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1 Measuring inorganics in biomass fast pyrolysis oils

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5 **Abstract**

6 Measurement of inorganics present in biomass fast pyrolysis liquids has been scarcely
7 investigated in the literature. In this work several analytical methods based on different
8 sample preparations were investigated and applied on a set of nine biomass fast pyrolysis
9 liquids covering a wide range of inorganics contents that have been measured using an ICP-
10 OES (Inductively Coupled Plasma-Optical Emission Spectrometer) analyser. Several
11 required mineralisation first steps were studied to completely dissolve the samples. Our
12 results show that the ISO 16967 method, initially developed for solid biomasses and adapted
13 here for bio-oils, was the most interesting one to quantify three major inorganics (i.e.
14 potassium, magnesium and sodium), measurement of calcium contents remaining a
15 challenge when applied to bio-oils while it provides good results for reference materials.

16 **Keywords**

17 Analysis, ICP, Inorganics, Pyrolysis, Bio-oil, Lignocellulosic biomass, Metals

18 **1. Introduction**

19 Transformation of lignocellulosic biomass (wood, forest residues, straw,...) through
20 thermo-chemical processes is currently one of the main promising pathways to
21 produce biofuels and chemical intermediates, in substitution to fossil fuels and
22 products. Fast pyrolysis is one of these thermochemical routes that enable biomass
23 direct liquefaction, breaking down the lignocellulosic matrix and converting the
24 heterogeneous solid into fast pyrolysis bio-oils (FPBO). These liquids are known to
25 be complex chemical mixtures composed of oxygen organics (*i.e.* sugar monomers
26 and oligomers, carboxylic acids, aldehydes, ketones, esters, alcohols and phenolics),
27 water and inorganics present in the forms of free ions or solid particles. Variety of
28 both fast pyrolysis processes and lignocellulosic biomass types contributes to the
29 large diversity of physical and chemical properties of the resulting bio-oils. Features
30 that are specific for each bio-oil should be taken into account to define which might
31 be the most relevant way of valorisation. Considering biomass fast pyrolysis liquids
32 as full or partial substitutes of fossil heavy fuels or natural gas in industrial boilers [1-
33 8] or as high-grade fuels for car engines after a suitable upgrading was one of the
34 main applications which attracted attention some decades ago. Many upgrading
35 approaches have been investigated, implying thermochemical treatments (*e.g.*
36 hydrocracking and hydrodeoxygenation), physicochemical treatments (*e.g.* ultrasonic
37 cavitation, plasma, electrochemical) or chemical and biological treatments (*e.g.*
38 esterification and transesterification). In their review, Hansel et al. [9] discussed the
39 key points of these upgrading strategies, concluding that electrochemical treatment,
40 based on the retention of hydrogen from bio-oil water content during deoxygenation,
41 could be a relevant alternative to thermo-chemical processes which are effective but

42 disadvantaged by their low process cost competitiveness due to high temperature and high
 43 pressure conditions.

44 More recently, other applications have also gained interest, especially those head towards
 45 valuable products coming from renewable resources, as enhanced by the present context of
 46 green chemistry. Bio-oils could be considered as sources of a large range of products such
 47 as hydrogen by steam reforming of bio-oils, biochemicals and commodities (olefins or BTX
 48 aromatics) achieved by a selective separation and/or after a hydrodeoxygenation step [10],
 49 binders for electrodes or asphalt production in relation to the high content of phenolics in bio-
 50 oils, functional carbonaceous materials or even plastics [11]. However bio-oils exhibit several
 51 undesirable features like a high acidity, a low thermal stability, a low heating value and a high
 52 viscosity that imply specific adaptations of current systems and/or additional prior upgrading
 53 steps. To go further, more fundamental and techno-economic studies are generally required
 54 to optimize separation and reaction pathways sections in order to respect fuels or products
 55 specifications and to rise from the early stages of technology development to commercial
 56 production scale with competitive costs when compared to current industrial processes
 57 especially for those based on transformation of fossil resources.

58 Fast pyrolysis of biomass is well known for more than 35 years but only recently reached
 59 industrial maturity, with a few industrial size plants. These pre-commercial and commercial
 60 size units for burner fuel application and for co-processing to refinery for advanced biofuels
 61 are currently located in North America and North Europe, with almost ten operational (or to
 62 be started soon) semi and fully commercial scale units (Table 1). Table 1 intends to gather
 63 the information recovered from publications, presentations, web-sites and press releases
 64 [12].

65 Table 1. Pre-commercial and commercial biomass fast pyrolysis units

Unit Location	Technology	In Operation since	Capacity			Fuel use
			Biomass (TPD)	Biomass (kt/y)	FPBO (kt/y)	

Fortum Joensuu Finland (1)		2014 Commercial	240		50	District urban heating from forest residue: needs of 10,000+ households.
Empyro/BTG_BTL (2) The Netherlands	VTT Fluid Bed	2015 Pre-commercial In production Namely capacity reached in 2017	120 (Wood residues)	35	24	12 years contract with Friesland-Campina (dairy producer) for FPBO co-combusted with natural gas for MP steam production and AKZO Nobel for sale of excess steam. The Empyro Plant became part of Twence on Jan ^{1st} , 2019 for FPBO commercial production and use.
BTG-BTL/TechnipFMC (2) Finland from wood sawdust	BTG Rotating Cone	April 2019 Commercial	4*120?			April 2, 2019 'In the Netherlands, Finland will invest EUR100 million for 4 scheduled facilities' that makes it possible to produce oil from various waste materials including wood waste with aEUR25 million investment for a 1 st facility.
BTG-BTL/TechnipFMC with Setra (wood industry) & oil company Preem (2), Sweden Bio-oil production scheduled to be started in 2021 from wood sawdust		October 2019 4th Commercial	120	35-40		Plan to build a production facility in Sweden to produce FPBO to be processed in refinery for advanced biofuels.
BTG-BTL & Goofuels, (3), The Netherlands Bio-oil for marine application from sawdust and roadside grass cuttings	BTG Rotating Cone	November 2019 Pilot plant			1	'Pilot refinery for converting pyrolysis oil into 100% sustainable marine biodiesel for ships, to demonstrate that continuous production is feasible'.
BTG Bioliquids: Green Fuel Nordic Oy (GFN) Lieksa, Finland (4,5,6)	BTG Rotating Cone	December 2020 Commercial	120		24	GFN is a Green Fuel Nordic subsidiary operating the plant in the Kevätmiemi industrial area in Lieksa.
BTG Bioliquids: Pyrocell Setra, Gävle, Sweden (4,5,6)	BTG Rotating Cone	Under construction, start-up in September 2021, Commercial	120 from sawdust	35-40	25	1 st announce in October 2019. Pyrocell is a Swedish J.V. between the wood industry Setra & Preem. Production unit built next to the Kastet sawmill of Setra in Gävle. FPBO to be co-processed in Preem refinery to produce advanced biofuels with 80-90% GHG reduction
RTP® (7,8) Renfrew Ontario-Canada	Ensyn CFB	2007 Pre-commercial	70		14	Memorial Hospital-New Hampshire (300,000 gal/y) since April 2014, Valley Regional Hospital Claremont (250,000 gal/y) since April 2015, Youngstown (Ohio) Thermal steam plant that powers district heating.
RTP® (7,8) Port Cartier, Quebec, Côte Nord, Ensyn, Arbec's sawmill and Groupe Rémabec	Ensyn - Envergent CFB	Completed 1 st Commercial Scale RTP®	200	65	46	FPBO for heating and for export to US: FPBO used for heating, and refinery Co-processing applications.
RTP® Aracruz Project (7,8) with Ensyn & Suzano from eucalyptus residues collocated to Suzano's 2.3 million t/yr pulp facility ;	Ensyn - Envergent CFB	Basic engineering completed Commercial			95 (22 million gal/y)	FPBO for heating and for export to US and refining application.
RTP® Viena Project, Georgia (7,8) with Ensyn, Renova & Roseburg Forest Products from mill residues, forest residues	Ensyn CFB	Project Commercial			86 (20 million gal/y)	FPBO to refineries for co-processing and/or heating & cooling clients.

(1) added to the existing fluidized bed boiler of the existing power Combined Heat and Power Plant

(2) <https://www.btg-btl.com/en>

(3) <http://www.biofuelsdigest.com/bdigest/2019/11/17/pyrolysis-party-and-whos-the-pilot-steering-the-ship-btg-and-goodfuels-to-invest-in-worlds-1st-marine-biofuel-refinery-based-on-pyrolysis-oil/>

(4) <https://www.btg-bioliquids.com/plants/>

(5) Virtual conference on "Co-Processing as route to deployment of advanced biofuels production" organised by the EU H2020 projects 4Refinery, Waste2Road, HyFlexFuel and the national Centre Bio4Fuels:

<https://www.etipbioenergy.eu/co-processing-as-route-to-deployment-of-advanced-biofuels-production-14-april-2021>

- (6) [BIOFIT Industry Forum on Bioenergy Retrofitting of Refineries, 17 June 2021: https://www.biofit-h2020.eu/news-and-events/biofit-industry-forum-on-bioenergy-retrofitting-of-refineries-17-june-2021/](https://www.biofit-h2020.eu/news-and-events/biofit-industry-forum-on-bioenergy-retrofitting-of-refineries-17-june-2021/)
- (7) Ensyn / Honeywell's Envergent RTP® Process
- (8) <http://www.ensyn.com/additional-expansion.htm>

66 Even if FPBO can be a first intermediate liquid to produce biofuels, their processing and
67 refining to drop-in biofuels is not yet fully demonstrated and remains at pilot scale level or at
68 an early pre-commercial step (refer to BTG Bioliquids: Pyrocell Setra, Gävle, Sweden in
69 Table 1 or to Equinor Kalundborg refinery test on the Distillate Hydrotreater) for
70 hydroprocessing. Regarding co-processing of FPBO, up to 5% by volume, a few trials have
71 been successfully performed on industrial Fluid Catalytic Cracking (FCC) units: Petrobras,
72 Equinor Monstad refinery, Ensyn-UOP, BTG, using an injection line of the FPBO. 5% to 10%
73 FPBO, co-processing has a very limited impact on the FCC product yields: gasoline
74 production yield does not significantly change, as well as coke formation, when dry gas, Light
75 Cycle Oil (LCO), the FCC atmospheric gasoil fraction, liquid FCC bottoms yields slightly
76 decreased. Oxygen from FPBO is converted to CO, CO₂ and water with a significant
77 production: 3 to 6% respectively with 5% and 10% FPBO co-processing. [13-16]. FCC co-
78 processing looks more mature than hydroprocessing.

79 Recently the International Maritime Organization(IMO) revealed its decarbonisation targets:
80 *'IMO has adopted mandatory measures to reduce emissions of greenhouse gases from*
81 *international shipping, under IMO's pollution prevention treaty (MARPOL) - the Energy*
82 *Efficiency Design Index (EEDI) mandatory for new ships, and the Ship Energy Efficiency*
83 *Management Plan (SEEMP)' [17]. 2023-2030 mid-term measures aim to reduce carbon*
84 *intensity (CI) of the fleet by 40% (30% reduction of the CI in 2025 and up to 50% for several*
85 *ships including container ships) while long term 2030-2050 program seeks to reduce CI by*
86 *70%, with at least 50% of total annual reduction of GHG by 2050 (requiring about 85% less*
87 *CO₂ emitted per ship).*

88 Today the main demonstrated application remains to replace fossil fuels in industrial size
89 boilers [5-8, 18]. Near future applications could also concern home size boilers and Internal
90 Combustion Engines such as adapted medium/low speed stationary diesel engines or
91 turbines for electricity and steam production [18].

92 Properties and behaviour of FPBO are completely different from mineral oils [19-21]. In order
93 to meet the national legislation requirements, to guarantee a suitable quality for FPBO used
94 in industrial size boilers in existing installations, to enable FPBO trading, as well as to make
95 possible the use of FPBO to produce green electricity by using stationary Internal
96 Combustion Engines or turbines, FPBO standardization is mandatory.

97 A first standard of FPBO, to be used in industrial boilers, was performed by the ASTM
98 International Committee D02 which established a method (ASTM D7544) defining two fuel oil
99 grades with two different solid and ash contents [22]. Since the legislation and emission limits
100 differ from Europe to North America, European standards were also needed. In 2013 CEN
101 received the mandate (M/525) from the European Commission to develop standards for
102 FPBO. A Working Group (WG41) was established under CEN/TC 19 (Gaseous and liquid
103 fuels, lubricants and related products of petroleum, synthetic and biological origin) in early
104 2014 to propose a standard for FPBO replacing light and heavy industrial boiler fuel oils, as
105 well as a Technical Specification (TS) for the quality for FPBO replacing fuel oils in stationary
106 ICE.

107 The deliverable from the WG 41 was the publication of the European Standard for FPBO use
108 in boilers with > 10 MW EN 16900 [23] with an Inter-Laboratory Study (ILS) launched end of
109 2015. The ILS gathered 17 laboratories (Europe and North America) and 8 FPBO samples
110 prepared from 9 representative FPBO produced from pilot plants and commercial units,
111 covering a very large range of properties and origins (Table 2). The results of the ILS were
112 incorporated in Annex C of the EN 16900 standard [23]. This ILS was the first of its kind
113 covering such a wide range of FPBO and such a number of analytical methods. The ILS
114 study revealed that some of the analytical methods derived from fossil fuels and used for
115 FPBO were not well adapted with a poor precision, especially for elementary analyses and
116 metals. Moreover only one of the 17 laboratories measured the metals contents (sodium,
117 potassium, calcium and magnesium). The WG 41 also issued a Technical Report for the
118 quality for FPBO replacing fuel oils in stationary ICE, because there were too few data from
119 public experimental works, a lack of feedback on usage from the manufacturers and a

120 significant lack of adapted analytical methods to propose a Technical Specification
 121 (document similar to a pre-standard for indication but without a standard status). Once again
 122 the measurement of metals was a main concern, as well as the maximum allowed level
 123 suitable to the existing adapted ICE technologies. Inorganics are well-known to be
 124 detrimental compounds responsible for several problems when using FPBO (fouling or
 125 corrosion in turbine systems, poisoning of reform catalysts, enhancement of coke formation
 126 during catalytic upgrading,...), giving importance to the accurate measurement of the
 127 inorganics contents in bio-oils.

128 Table 2. EN 16900 ILS FPBO typical range of physical and chemical properties

Property	Unit	Range
Density	kg/m ³	1185 - 1248
Viscosity at 40°C	mm ² /s	10.7 - 1172
Water	wt%	14 - 31
Solid	wt%	0.03 - 6.8
Flash Point	°C	<40 - 58
Pour Point	°C	(-39) - (-9)
Carbon content	wt%	38 - 46
Hydrogen content	wt%	7.5 - 8.0
Nitrogen content	wt%	0.1 - 0.8
Sulfur content	wt%	0.005 – 0.46
Sodium content	mg/kg	<2 - 5
Potassium content	mg/kg	<20 - 250
Calcium content	mg/kg	<20 - 450
Magnesium content	mg/kg	<10 - 70

129 A significant number of works has already been published on the behaviour of inorganics
 130 during fast pyrolysis of lignocellulosic biomass and how these inorganics are distributed in
 131 the bio-oils and their ashes. However there are still very scarce literature studies related to
 132 analytical measurements of inorganics in chemically complex fast pyrolysis liquids.

133 Inorganics are usually quantified by a two-steps approach implying a first mineralisation step
134 aimed to completely dissolve liquid or solid samples (*i.e.* bio-oils or their ashes), followed by
135 a measurement of the aqueous resulting solutions by ICP-OES (Inductively Coupled Plasma-
136 Optical Emission Spectrometer) technique. Mineralisation conditions are the main key
137 parameters of this analytical methodology, based on digestion of the sample using specific
138 acids: for instance literature works reported the use of nitric and/or hypochlorous acids [24,
139 25], mixtures of hydrofluoric and hypochlorous acids [26], hydrogen peroxide, nitric and
140 hypochlorous acids [27] or hydrogen peroxide and nitric acid [28]. Mineralisation conditions
141 deeply depended on the laboratories and needed to be uniformed. Some years ago, a
142 standard method ISO 16967 has been published for the determination of major elements (*i.e.*
143 aluminium, calcium, iron, magnesium, phosphorus, potassium, silicon, sodium and titanium)
144 in solid biofuels. As far as we know, this method has already been applied to biomass fast
145 pyrolysis ashes, but not to bio-oils themselves.

146 From a larger viewpoint, inorganics analysis has been a topical issue since a long time
147 considering other matrices like water [29], petroleum products [30] or even more recently
148 biodiesel and bioethanol [31]. As already mentioned, the approaches for organic matrices
149 use three types of protocols. The first one allows the direct introduction of the organic
150 substances (if those are liquid or soluble in a suitable solvent at room temperature) within the
151 plasma of an ICP-OES. The second one is based on the mineralization of the organics in
152 order to collect an aqueous fraction also analysed by ICP-OES. The last one is based on a
153 production of ashes from the material, that are also mineralized to be analysed by ICP-OES.
154 Anyhow, such feedback for the analysis of FPBO is not existing and various assays have
155 been done in the past without real success for the analysis of inorganic contaminants in
156 FPBO.

157 In this work several analytical methods based on different sample preparations were
158 investigated and applied on a set of ten biomass fast pyrolysis liquids to measure the
159 inorganics contents using an ICP-OES analyser. Results will be compared in this

160 experimental study to define the most relevant analytical approach to determine the major
161 inorganics present in bio-oils.

162 2. Material and methods

163 2.1. Samples

164 Nine samples produced from three different fast pyrolysis processes as well as from different
165 types of lignocellulosic biomasses, were investigated in this study (Table 3). Sample A was
166 produced from a Circulating Fluidised Bed fast pyrolysis demonstration plant of a hardwood
167 feedstock. Samples B, C, D and E resulted from fast pyrolysis (feedstock origins are
168 unknown). Samples F and G were produced from fast pyrolysis of wood and grass feedstock
169 respectively. Samples H and I were obtained after solids removal by filtration of samples F
170 and G respectively.

171 Table 3. Physical and chemical properties of the investigated bio-oils (results expressed on
172 a wet basis)

Property	Unit	Samples								
		A	B	C	D	E	F	G	H	I
Density at 15°C	g/cm ³	1.2361	1.2352	1.2300	1.2068	1.2073	1.1978	1.1895	1.1949	1.1976
Conradson carbon content	wt%	24.6	22.5	21.2	17.5	18.5	18.5	21.8	17.6	21.7
Carbon content	wt%	46.6	40.5	40.7	35.2	35.3	43.3	42.1	43.6	40.3
Hydrogen content	wt%	7.14	7.55	7.72	7.97	7.98	7.60	7.83	7.72	7.77
Oxygen content	wt%	45.06	51.36	51.34	55.61	55.80	47.96	48.33	48.06	49.79
Nitrogen content	wt%	0.277	0.1085	0.1315	0.183	0.1865	0.123	1.109	0.125	1.140

173 2.2. Chemicals

174 Aqueous multi-elemental standards were obtained from a stock solution (Spex Multiprep,
175 Stanmore, UK). All the aqueous solutions were prepared using ultrapure water (>18.2MΩ)
176 produced from a Millipore IQ 7003 water-purification system (Millipore, Molsheim, France).

177 Nitric acid (HNO₃, Suprapur) and methanol (MeOH, Normapur) used for the organic dilution
178 and calibration of the instrument were purchased from VWR Chemicals (Fontenay sous Bois,

179 France). hydrofluoric acid acid (HF, Suprapur) and hydrogen peroxide (H₂O₂, Suprapur) were
180 obtained from Merck (Darmstadt, Germany).

181 Reference materials (bush branches and leaves, NCS DC 73349 and wood fuels NJV945)
182 were purchased from LGC (Molsheim, France) and Analytical Standard (Molnlycke,
183 Sweeden) respectively.

184 2.3. *Sample preparation*

185 The following protocols of sample preparation were performed prior to ICP-OES analyses.

186 **ISO 16967 Method.** The protocol was adapted from the standard method ISO 16967 ‘Solid
187 biofuels - Determination of major elements - Al, Ca, Fe, Mg, P, K, Si, Na and Ti’ originally
188 dedicated to the analysis of solid biomass samples. In our work the solid biofuels were
189 replaced by bio-oils and the determination of aluminium, calcium, iron, magnesium,
190 phosphorus, potassium, silicon and sodium contents was obtained after a digestion of the
191 samples using hydrogen peroxide, nitric acid and hydrofluoric acid reactants under pressure
192 and temperature in a closed vessel. Based on a two-stages protocol occuring at 190°C and
193 150°C, this method used an oxidative acid mixtures combined to hydrofluoric acid. Such
194 mixture has the ability to digest most of the major and minor contaminants of a bioproduct.
195 The excess of hydrofluoric acid was neutralised and the remaining solution was analysed
196 using ICP-OES (Appendix 1). Data obtained with reference or ‘spiked’ materials are
197 available in Appendix 2.

198 **Protocol based on the method developed by Wondimu et al.** Based on a method
199 described by Wondimu et al [32], a protocol designed in this work as ‘Wondimu protocol’ was
200 performed to mineralize 0,1 g of a bio-oil prior to the analysis by ICP-OES of the resulting
201 aqueous solution. This sample preparation involved the use of a hydrogen peroxide and nitric
202 acid mixture (10 mL) as well as a microwave Teflon bomb operating at 800 W under a
203 temperature gradient (maximum at 230°C). This mixture of acid was also oxidative and very
204 attractive to digest carbonaceous material, but the absence of hydrofluoric acid would

205 hamper the digestion of some refractory oxides present in the material. Temperatures up to
206 230°C were applied, involving several different temperature ramps and residence times as
207 described in Appendix 1.

208 **Protocol by methanol dilution.** This third approach used in this work was based on a
209 method proposed by WG41 for the analysis of pyrolysis oils. It consisted of diluting a bio-oil
210 before filtration with a paper filter to eliminate undissolved materials and of a direct
211 introduction into the ICP-OES device. The protocol was modified from method EN 16476
212 where the sample is dissolved in kerosene and the viscosity change was corrected by the
213 use of an internal standardization. Since FPBO are not soluble in hydrocarbons, kerosene
214 was replaced by methanol and the 2 times dilution was also adapted and reduced to 20
215 times dilution in the solvent to minimize the viscosity difference that would not be corrected
216 by the use of the internal standard.

217 **Protocols for ashes production and their mineralisation.** Ashes were first produced by
218 calcination of a bio-oil (sample A) using a Carbolite furnace and a Eurothem control system.
219 For each experiment, 3 g of bio-oil were placed in a platinum crucible heated from room
220 temperature to 775°C with a heat temperature program adapted to prevent any foam
221 phenomenon. Once the final temperature was reached, the furnace temperature was
222 maintained at 775°C during 3 hours before cooling. Based on reproducibility implying 21
223 calcinations, the ashes content of sample A was determined to be 0.26 %wt \pm 0.01 %wt (on
224 wet basis). In order to supply enough matter for ICP and WXRf analyses (*i.e.* 0,3 g), 40
225 calcination experiments were performed on sample A. In a second time, a mineralisation step
226 was carried out on ashes (0.1 g) prior to ICP-OES analysis: 0.1 g of ashes were introduced
227 in a microwave bomb Teflon operating at 800 W under a temperature gradient up to 180°C in
228 presence of 8 mL of nitric acid. Then 2 mL of hydrofluoric acid were added in the bomb and
229 the mixture was heated at 220°C during 15 min at 800 W. The resulting solution was
230 submitted to an evaporation step to remove hydrofluoric acid ; 1 mL of nitric acid and some
231 water (q.s. 25 mL) were finally added.

232 **2.4. Apparatus and analytical conditions**

233 The ICP-OES instrument was a Spectro Arcos device equipped with different nebulizers
234 depending on the type of solution to be analysed. For conventional nitric acid solution, the
235 instrument was equipped with a modified Lichte nebulizer mounted on a cyclonic chamber
236 and the plasma was monitored under aqueous conditions (refer to Table 4). For solution still
237 containing hydrofluoric acid, the instrument was equipped with a Burgener Miramist nebulizer
238 and the nebulization chamber was a cyclonic chamber made of Teflon, but the aqueous
239 conditions of the plasma were kept constant. For organic solutions, the ICP Arcos was
240 equipped with a cooled (-10°C) cyclonic chamber and a Burgener T2002 nebulizer. The ICP-
241 OES was tuned in order to sustain organic introduction (refer to Table 4). The calibration
242 curves mostly covered 0 to 100 mg/L with 11 standards, including 5 standards between 0 to
243 1 mg/L.

244 **Table 4. Plasma and nebulization conditions for the ICP-OES analysis**

Parameter	Unit	Conditions for analysis of aqueous samples	Conditions for analysis of organic samples
Plasma power	W	1350	1650
Carrier gas flow	L/min	0.95	0.60
Auxiliary gas flow rate	L/min	0.80	2.00
Plasma gas flow	L/min	12	16
Pump speed	rpm	30	15
Rinse time with samples	s	300	200
Injector diameter	mm	1.8 (2.5 for hydrofluoric acid analysis)	1.2

245 The WDXRF device used for the semi-quantitative determination of the composition of the
246 ashes (~70 elements determined) was a Thermo Perform'X apparatus (4,2 kW) using
247 Uniquant 5.0 incorporated to OXAS V2 Software. The broad spectrum was acquired by a
248 peak-hopping procedure proposed by the instrument and the intensity for each line was
249 compared to sensitivity coefficient already integrated in the Uniquant Software.

250 **3. Results and discussion**

251 **3.1. Inorganics measurement by mineralisation and ICP-OES analyses**

252 Major inorganics contents in a FPBO (sample A) were measured using several protocols, all
253 based on a mineralisation first step and a ICP-OES analysis second step. On one hand,
254 measurements were performed on the bio-oil using the ISO 16967 method or Wondimu
255 protocol, while, on the other hand, measurements were carried on the ashes resulting for
256 calcination of sample A. For all type of measurements, the analysis was duplicated to verify
257 the repeatability of the procedure. Ashes were also directly analysed by a semi-quantitative
258 WXRf method to compare data with the one got by mineralisation and ICP-OES analysis.

259 Inorganics contents measured using the method ISO 16967 or Wondimu protocol directly
260 applied on the bio-oil are reported in Table 5. When both results issuing from the duplicate
261 analysis were within the 10% difference, only one result was reported. If this difference was
262 higher than 10%, both results are reported. Furthermore contents of inorganics in bio-oil
263 were calculated taking into account the ashes content of sample A (*i.e.* 0,26 %wt) and the
264 contents measured directly on the ashes; these calculated contents are also presented in
265 Table 5. According to these data, iron was the most abundant inorganic element quantified in
266 the bio-oil A. Its unexpected high level (952 mg/kg determined by the method ISO 16967) in
267 comparison with literature data [5] indicates that the bio-oil may have been probably
268 contaminated with iron oxide under inappropriate storage conditions [33]. Other major
269 elements in this sample were potassium, phosphorus and calcium with contents ranging from
270 100 to 200 mg/kg. Mainly concentrated in ashes, silicon certainly came from sand particles
271 used in the fluidised bed reactor for wood fast pyrolysis [4]. In addition, lower contents of
272 aluminium, sodium, magnesium and platinum, each inferior to 20 mg/kg, were measured
273 from the bio-oil.

274 As regards the comparison of the analytical methods used in this work, results about iron and
275 potassium contents are in good agreement, whether they were obtained by using the ISO
276 16967 method or Wondimu protocol. These elements were mainly concentrated in ashes
277 whose analyses by ICP-OES and WRXF were both consistent. Concerning silicon, the
278 content measured by applying the Wondimu protocol on bio-oil is much inferior to the one

279 determined using the ISO 16967 method or the ones calculated from ICP or WRFX analyses
280 of ashes. This underestimation of Wondimu protocol is explained by the fact that the nitric
281 acid and hydrogen peroxide mixture used was not suitable to get a good solubilisation of
282 silica during the mineralisation step, on the contrary to the method ISO 16967 which required
283 the use of hydrofluoric acid.

284 Table 5 shows that quantifications of calcium, phosphorus and sulphur in the investigated
285 FPBO (sample A) using different approaches were not successful. This is an unexpected
286 result for calcium and phosphorus as their quantification was not an issue when using
287 reference materials like bush and branches or wood fuel material (refer to Appendix 2).

288 This reveals that the difference is probably not due to loss of phosphorous by volatility or loss
289 of calcium by incomplete dissolution, as these elements were validated with reference
290 materials. For phosphorous, the value around 130 mg/kg is consistent for both ISO 16967
291 and Wondimu protocols performed directly on the bio-oil. Nevertheless the two values
292 obtained with the ISO 16967 protocol reveal that phosphorous might be associated to
293 sludges that are not homogeneous in the sample. One of the limitation of the digestion by
294 micro-wave in closed vessel is the limited mass of sample (100 mg) that is used in the
295 experiment. Perfect homogeneity with such low mass of sample is difficult to reach and this
296 is why two replicates are systematically carried out in order to reveal such heterogeneity.
297 However phosphorus contents measured on the ashes by ICP and WRXF were both in a
298 good agreement and were clearly lower than the ones resulting from the direct analysis of
299 the bio-oil, which tends to confirm the assumption of loss of phosphorus during calcination
300 experiments to produce the ashes. Analyses of ashes showed that phosphorus was probably
301 not initially present as phosphates in bio-oils and that phosphorus may be more likely
302 integrated as a part of organic molecules, maybe as particles forms, being consistent with
303 the fact that phosphorus could be largely retained in (lignin-rich) char after fast pyrolysis [34].
304 The case of calcium is a little bit more difficult to cope with. Values are varying widely
305 between 59 to 238 mg/kg in the investigated FPBO (sample A) using several analytical

306 procedures. Once again, the ISO 16967 protocol was validated for calcium using the
 307 reference materials (refer to Appendix 2). It is interesting to see that the two values
 308 measured on ashes materials are consistent and that, in the case of protocols using a small
 309 mass of sample (ISO 16967 and Wondimu protocols), the results reveal potential
 310 heterogeneity with significantly different values coming from replicates. However mean
 311 contents for both protocols (147 mg/kg for ISO 16967 and 166 mg/kg for Wondimu) even if a
 312 little bit higher, are consistent with the mean value obtained with ashes.

313 Like phosphorus, sulphur is known to be difficult to be analysed by ICP technique following a
 314 mineralisation step in the case of fossil fuels. Sulphur was quantified at 117 mg/kg in the bio-
 315 oil with the Wondimu protocol while its content was much more lower in the ashes (35-46
 316 mg/kg). This element might have been lost during calcination experiments carried out at
 317 775°C to produce ashes from the bio-oil whereas losses might have been less important or
 318 not possible when closed system are used. This is the case of the micro-wave digestion in
 319 closed vessel at moderate temperatures such as the ones employed during the method ISO
 320 16967 and Wondimu protocol.

321 According to results obtained with the method ISO 16967, other elements (*i.e.* aluminium,
 322 sodium, magnesium and platinum) were also quantified in the sample A with contents inferior
 323 to 25 mg/kg. Except for aluminium whose quantification by Wondimu protocol suffered from a
 324 lack of repeatability, overall data coming from the analysis of the bio-oil or the ashes were
 325 globally consistent, being within the same order of magnitude. Nevertheless one should keep
 326 in mind that sodium quantification is usually a challenging task, due to frequent
 327 contamination from the glassware used for sample preparation prior to analysis [33].

328 Table 5. Contents of major inorganics in a bio-oil (sample A) determined according several
 329 analytical methods (mean values are reported except for significantly different results)

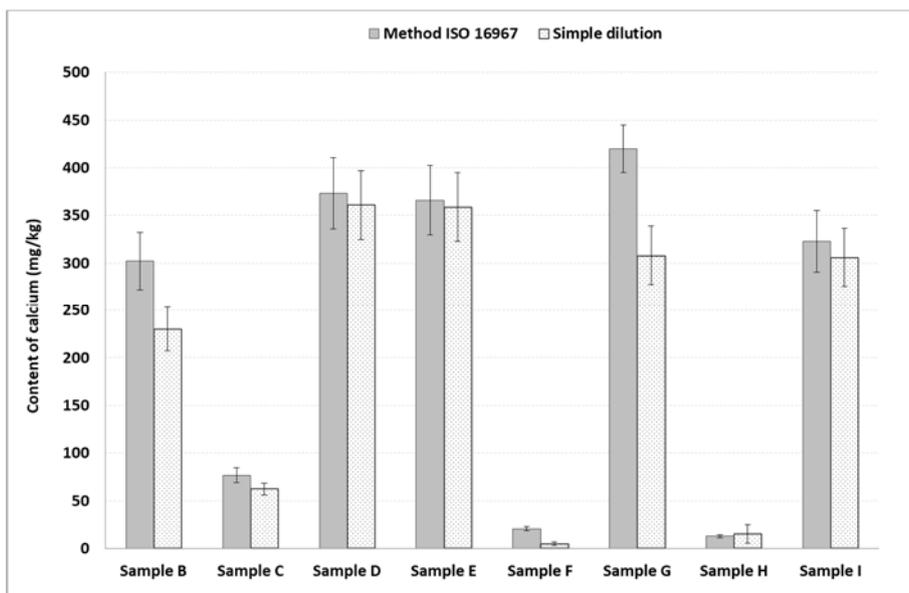
Element	Contents measured from the bio-oil analysis [mg/kg]		Contents calculated from the ashes analysis [mg/kg]	
	ISO 16967 protocol	Wondimu protocol	ICP-OES	WXRF

Fe	952.0 ± 95.2	812.0 ± 81.2	734.0	682.0
Si	271.0 ± 27.1	45.3 ± 4.5	292.0	291.0
K	159.0 ± 15.9	176.0 ± 17.6	136.0	134.0
Ca	59.0 ; 235.0	238.0 ; 94.3	97.3	109.0
P	10.3 ; 132.2	160.0 ± 16.0	2.9 ; 2.3	5.0
S	not measured	117.0 ± 11.7	46.3 ; 40.2	35.0
Al	22.3 ; 19.8	37.6 ; 78.6	15.2	12.0
Na	13.5 ; 17.6	13.8 ± 1.4	10.2	7.0
Mg	16.0 ± 0.2	<25.0	14.0	12.0
Pt	not measured	<12.5	1.6	15.0

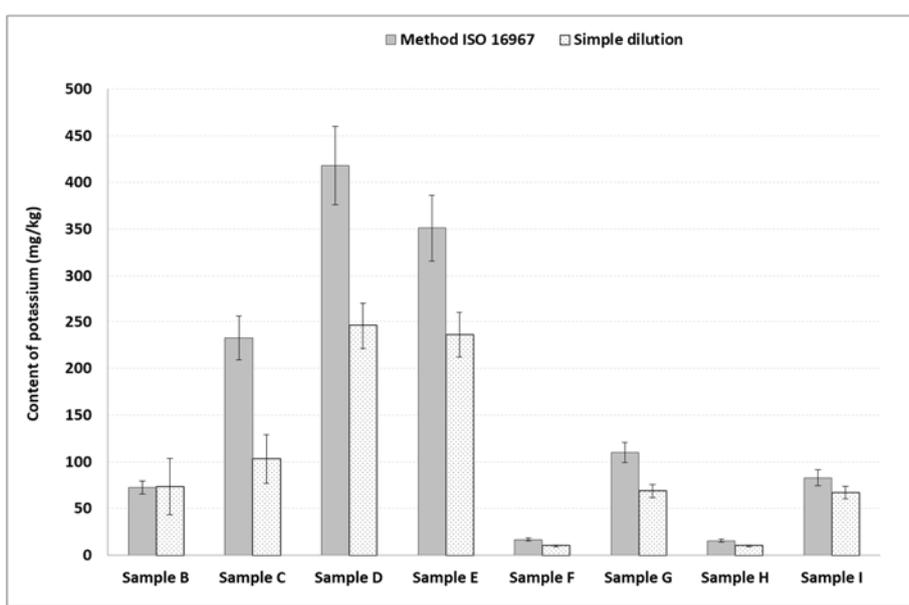
330 **3.2. Comparison of method ISO 16967 and method by simple dilution and ICP-OES**
331 **analysis**

332 In the previous part, the ISO 16967 method proved to be relevant for measuring major
333 inorganics contents in a FPBO. This method was then applied to the analysis of eight other
334 bio-oils coming from different fast pyrolysis conditions and different lignocellulosic biomasses
335 (samples B to I). On the same time, these bio-oils were also analysed by ICP-OES after
336 being simply diluted by 20 times in methanol and filtrated ; as yet explained, this approach
337 had been proposed during a previous inter-laboratory study organised by the working group
338 WG41 from CEN/TC 19 committee.

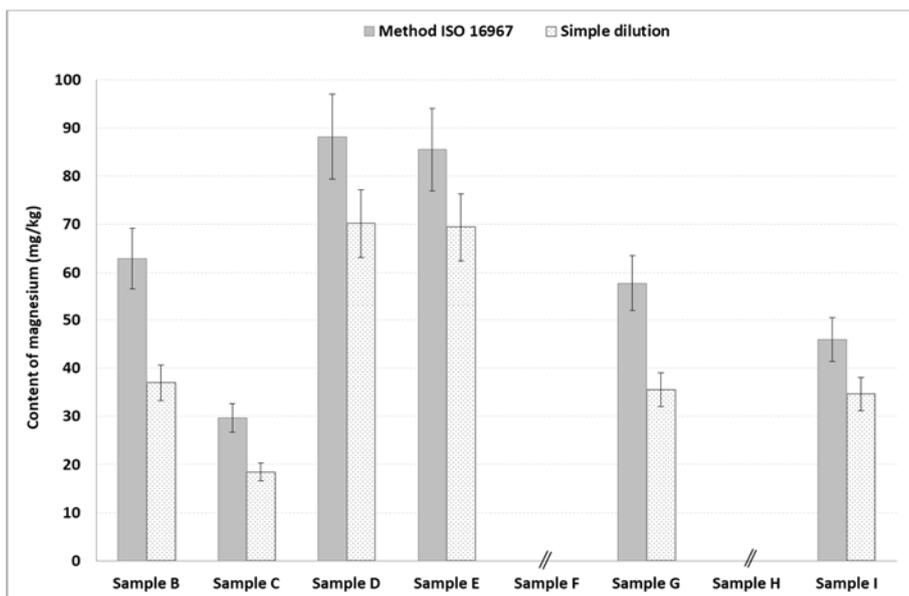
339 Reported in Figures 1 to 4, contents of the four main alkali inorganics (*i.e.* potassium,
340 calcium, magnesium, sodium) of samples B to I varied over a large range of values,
341 depending on the element and on the bio-oil. Contents measured using the method ISO
342 16967 were systematically significantly higher than the ones obtained by methanol dilution
343 and ICP-OES analysis, except for a few cases (*i.e.* potassium for samples B and D, calcium
344 for samples D, F and G, sodium for sample F). The drawback of analytical method based on
345 simple dilution is that it tends to under-estimate alkali contents and, because of a partial
346 solubilisation of the oil in methanol during sample preparation, it does not allow to take into
347 consideration inorganics that were not methanol-soluble and that were retained during
348 filtration priori to injection in the ICP-OES analyser. Such results are consistent with previous
349 VTT recommendations [12].



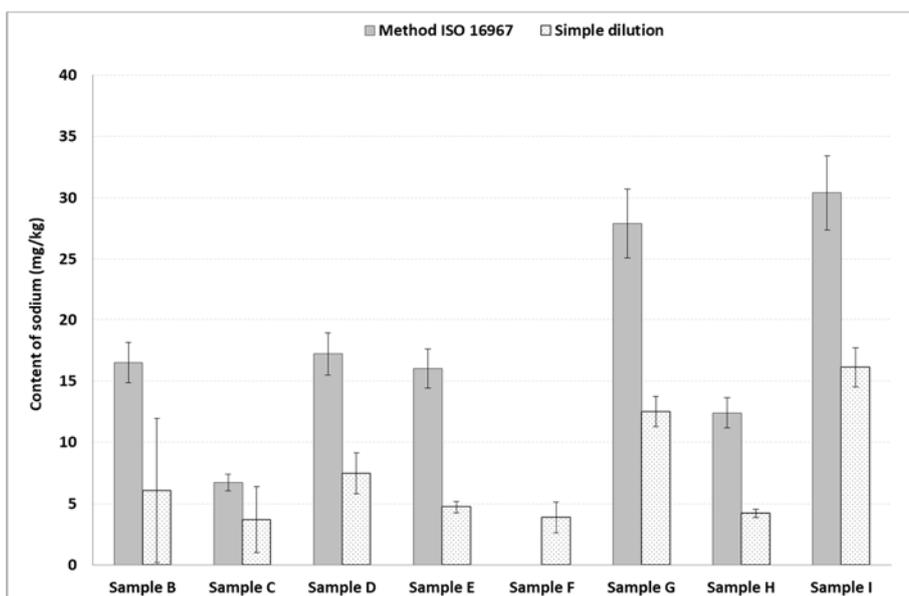
350 **Figure 1.** Contents of calcium in bio-oils (samples B to I) measured by the method ISO
 351 16967 (grey bars) and by the method based on simple dilution of the samples prior to ICP-
 352 OES analysis (dotted bars).



353 **Figure 2.** Contents of potassium in bio-oils (samples B to I) measured by the method ISO
 354 16967 (grey bars) and by the method based on simple dilution of the samples prior to ICP-
 355 OES analysis (dotted bars).



356 **Figure 3.** Contents of magnesium in bio-oils (samples B, C, D, E, G and I) measured by the
 357 method ISO 16967 (grey bars) and by the method based on simple dilution of the samples
 358 prior to ICP-OES analysis (dotted bars).



359 **Figure 4.** Contents of sodium in bio-oils (samples B to I) measured by the method ISO
 360 16967 (grey bars) and by the method based on simple dilution of the samples prior to ICP-
 361 OES analysis (dotted bars).

362 **4. Conclusion**

363 Dealing with inorganics is one of the key issue for the industrial valorisation of biomass fast
364 pyrolysis oils (FPBO) as substitutes of petroleum products in the fields of energy or chemical
365 products. However characterization of inorganics in such liquids has been very scarcely
366 reported in literature and no analytical method has been yet universally adopted to measure
367 their contents. Experimental conditions are varying very largely depending on each
368 laboratory practices, without any real consensus on the subject from the scientific
369 community. This study was dedicated to the measurement of inorganics in bio-oils and their
370 ashes. Several methods were investigated, showing that the ISO 16967 method, initially
371 developed for solid biomasses, and adapted for bioliquids, was the most interesting one to
372 quantify three major inorganics (*i.e.* potassium, magnesium and sodium) in FPBO,
373 measurement of calcium contents remaining a challenge when applied to bio-oils while it
374 provides good results for reference materials.. Further work is now required implying for
375 instance round robins based on this method to assess this analytical approach at a larger
376 scale of samples, before it could be introduced as a standard analytical method.

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383

384 **6. References**

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