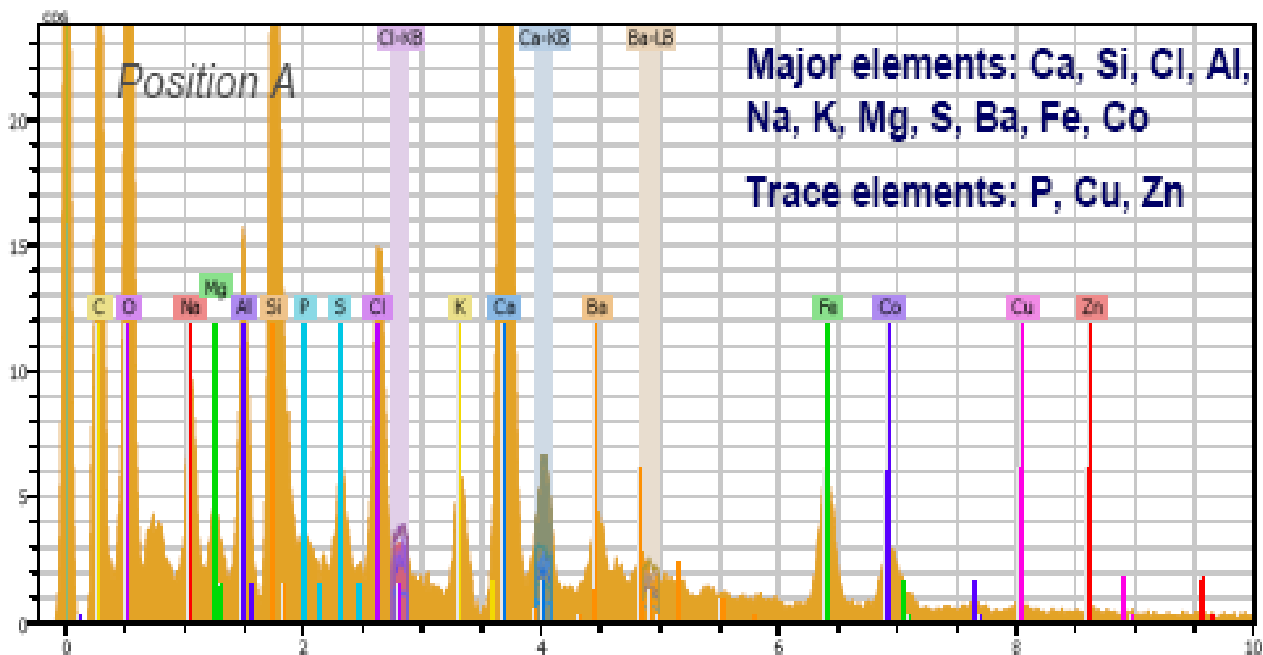


Figure 6 : Elements identified in the filter particles for seaweed

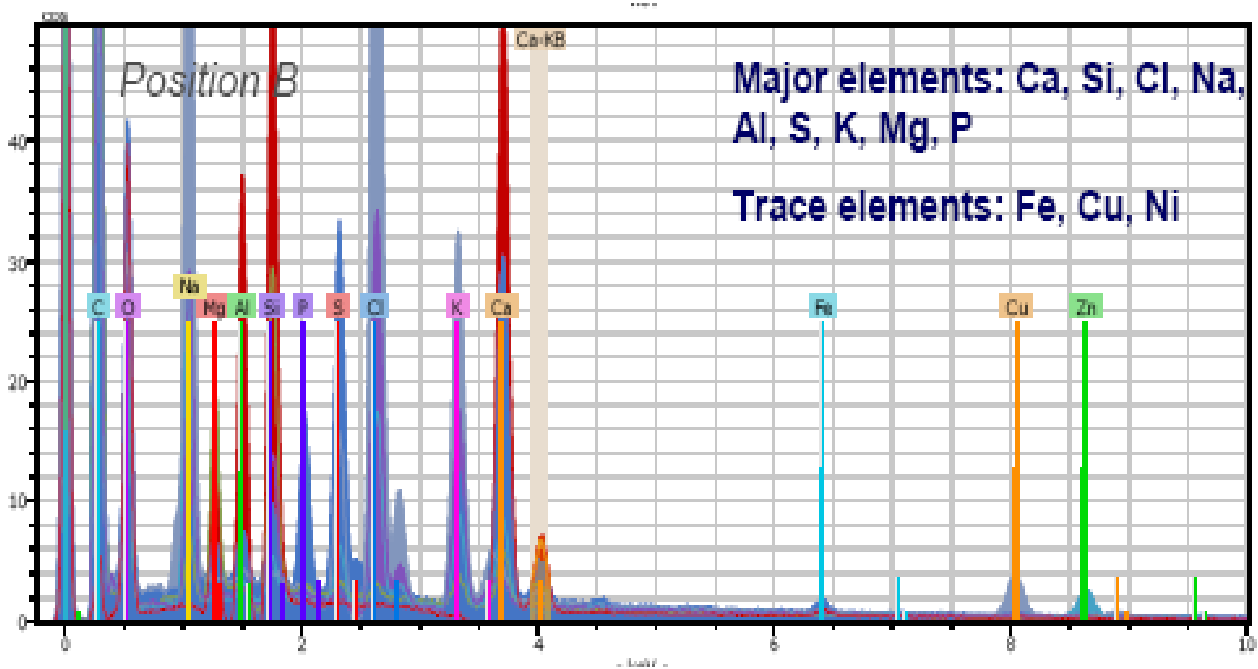


Figure 7 : Elements identified in the filter particles for seaweed

4.3 Determination of Sulphur in biofuel by isotope dilution

For the determination of sulphur by isotope dilution two samples with different content of Sulphur were tested. The Sulphur results for biofuel sample from BioNorm I project rapestraw is 0,188 % ± 0.004 % and seaweed is 1,87 % ± 0.04 %. After combustion of the sample in a calorimetric bomb the measurements of the receiving solution were performed using isotope dilution with inductively coupled plasma mass spectrometry (ICP-MS). The calibration is based on an isotope spike of ³⁴S - IRMM646.

In detail for the combustion about 1 g of undried biofuels were dissolved by combustion in a calorimetric bomb according to CEN/TS 15289:2006 and diluted to 200 ml. The blank from digestion was subtracted from the result. Isotopic spike was added to the digested sample and measurements were performed with a high resolution ICP-MS instrument Element2 in medium resolution. The differences in sensitivity for different masses were calibrated with a massbias solution prepared by mixing the isotope spike with natural sodium sulphate.

The samples were run in the following order: acid-blank, massbias, massbias, acid-blank, sample, sample, acid-blank, massbias, massbias, acid-blank, acid-blank. After a preflush of 2 min the ion intensities of mass 30 and 34 were measured for a period of 3 minutes. The average value of massbias and sample was used for the concentration calculations. The value of the acid-blank, determined before and after the measurement was subtracted before ratio calculations.

After this procedure the results were corrected for dry mass basis and are summarized in table 7.

Table 7 Results for S in % in the biofuels (laboratory SP)

| | S wt-% d.b. | U, K=2 % |
|-------------------|-----------------------|--------------------|
| Rape straw | 0,188 | ±0,007 |
| Sea weed | 1,87 | ±0,04 |

The method can be used for the determination of Chlorine, but the combination of Chlorine with more elements like Sulphur, Bromine etc. in the bomb digestion method using ionchromatography makes more useful. The method also shows that small losses of Chlorine could happen in the Bomb.

4.4 INVESTIGATION OF THE ADDITION OF MINERALS AND RECEIVING SOLUTIONS

In order to evaluate if the addition of minerals or different receiving solutions could enhance the recoveries of Sulphur and Chlorine, several tests were performed using different samples. In addition, these tests were carried out to find out if the reference method could be extended for fluorine, bromine and iodine.

Previous experiments were carried out by analysing a cellulose sample polluted with high contents of F, Cl, Br, S and I. In this first set of experiments the following absorption solutions were tested: ultrapure water (UW), and an aqueous solution containing 0.05 wt% NaOH and 0.05 v% H₂O₂. To find out if ascorbic acid enhances the iodine recovery, a solution containing a small amount of ascorbic acid (1 wt%) was also tested.

Moreover, a 10 wt% of different additives such as kaolin, MgO and the mixture Eschka(1:2 Na₂CO₃ – MgO), which is used in the Eschka procedure of determination of Chlorine, were added to the sample and the obtained blend was burnt in the calorimeter. The absorption solution was UW containing 0.05 wt% NaOH and 0.05 v% H₂O₂ when mineral additives were used.

Recoveries and repeatability, expressed as a coefficient of variation, as well as the number of replicates for each test are included in table 8.

Table 8 Recoveries and repeatability when analysing a polluted sample of cellulose.

| | %Recoveries (%C.V.) | | | | | n |
|---|---------------------|------------|-------------|------------|-----------|---|
| | F | Cl | Br | S | I | |
| UW | 102.0 (3.2) | 97.2 (7.5) | 94.6 (21) | 96.7 (8.6) | 6.7 (24) | 3 |
| UW-NaOH-H₂O₂ | 85.2 (3.0) | 98.6 (4.0) | 89.6 (29) | 99.4 (5.8) | 8.0 (46) | 6 |
| Kaolin | 69.8 (1.1) | 87.0 (0.7) | 103.0 (5.4) | 89.6 (0.2) | 5.4 (1.0) | 3 |
| MgO | 68.5 (3.1) | 83.0 (3.1) | 66.3 (6.2) | 89.8 (5.2) | 7.1 (12) | 3 |
| Eschka | 69.2 (1.8) | 86.9 (1.7) | 73.0 (1.1) | 92.1 (3.3) | n.d. | 3 |
| Ascorbic acid | | | | | 97.4 (30) | 5 |

n= No. Replicates; *n.d.*= not detected

Results for each element are depicted in figures 8-11. Red line represents the theoretical concentration, which means the amount of each element that has been added to the polluted cellulose sample, while the blue one is corresponded with the obtained concentration for each experiment.

From the results, it can be deduced that recoveries for Sulphur and for the remaining halogens (Cl, F, Br and I) are not improved by adding kaolin, MgO, or Eschka mixtures as additives. Neither does an aqueous solution containing 0.05 wt% NaOH and 0.05 v% H₂O₂, comparing to the recoveries obtained when using an ultrapure water solution. The chromatogram for a polluted cellulose sample when using an aqueous solution containing ascorbic acid (1 wt%) can be observed in figure 13. The background is greatly increased. Nevertheless, quantitative mean iodine recoveries (97 %) were obtained with this receiving solution, although poor repeatability was achieved (C.V. = 30 %).

Figure 8: Theoretical and obtained concentrations for Chlorine element under different conditions.

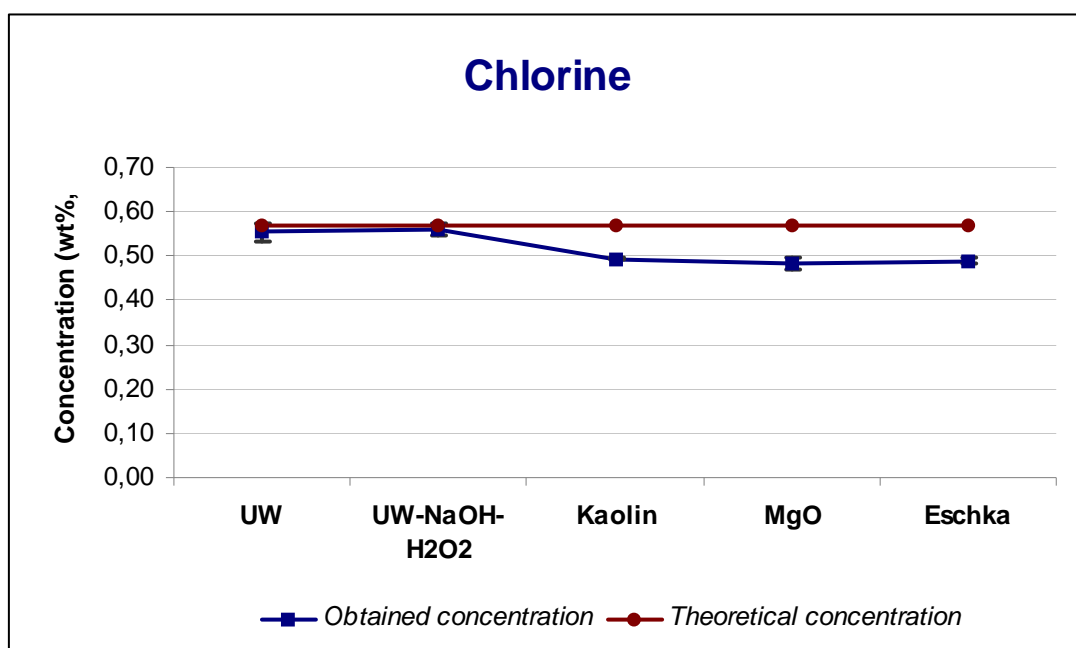


Figure 9: Theoretical and obtained concentrations for Sulphur under different conditions.

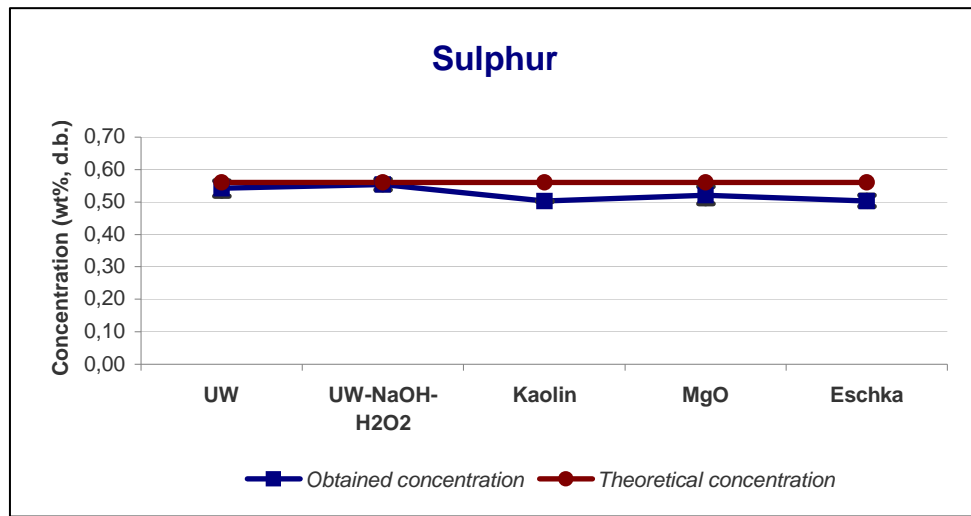


Figure 10: Theoretical and obtained concentrations for Bromine under different conditions.

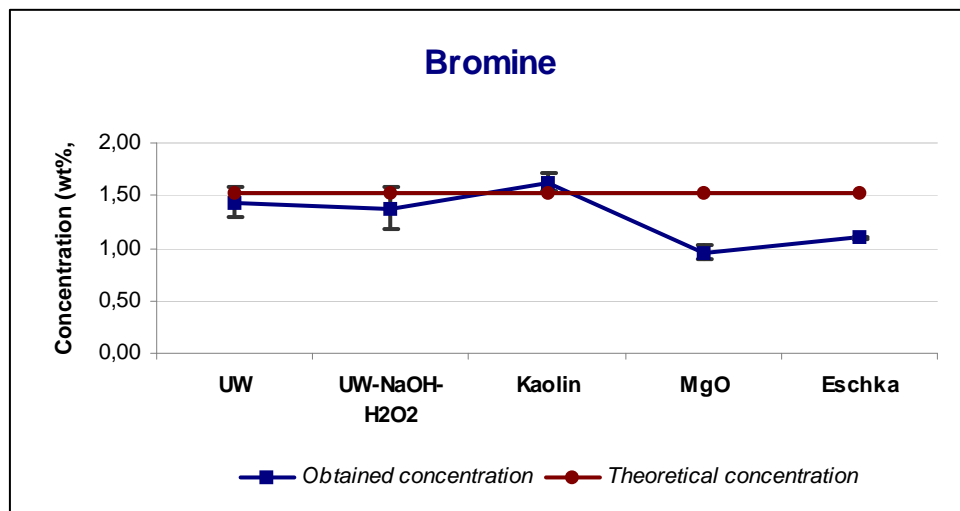


Figure 11: Theoretical and obtained concentrations for Fluorine under different conditions.

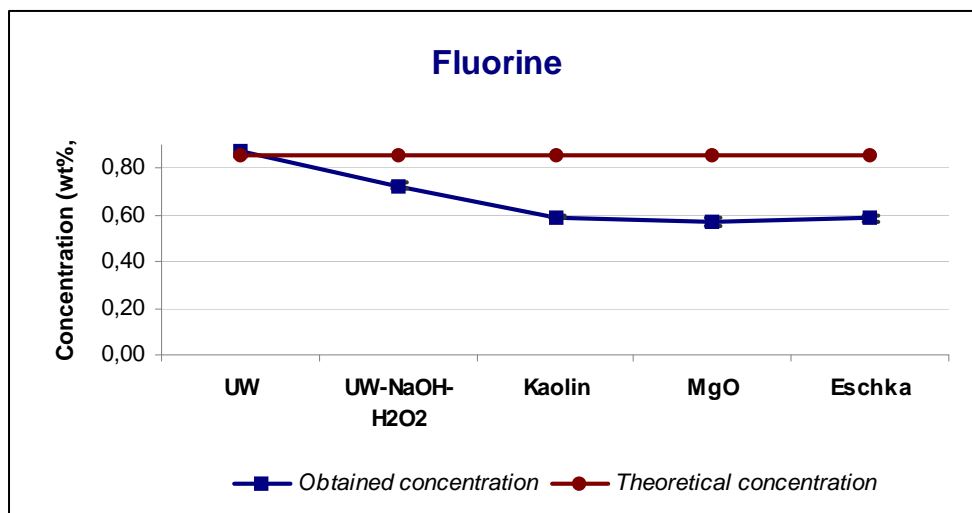


Figure 12: Theoretical and obtained concentrations for Iodine under different conditions.

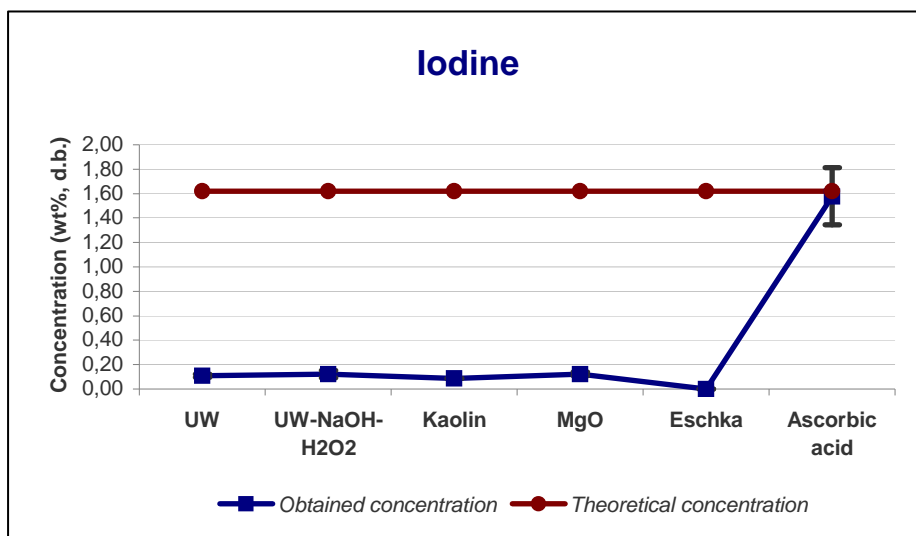
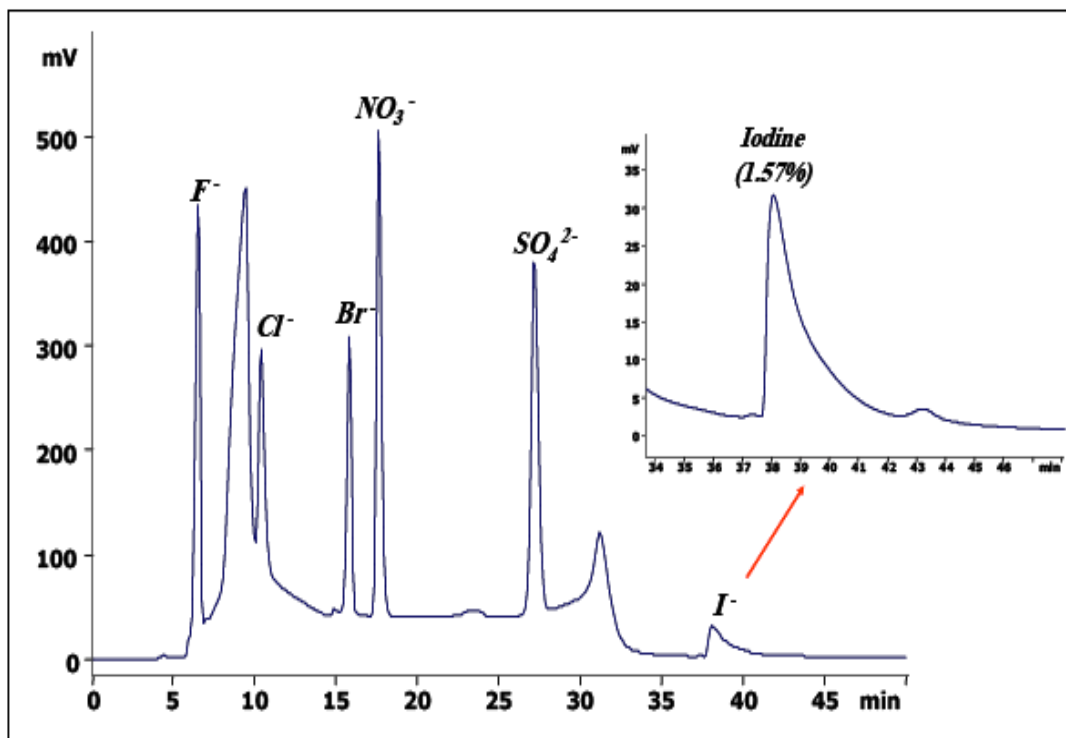


Figure 13: Chromatogram using UW/ascorbic acid for a polluted sample of cellulose.



With the aim of testing different receiving solutions using real biomass samples, a second set of experiments were performed analyzing polluted hemp and tobacco samples provided by ofi.

Besides the receiving solutions tested in the first set of experiments (UW, an aqueous solution containing 0.05 wt% NaOH and 0.05 v% H2O2, and an aqueous solution containing 1 wt% ascorbic acid), other solutions containing different quantities of sodium hydroxide were also included because alkaline solutions are recommended when Chlorine or Sulphur contents exceeds 2 % to neutralise the acidic compounds produced during combustion [4]. Thus, aqueous solutions with different amounts of NaOH ranging from 0.05 to 0.48 wt% were tested. Another test was performed by adding 1.5 ml of an aqueous solution containing 32 wt% NaOH inside the bomb, to find out if the addition of an alkaline solution inside the bomb makes any difference in the recovery of the ana-

lytes. This solution provides 0.48 g of sodium hydroxide inside the bomb, exactly the same amount presented in the aqueous solution containing 0.48 wt% NaOH.

For higher Sulphur contents, the addition of hydrogen peroxide to the absorption solution before combustion to improve the oxidation of Sulphur is recommended both in calorimetric bomb and Schöniger flask combustion methods in CEN technical specification 14582 [2]. According to CEN technical specification 15289 [4], hydrogen peroxide shall be used for the digestion in the closed vessel method to avoid losses of Chlorine. For that reason, the addition of hydrogen peroxide to an aqueous receiving solution was considered interesting, and an ultrapure water solution containing 0.25 v% of H₂O₂ was also finally included in the study.

Figures 14-16 show the obtained concentrations for Chlorine, Sulphur, and bromine when analysing the hemp and tobacco samples using the aforementioned receiving solutions.

Obtained concentrations for real biomass samples when using different receiving solutions.

Figure 14: Obtained concentrations for real biomass samples when using different receiving solutions.

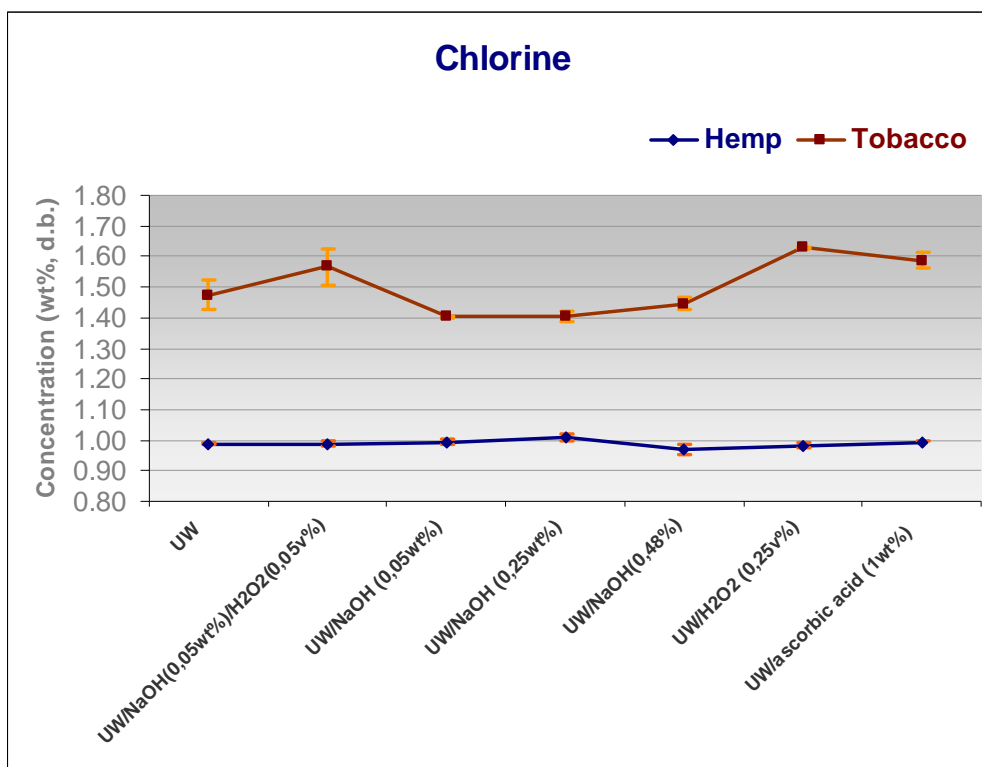


Figure 15: Obtained concentrations for real biomass samples when using different receiving solutions.

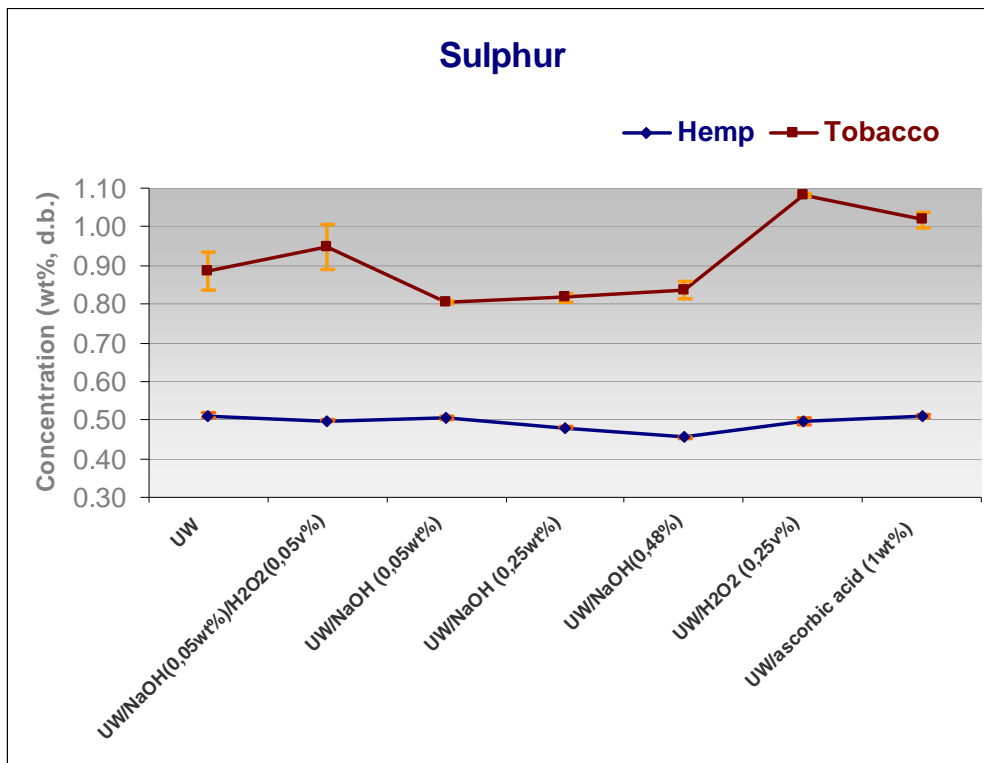
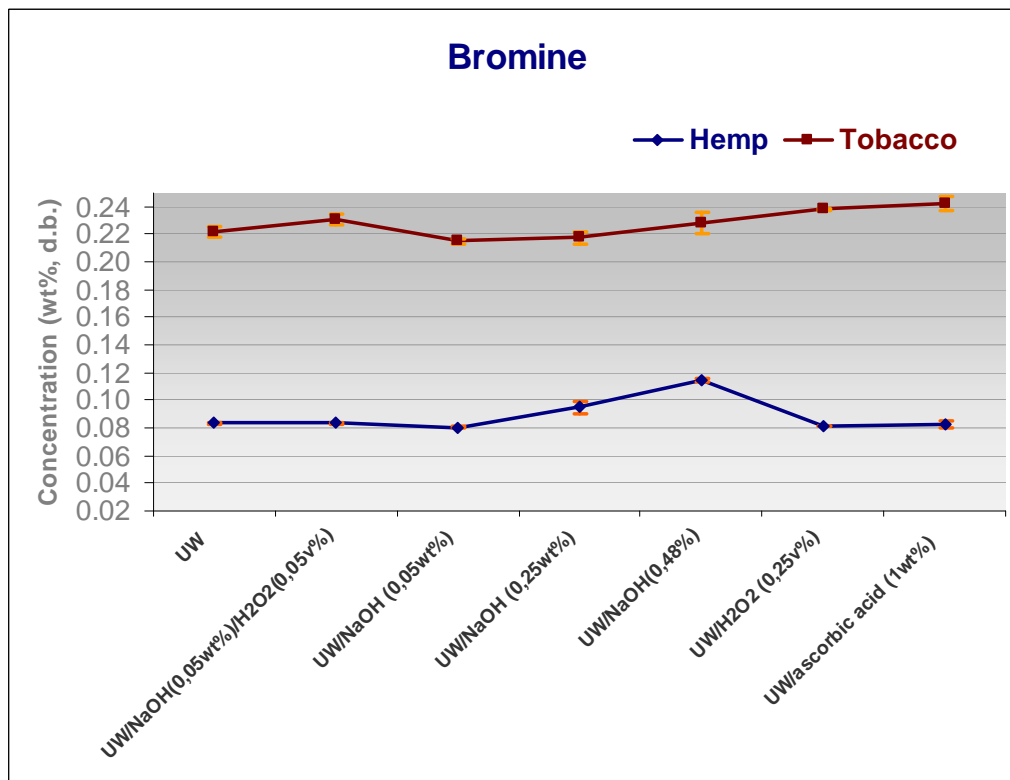


Figure 16: Obtained concentrations for real biomass samples when using different receiving solutions.



The obtained concentrations, as well as the repeatability, expressed as relative standard deviation (R.S.D.) can also be consulted in table 8. The number of replicates for each analysis is also included in this table.

Table 9: Obtained concentrations and repeatability when analysing real biomass samples using different receiving solutions.

| % Concentration (% R.S.D.) | | | | | | |
|-------------------------------|------|--------------|--------------|--------------|------|---|
| Hemp sample | | | | | | |
| | F | Cl | Br | S | I | n |
| UW | n.q. | 0.99 (0.004) | 0.08 (0.002) | 0.51 (0.01) | | 3 |
| UW/NaOH(0,05wt%)/H2O2(0,05v%) | n.q. | 0.99 (0.02) | 0.08 (0.002) | 0.50 (0.01) | | 3 |
| UW/NaOH (0,05wt%) | n.q. | 0.99 (0.02) | 0.08 (0.001) | 0.51 (0.01) | | 3 |
| UW/NaOH (0,25wt%) | n.q. | 1.01 (0.02) | 0.09 (0.01) | 0.48 (0.004) | | 3 |
| UW/NaOH(0,48%) | n.q. | 0.97 (0.03) | 0.11 (0.003) | 0.46 (0.005) | | 3 |
| UW/H2O2 (0,25v%) | n.q. | 0.98 (0.01) | 0.08 (0.001) | 0.50 (0.02) | | 3 |
| UW/ascorbic acid (1wt%) | n.q. | 0.99 (0.01) | 0.08 (0.004) | 0.51 (0.01) | n.q. | 3 |
| Tobacco sample | | | | | | |
| | F | Cl | Br | S | I | n |
| UW | n.q. | 1.47 (0.09) | 0.22 (0.009) | 0.89 (0.10) | | 3 |
| UW/NaOH(0,05wt%)/H2O2(0,05v%) | n.q. | 1.57 (0.12) | 0.23 (0.008) | 0.95 (0.12) | | 3 |
| UW/NaOH (0,05wt%) | n.q. | 1.4 (0.004) | 0.22 (0.04) | 0.81 (0.01) | | 3 |
| UW/NaOH (0,25wt%) | n.q. | 1.41 (0.03) | 0.22 (0.01) | 0.82 (0.02) | | 3 |
| UW/NaOH(0,48%) | n.q. | 1.44 (0.04) | 0.23 (0.02) | 0.84 (0.04) | | 3 |
| UW/H2O2 (0,25v%) | n.q. | 1.63 (0.001) | 0.24 (0.001) | 1.08 (0.01) | | 3 |
| UW/ascorbic acid (1wt%) | n.q. | 1.59 (0.05) | 0.24 (0.01) | 1.02 (0.05) | n.q. | 3 |

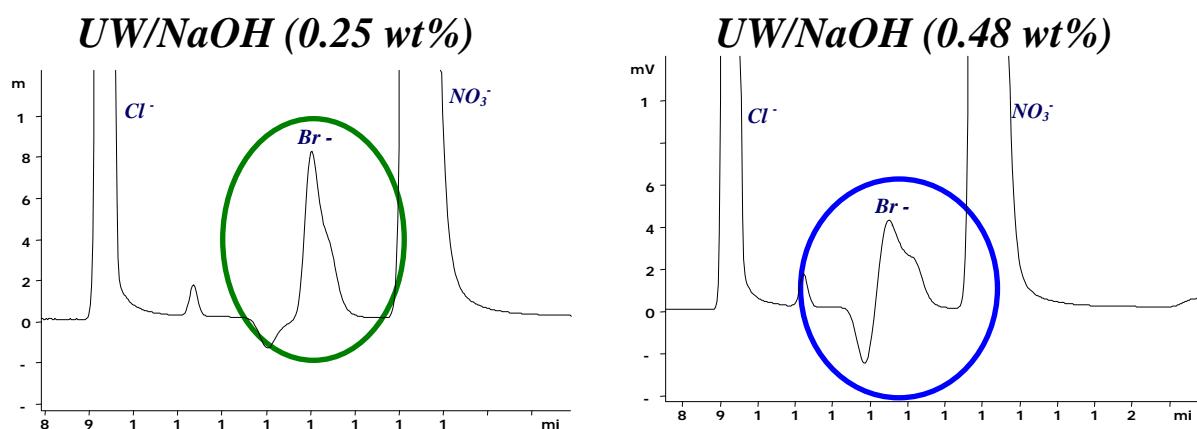
n. q. = not quantified

It should be mentioned that fluorine and iodine contents were not quantified in the hemp and tobacco samples because it was found that their concentrations were below the limits of quantification when using ion chromatography as the determination technique. The expected fluorine, and iodine contents in real biomass samples are very low. For that reason, if this method is going to be applied for unpolluted biomass samples, its sensitivity should be improved by using e.g. other specific chromatographic columns and/or different detection systems as ICPMS.

It is worth mentioning that an aqueous solution containing 0.25 v% H2O2 enhances the recovery of Chlorine and Sulphur when analysing the tobacco sample (see figures 17 and 18 table 8), obtaining a concentration of 1.63 %, closer to the value encountered by the well-known Eschka procedure (1.67 %). However, the same trend was not observed for the hemp sample, probably due to its lower Chlorine and Sulphur content.

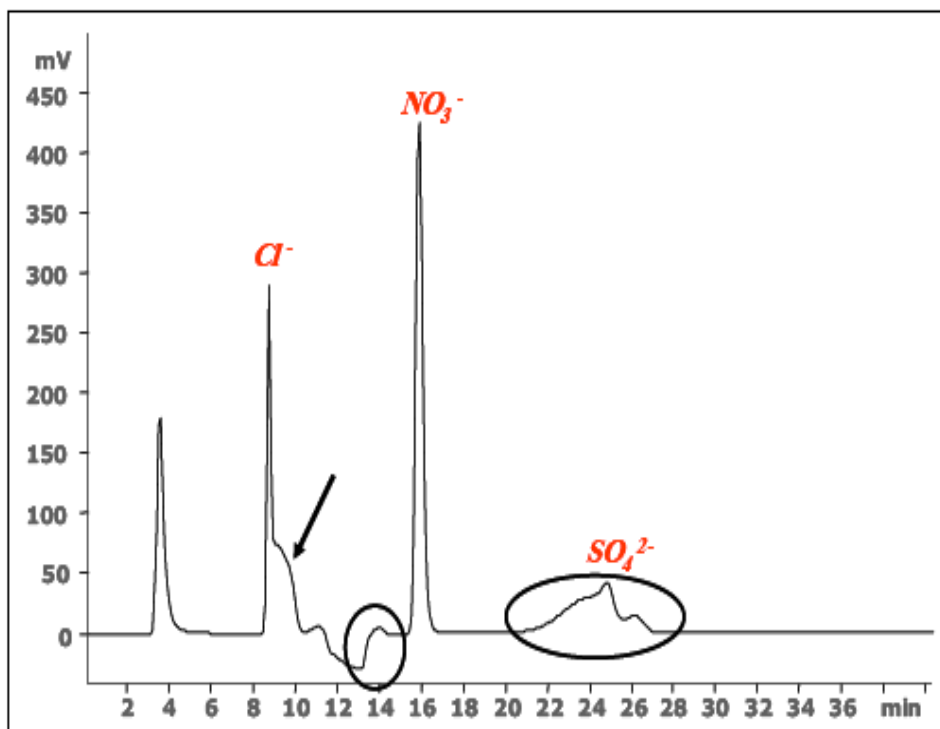
As it can be seen in figure 15, and table 8, the tested alkaline solutions do not improve the recoveries of Sulphur and Chlorine. Neither does an aqueous solution containing 0.05 wt% NaOH and 0.05 v% H2O2. Figure 17 shows the chromatogram area where the bromide ion elutes when the receiving solution contains 0.25 and 0.48 wt% of NaOH. Apparently, more bromine was recovered when using receiving solutions with higher contents of sodium hydroxide (see figure 17). Nevertheless, it is an artefact because another peak was found to be overlapped with the bromide peak (notice the shoulder in figure 16; more pronounced at higher contents of sodium hydroxide). Although this peak could not be identified, it could correspond to the hypobromite anion. In a basic media, bromide anion can form hybromous acid, which dissociates into hypobromite anion. Thus, it can be concluded that the tested receiving solutions do not improved bromine recoveries.

Figure 17. Bromine area of the obtained chromatograms when using aqueous solutions with high contents of NaOH.



The obtained chromatogram when the sodium hydroxide solution was placed inside the calorimetric bomb before the combustion is shown in figure 18. New peaks co-elute with chloride and sulfate, while the bromide peak becomes broader and smaller. Thus, and under these conditions the determination is not reliable.

Figure 18: Chromatogram when 1.5 ml of an ultrapure water solution containing 32 wt% NaOH is placed inside the bomb.



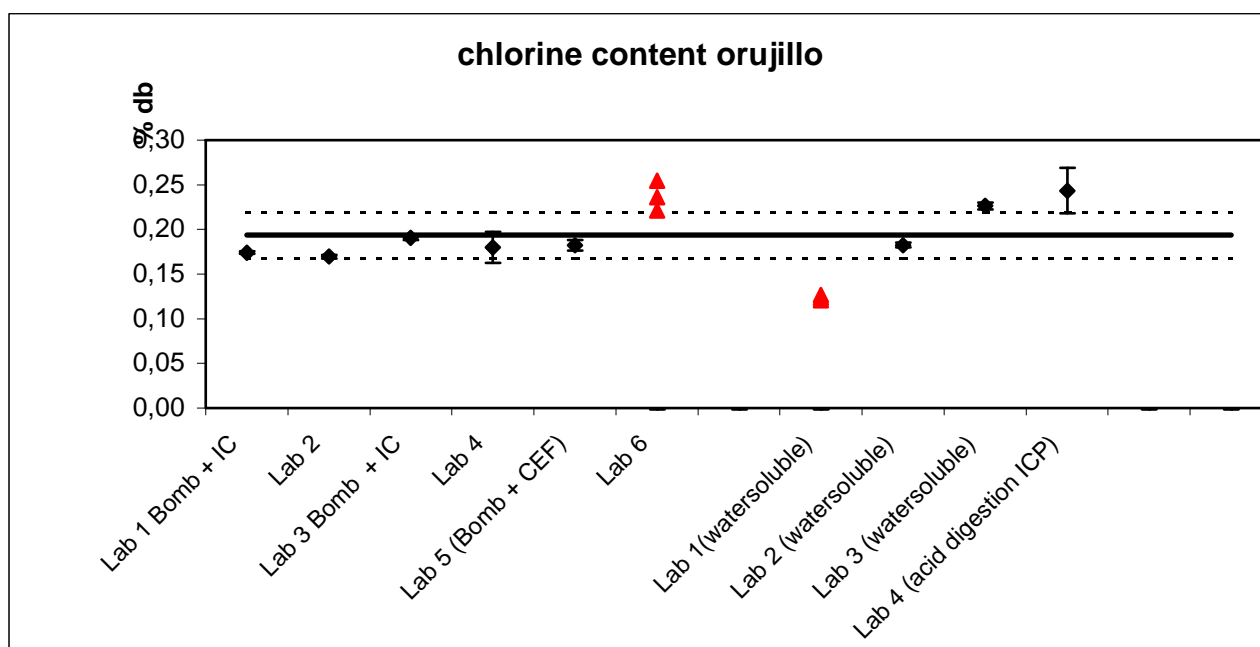
4.5 Investigation of difference of water soluble Chlorine and Chlorine determination with bomb combustion

During the BioNorm I project the water soluble method achieved on special samples better results for Chlorine determination.

The most important point during this test is the laboratory practice. The method seems to be very simple but all steps should be performed very carefully to achieve satisfying results. It is for example very important to close the “digestion” vessel very tight and also during the filtration step mistakes can happen. If the laboratory is using a folded filter out of bleached paper, the Chlorine content could be influenced. During the test series different filter types were tested and just few filter types does not have high blank values for Chlorine. For this method the measurement of a blank is essential.

If a laboratory has enough practice on this method, the results show that the Chlorine determination of samples with high ash content and a higher Chlorine content is better.

Figure 19: Chlorine determination results from round robin



5 Conclusion

The recoveries of Sulphur and Chlorine in the bubbler are negligible compared to the percentage recovered in the bombs. Thus, the dissolution of Chlorine and Sulphur compounds in the aqueous phase in the bomb is quantitative. Only some traces of deposit, that were dragged from the bomb while passing the gas stream (aerosols), were found on filters. Particle recoveries can be considered negligible. Detected particles on the filter are characterized by a poor density. More and bigger particles were detected in the filters when analysing seaweed compared to those found in Cyanara. EDX analysis of the filter deposits revealed the presence of mainly Na, Al, Si, Cl, Ca, S, P, Mg and K.

Also the recoveries for Sulphur and for the remaining halogens (Cl, F, Br and I) are not improved by adding kaolin, MgO, or Eschka mixture as additives and the tested alkaline solutions do not improve S, Cl, or Br recoveries. Neither does an aqueous solution containing 0.05 wt% NaOH and 0.05 v% H₂O₂. Only quantitative mean Iodine recoveries were obtained when using an aqueous

solution containing 1 wt% ascorbic acid as the receiving solution, although poor repeatability was achieved.

When analysing the tobacco sample, an aqueous solution containing 0.25 v% H₂O₂ enhanced the recovery of Chlorine and Sulphur, although the same trend was not observed when analysing the hemp sample, probably due to its lower Chlorine and Sulphur content.

The test series with combustion aids show that the recovery of Chlorine and Sulphur is not significant much better than without, but in some cases e.g. loos powder, samples with high content of ash combustion aids are grate help during the combustion.

Between the Chlorine determination with bomb digestion and water soluble method differences exist. The assumption that during the combustion, Chlorine and Sulphur is bound in the “ash” (solid combustion residues) based on the this test series is plausible. So the water soluble method is better samples with high ash and Chlorine content.

Also comments from other technical committees were studied and result in additional laboratory tests. The difference between solid biofuels and e.g. solid recovery fuels is to high to adapt existing method from other committee without tests.

All this results were included into the draft standard pr EN 15289 “Solid biofuels – Determination of total content of Sulphur and Chlorine”.

6 References

- [1] CEN TS 14775 “Solid biofuels – Determination of ash content”.
- [2] CEN TS 14582 “Characterization of waste – Halogen and Sulphur content – Oxygen combustion in closed systems and determination methods”
- [3] CEN TS 14774-3 “Solid biofuels – Determination of moisture content – Part 3 Moisture in general analyse sample”.
- [4] CEN TS 15289 “Solid biofuels – Determination of total content of Sulphur and Chlorine”.