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Bio-oil Inorganic Analysis: A Minireview of Current Trends, Challenges, and Future Perspectives

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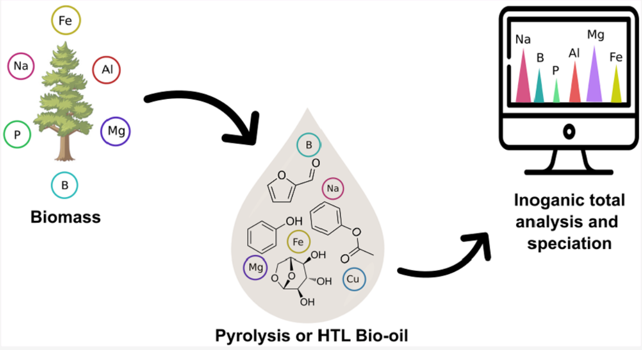
ABSTRACT: The analysis of the inorganic content of bio-oils has not been widely reported in the literature. In this work, the analytical methods employed for the quantification and speciation of inorganic species in bio-oils are summarized. Total inorganic analysis of bio-oils is commonly performed using inductively coupled plasma optical emission spectrometry and inductively coupled plasma mass spectrometry techniques; however, other quantitation techniques are compiled and discussed in this review. Additionally, the few studies that have recently been reported on the inorganic speciation of bio-oils by supercritical fluid chromatography−inductively coupled plasma mass spectrometry, gel permeation chromatography−inductively coupled plasma high-resolution mass spectrometry, and electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry are also addressed. Cumulatively, the reports suggest that the lack of standard analytical methods in the total inorganic analysis of bio-oils is a major contributor to inaccurate results. Thus, future research with analytical methodologies already applied in crude oils should be adapted to account for the unique bio-oil(s) matrix. Such a strategy offers a path toward more accurate inorganic speciation/quantitation of inorganics in bio-oils, which might be the key to the understanding of production problems, storage stability, and upgrading processes commonly encountered with such samples.



1. INTRODUCTION

One of the biggest challenges in the energy industry is the transition from fossil-based fuels to those derived from biomass (biofuel). Biofuels represent a renewable energy alternative with a lower environmental impact. Therefore, the European Commission recently proposed changes to the legislation Renewable Energy Directive for 2021−2030 (RED II), which had stipulated that at least 14% of transport fuel in Europe must be biofuel.[1] The revised proposal raises the ambition of this target to a 13% reduction in greenhouse gas (GHG) intensity for transport for 2030 compared to 1990 levels, which implies consumption of biofuels of higher than 14%.[2] Unlike fossil fuels, which are derived from the extraction and processing of crude oil, biofuels can be obtained through chemical, biochemical, and thermochemical processing of various sources of biomass feedstocks.[3−6] The properties of biofuels can be as complex as those of crude oil. Therefore, there is a need for the development of new standardized analytical methods for quality assurance of biofuels concurrent with the industrial energy transition. Among the properties of interest, inorganic content in bio-oils plays an important role in the yield, composition, stability, and performance.[7,8]

Although bio-oil is primarily composed of organic compounds, the presence of trace metals and heteroatomic compounds can accelerate the aging processes and even poison the catalysts used in upgrading processes, like hydrodeoxygenation (HDO).[9,10] Therefore, it is crucial to develop standard analytical methods with good precision and accuracy for the quantification and speciation of metals and metalloids in bio-oils to ensure their quality before subsequent upgrading processes. While standard methods of total inorganic analysis have been established for crude oil and its fractions over many years,[11] there are currently no standardized methods for bio-oil matrices. Moreover, the number of reported bio-oil inorganic analyses is significantly lower than that for biodiesel and its feedstocks (vegetable oils, animal fat, and used cooking oil).[12] The most common method of total inorganic analysis involves mineralization of the sample in a strong acidic mixture using a microwave,

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followed by quantification using inductively coupled plasma optical emission spectrometry (ICP−OES). Notably, the most common trends found in the literature focus on the distribution of metals in the pyrolysis products from phytoremediation waste[13,14] and in the hydrothermal liquefaction (HTL) products from sewage sludge.[15] The study of inorganic content in bio-oils started before 2010, but it gained importance after 2015. This increase was likely linked to industrial growth, especially with the setup of commercial biomass pyrolysis units around the globe.[16] This trend is depicted in Figure 1.

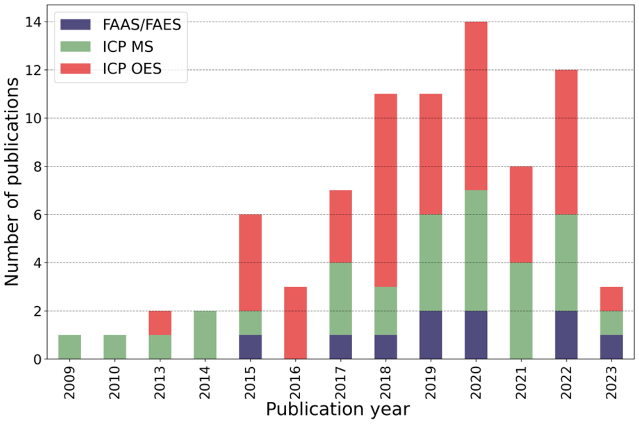


Figure 1. Publication record count given on the Scopus citation database with the keywords: bio-oils, biocrude, metal determination, inorganic analysis, inorganic speciation, trace metal, inorganic determination, flame atomic absorption spectrometry, flame atomic emission spectrometry, inductively coupled plasma−optical emission spectrometry, and inductively coupled plasma−mass spectrometry.

The aim of this work is to critically review the current advances and challenges in the inorganic analysis of bio-oils. It is presented as an exhaustive compilation of analytical techniques reported for total inorganic analysis of bio-oil, including examples of commonly used ICP−OES. Furthermore, the bio-oil inorganic speciation examples reported thus far are discussed, describing the advantages of the development of these analytical methods and the promising outlooks that complementary mass spectrometry techniques can offer to this challenge.

2. BIOFUEL TYPES AND GLOBAL PRODUCTION

Biofuels can be obtained from different biomass feedstocks through various processes, such as fermentation, transesterification, HDO, pyrolysis, and HTL. These processes yield different types of biofuels, such as bioethanol, biodiesel, and bio-oils, which are classified in different ways worldwide. However, this review will adopt the terminology of the European Commission for consistency (see Figure 2). The European Commission defines biofuels as follows: First-generation biofuels are derived from edible biomass feedstocks, which encompass sugar and starch crops, such as sugar cane, corn, wheat, and vegetable oils, like soybean, palm, and sunflower.[17] On the other hand, the advanced biofuels, known as second- and third-generation biofuels, are derived from non-edible biomass feedstocks. Second-generation biofuels utilize lignocellulosic materials, including agricultural and forestry residues, and municipal solid waste.[17] Meanwhile, third-generation biofuels use microalgae as feedstock.[17] Biofuels generated from used cooking oil and animal fat waste are not considered in the aforementioned classifications and are, hence, referred to as "other biofuels".[1,18]

However, in the United States, the Revised Renewable Fuel Standard (RFS2) bifurcates biofuels into two categories: conventional biofuels (corn starch) and advanced biofuels (lignocellulosic materials, animal and food waste, and sugar and starch crops other than corn).[19] Furthermore, Haldor Topsøe, a Danish enterprise, has its own classification. It categorizes virgin oils as first-generation biofuels, waste oils and fats as second-generation biofuels, and solid waste biomass, such as forestry

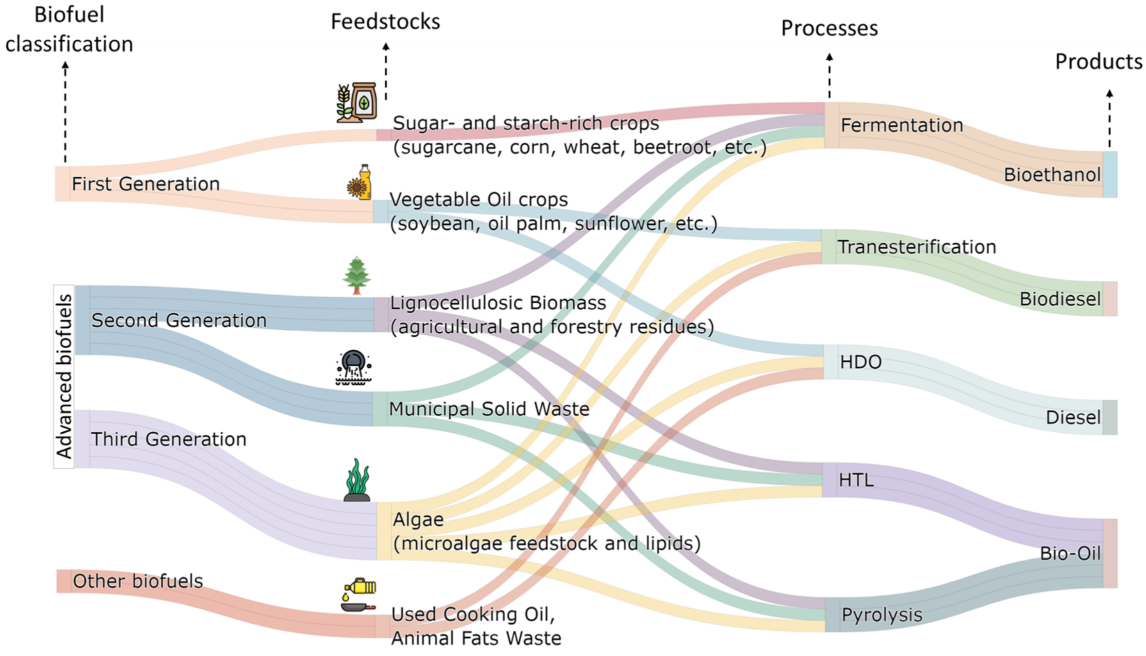


Figure 2. General scheme of the different sorts of liquid biofuels according to the European Commission.[1,17,18]

residue, sewage sludge, plastic waste, and end-of-life tires, as well as non-edible crops, like carinata, castor, pongamia, and microalgae, as third-generation biofuels.[20] Although first-generation biofuels have been extensively studied and developed as a significant energy source, the use of edible biomass as feedstock raises ethical concerns.[21] Therefore, the second and third generations of biofuels are increasingly viewed as a more feasible alternative to meet the growing demand for the energy transition.

The three main liquid biofuels are bioethanol, biodiesel, and bio-oils. Current global biofuel production is approximately 2 million barrels per day (BPD),[22] with the following breakdown: 65.7% ethanol, 27.8% fatty acid methyl esters (FAMEs)/biodiesel, and 6.5% renewable diesel/hydrotreated vegetable oil (HVO).[23] These biofuels can be derived from various feedstocks and belong to multiple generations (Figure 2). Bioethanol is typically made from crops but can also come from lignocellulosic biomass and microalgae.[21,24] Biodiesel is a mixture of FAMEs derived from triglycerides, while renewable diesel is a deoxygenated version of biodiesel.[25] Both are produced from edible and non-edible feedstocks, such as vegetable oils, used cooking oil, animal fats, and algal lipids.[26−28] The concentration of alkali and alkaline earth metals (AAMEs, e.g., Na, K, Mg, and Ca) and other inorganic species in bioethanol and biodiesel primarily depends upon the type of biomass used, the production process, and storage conditions. Accurately measuring these concentrations is crucial, given their potential influence on engine performance and environmental impact. For instance, Brazil's National Agency of Petroleum, Natural Gas and Biofuels (ANP) sets maximum concentrations for AAMEs, sulfur (50 ppm), and phosphorus (10 ppm) in biodiesel.[29] Similarly, ASTM International and the European Committee for Standardization (CEN) prescribe allowable limits for trace elements in ethanol and diesel.[30−32] Bioethanol and biodiesel of first generation benefit from validated analytical methods for inorganic content determination, with applicable standards from organizations, like the International Organization for Standardization (ISO), CEN, and ASTM International.[33−41] The efficacy and drawbacks of several analytical techniques for the inorganic analysis of these biofuels have been extensively researched and discussed elsewhere.[42] However, this minireview does not aim to explore these developments. Instead, it will primarily focus on studies pertaining to bio-oils.

3. FOCUS ON BIO-OILS

Bio-oils are a type of liquid biofuel derived from the thermal decomposition of lignocellulosic biomass, organic waste, or algae (see Figure 2). The main advantage of bio-oils is their derivation from non-edible biomass, rendering them distinct from first-generation biofuels.[43−46] The two main processes used to produce bio-oils are pyrolysis and HTL. Pyrolysis can be divided into several types, including slow, fast, catalytic, and hydropyrolysis. In fast pyrolysis, dry biomass is exposed to high temperatures in an oxygen-free atmosphere for a short time, resulting in the formation of liquid bio-oil, biochar, and non-condensable gases.[47] In HTL, biomass is exposed to a high pressure and temperature with a solvent for several minutes (10−60 min), producing bio-oil, biochar, syngas, and water-soluble compounds.[43,46] Bio-oils are characterized by a complex organic matrix, which can vary based on the type of biomass from which they are produced. When derived from lignocellulosic feedstock, bio-oils are composed of several organic families, including acids, alcohols, aldehydes, ketones, phenols, sugars, and oligomers from the fragmentation of lignin, cellulose, and hemicellulose, with a relatively high oxygen content. This makes them significantly different from bioethanol and biodiesel.[45] In contrast to crude oil, the aging tendency of bio-oils is notable, owing to the polymerization of reactive oxygen-containing compounds, which results in increased viscosity and water content.[48] Furthermore, the high oxygen content in bio-oils reduces their heating value. Therefore, catalytic processes, such as HDO, have been employed to obtain upgraded biofuels and reduce the oxygen content.[49] Given the rich diversity of organic compounds in bio-oils and the aforementioned issues, various analytical speciation methods have been reported to date, including gas chromatography (GC),[50] comprehensive two-dimensional gas chromatography (GC × GC),[51] flash chromatography,[52] high-performance liquid chromatography (HPLC),[53,54] gel permeation chromatography (GPC),[55] and detection systems, such as ultraviolet−visible (UV−vis),[54] refractive index detector (RID),[53] Fourier transform infrared spectroscopy (FTIR),[56] nuclear magnetic resonance (NMR),[52,56] mass spectrometry (MS) system,[51] and high-resolution mass spectrometry (HRMS).[52,57−60]

The metal and metalloid contents of bio-oils originate from the macro- and micronutrients present in the biomass.[61,62] Nevertheless, there is a discrepancy in the literature regarding the influence of metals on bio-oil production. Some studies suggest that metals from phytoremediation act as catalysts, thereby increasing the yield of bio-oil during pyrolysis. Moreover, at specific temperature conditions, most metals remain in the biochar.[13] Conversely, other researchers argue that the presence of metals in biomass, such as AAMEs, catalyzes the degradation of lignocellulosic materials to low-molecular-weight molecules rather than oligomer products with a higher energy value.[63] Experimental support for this was observed in the results of Patwardhan et al.[7] using pyrolysis products of cellulose impregnated with AAMEs (Na, K, Mg, and Ca) as well as in the results of Cen et al.[63] with the leaching of AAMEs from Moso bamboo biomass prior to pyrolysis. In addition, Facas et al. in a theoretical approach observed the activation of cellulose chains for thermal decomposition in the presence of Ca^{2+} ions using the density functional theory (DFT).[64] A comprehensive summary of the effect of metals on pyrolysis bio-oils has been provided by Giudicianni et al.[65]

During pyrolysis or HTL processes, inorganic nutrients in biomass are distributed among the various products. It is well-established that the majority of inorganic content is retained in biochar, while only a small fraction passes into bio-oils and non-condensed gases.[13] Leijenhorst et al.[76] found that the transfer percentage of inorganic nutrients from biomass to bio-oil is related to the initial concentration of metals, with Ca and Mg transfer percentages around 5% and sulfur transfer percentage around 50%. The diversity of metals and metalloids present in bio-oils is generally higher than in crude oils, where the main trace metals are generally Ni (<120 ppm) and V (<1200 ppm), with sulfur as the main inorganic component at 0.05−6.00 wt % (500−60 000 ppm).[73] The left side of Figure 3 shows a spider diagram, which represents a compilation of the highest and lowest concentration values of trace elements in bio-oils reported in some of the papers from Table 2,[13,55,66−72] while on the right side, a similar diagram was plotted with the typical trace elements in crude oils,[75] and the usual range of Ni and V in Venezuelan crude oil[74] as well as the range of the sulfur content expected for crude oils.[73] Given the inherent complexity of the inorganic content in bio-oil, dedicated analytical methods are

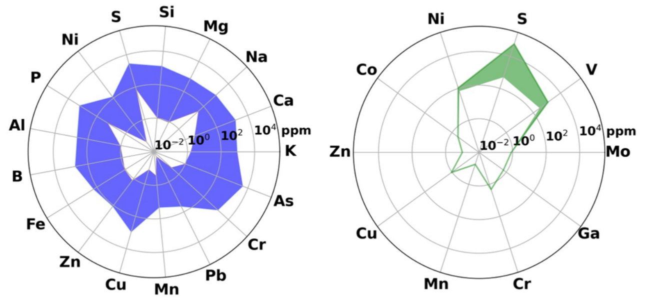


Figure 3. Representation of inorganic content of bio-oils[13,55,66−72] (left, blue) and crude oil[73−75] (right, green).

required. To begin addressing this demand, an exploration of the most recent analytical methods for the total inorganic analysis and speciation of bio-oils will be presented in the following sections.

4. TOTAL INORGANIC ANALYSIS OF BIO-OILS

Total inorganic analysis of bio-oils refers to the quantitative determination of their metal and metalloid contents. Table 1 summarizes the analytical methods for total inorganic analysis determinations reported to date for bio-oils. Flame atomic absorption spectroscopy (FAAS) stands as a simple and cost-effective method, mainly suitable for analysis of high-concentration elements; however, it falls short in terms of sensitivity and can only perform single-element analysis. In contrast, graphite furnace atomic absorption spectroscopy (GF AAS) and high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) significantly increase sensitivity, although their complexity and requirement for optimization introduce a trade-off. On the other hand, higher sensitivity and multielement analysis capabilities are provided by plasma-based methods, such as inductively coupled plasma mass spectrometry (ICP−MS) and inductively coupled plasma optical emission spectroscopy (ICP−OES). However, the requirement for sample digestion and the substantial cost of the equipment represent an important parameter to be considered. An alternative route is presented by total reflection X-ray fluorescence (TXRF), which requires tiny samples and offers a non-destructive and multielement analysis, although being limited to surface analysis. Ion chromatography (IC) is a moderately complex method, primarily dedicated to ionic species. All of these techniques offer unique strengths and bear specific drawbacks, emphasizing the importance of technique selection based on the requirements of the specific analytical task at hand. While FAAS is an affordable choice for high-concentration elements, more sensitive and complex methods, like ICP−MS or ICP−OES, might be preferable for multielement and isotopic analysis. Techniques such as TXRF and IC provide additional options for specific needs, demonstrating the wide array of tools available for modern element analysis.

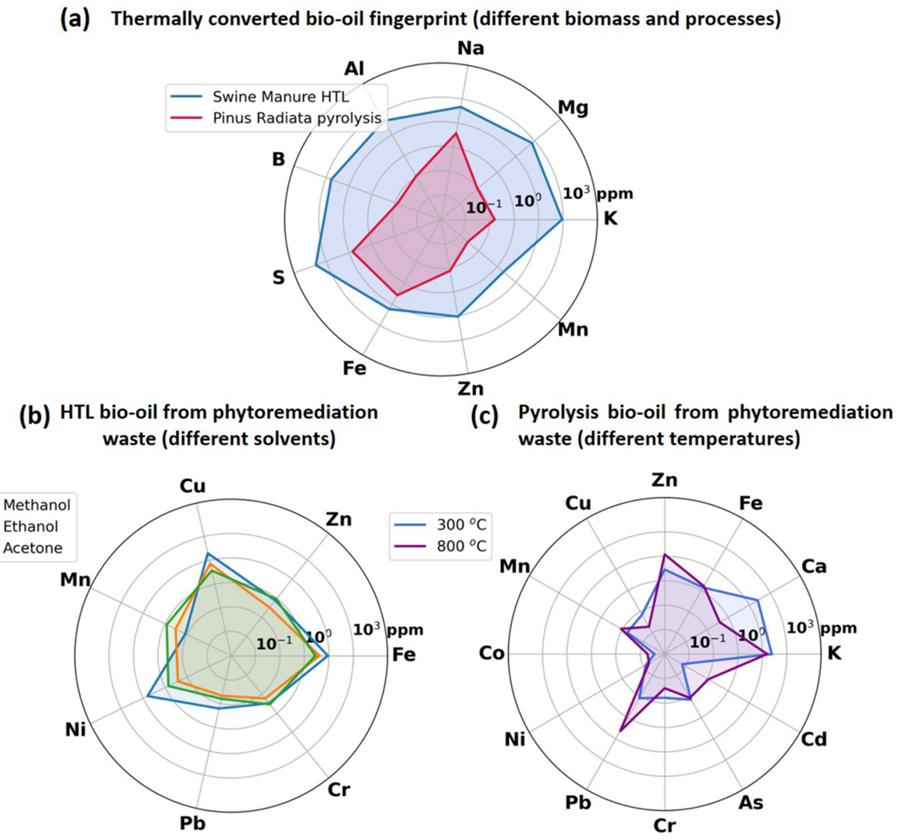
Table 2 outlines the sample preparation methodologies and analytical techniques employed for the total inorganic analysis of bio-oils. Unsurprisingly, ICP−OES is the predominant choice for such analysis. This preference stems from its superior sensitivity and ability to perform multielement analysis. Furthermore, in comparison to its counterpart, i.e., ICP−MS, ICP−OES is a more robust option for batch analysis and demands less technical expertise. Thus, Table 2 is limited to a few examples of the use of the ICP−OES technique, with all of

Table 1. Summary of Analytical Methods Used for Total Inorganic Content Determination in Bio-oils

technique	principle	complexity	sample volume	advantages	disadvantages	usual limit of detection (LOD)
flame atomic absorption spectroscopy (FAAS)	measures the absorption of light by atoms in a flame	low	1−10 mL	easy to use, relatively cheap, good for high-concentration elements	limited to single-element analysis, lower sensitivity compared to other methods	ppm level
graphite furnace atomic absorption spectroscopy (GF AAS)	measures the absorption of light by atoms in a graphite furnace	medium−high	<1 mL	high sensitivity, small sample volume	limited to single-element analysis, requires optimization (time-consuming)	ppb level
high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS)	measures the absorption of light by atoms in a graphite furnace	high	<1 mL	high sensitivity, small sample volume, multielement analysis	requires complex optimization, expensive equipment	ppb level
inductively coupled plasma mass spectrometry (ICP−MS)	uses ionized atoms and mass spectrometry for element analysis	high	1−10 mL	high sensitivity, multielement analysis, isotopic analysis	requires sample digestion, expensive equipment	ppt level
inductively coupled plasma optical emission spectroscopy (ICP−OES)	uses ionized atoms and optical emission for element analysis	high	1−10 mL	multielement analysis, wide dynamic range	requires sample digestion, expensive equipment	ppm to ppb level
total reflection X-ray fluorescence (TXRF)	measures the fluorescent X-rays emitted by a sample	medium	<10 μL	small sample volume, non-destructive, multielement analysis	limited to surface analysis, may require specific standards	ppb level
ion chromatography (IC)	separates and quantifies ions in a liquid sample	medium	1−10 mL	relatively easy to use	limited to ionic species, may require derivatization for certain analyses	ppm to ppb level

Table 2. Total Analysis Methods for the Inorganic Content in Bio-oils

production process	bio-oil sample type	sample preparation	technique	elements analyzed	reference
slow pyrolysis	*Avicennia marina* (phytoremediation)	microwave digestion of sample in HNO_3 + HCl (3:1), following U.S. EPA 3051A standard method	ICP−MS	Cr, Mn, Co, Ni, Fe, Cu, Zn, As, Cd, and Pb	He et al.[13]
			TXRF	K and Ca	
	Miscanthus grass	microwave digestion of sample in HNO_3 + HCl (3:1), following U.S. EPA 3050B standard method	ICP−MS	As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni, Se, Sb, Ag, Tl, U, V, and Zn	Arnold et al.[82]
	Avicennia marina (phytoremediation)	microwave digestion of sample in HNO_3 + HCl (3:1), following U.S. EPA 3051A standard method	ICP−MS	Cr, Cd, As, Pb, Ni, and Fe	He et al.[83]
pyrolysis	water hyacinth (phytoremediation)	microwave digestion of 200 mg of sample in 5.00 mL of HNO_3 and then diluted to 50 mL in water	FAAS	Pb	Jiu et al.[77]
	water hyacinth (phytoremediation)	microwave digestion of 200 mg of sample in 5.00 mL of HNO_3 and then diluted to 50 mL in water	FAAS	Cr	Lin et al.[78]
	peach pit, rice husk, sugar cane straw	direct weighing of the sample on a graphite platform (5 and 10 mg)	HR-CS GF AAS	Pb	Duarte et al.[80]
	palm tree fiber, coconut fiber, and peach pit	dilution of the sample in 1-propanol (from 1:4 to 1:10 dilution factor) and then weighing (4−10 mg) on a graphite platform	HR-CS GF AAS	Si	Nakadi et al.[72]
	pine and cottonwood	microwave digestion of 500 mg of sample in 10.00 mL of HNO_3 and 2.00 mL of H_2O_2	ICP−OES	Ca, K, Mg, Na, P, and S	Naske et al.[67]
	municipal solid waste	wet digestion of samples in a solution of HNO_3, $HClO_4$, and HF (3:2:1 by volume)	FAAS	Zn and Pb	Ding et al.[69]
			GF AAS	Cd	
	Sedum plumbizincicola (phytoremediation)	wet digestion of samples in a solution of HNO_3, $HClO_4$, and HF (3:2:1 by volume)	FAAS	Zn and Pb	Zhong et al.[81]
			GF AAS	Cd	
	biosludge	wet digestion of the samples in 20 mL of $HNO_3/HClO_4/HF$ (3:5:2) in a Teflon-lined closed vessel, placed in a high-pressure digestion oven (170 °C for 5 h), and then heated at 90 °C to concentrate to 0.2 mL; finally, the concentrated mixture was diluted to 25 mL by 2% nitric acid	ICP−OES	Al, Ca, Fe, K, Mg, Na, S, Co, and Zn	Chiang et al.[84]
			ICP−MS	As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Sb, Se, Sr, Ag, and V	
flash pyrolysis	willow plant stems and leaves (phytoremediation)	microwave digestion of 250 mg of sample in 4.00 mL of HNO_3 and 2.00 mL of H_2O_2 and then diluted to 25 mL in water	ICP−OES	Zn, Cd, and Pb	Stals et al.[79]
fast pyrolysis	chromated copper arsenate-treated wood (CCA-W) and alkaline copper quaternary compound-treated wood (ACQ-W)	microwave digestion of 500 mg of sample in 10 mL of $HNO_3/HCl/H_2O_2$ (8:1:1, v/v/v) and then diluted to 50 mL in water, followed by filtration	ICP−OES	As, Cu, Cr, Al, Ca, K, Mg, Na, P, and Si	Kim et al.[55]
	Pinus radiata	microwave digestion of 300 mg of sample in 2.50 mL of HNO_3 and 2.50 mL of H_2O_2 and then diluted to 25 mL in water	ICP−OES	Li, Na, K, Mg, Ca, Ba, Cr, Cu, Fe, Mn, Ni, Zn, Cd, Co, V, Al, Pb, P, S, As, and B	Wigley et al.[71]
	commercial bio-oils	microwave digestion of 200 mg of sample in 20.00 mL of HNO_3, HCl, and H_2O (at a volume ratio of 10:0.5:9.5) following the modified EN13805:2002/U.S. EPA 3052 method	ICP−OES	Na, K, Mg, and Ca	Zhang et al.[85]
		evaporation−ashing−digestion−IC method	IC		
thermochemical liquefaction (supercritical conditions)	*Camellia oleifera* cake	wet digestion of 0.5 g of sample in 10 mL of HNO_3 + H_2O_2 (2:1, v/v) for 10 min at rt, then heated at 80 °C until clear solutions, then evaporated and dissolved in 5 mL of 0.2 M HNO_3, filtered through 0.22 μL filter paper, and made up to 10 mL with water	ICP−OES	Zn, Pb, Cd, Ni, Fe, Mn, Cr, and Cu	Chen et al.[68]
microwave-assisted pyrolysis	waste office paper	dilution in acetone (dilution factor not reported)	ICP−MS	Na, Mg, Al, Si, K, Ca, Cr, Mn, Fe, Cu, Zn, As, Nb, Pd, Sn, Ir, Pt, Au, and Pb	Zhang et al.[70]
liquefaction	swine manure	microwave digestion of sample (200 °C and 2 MPa) in HNO_3/HCl	ICP−OES	Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Si, Sr, Tl, V, and Zn	Xiu et al.[66]
HTL	microalgae	dilution of the sample (about 50−100-fold) by ethylene glycol butyl ether	ICP−OES	Na, K, Mg, Ca, P, S, Zn, Cu, Al, Ni, Mn, and Fe	Jiang et al.[62]



(a) Thermally converted bio-oil fingerprint (different biomass and processes)

(b) HTL bio-oil from phytoremediation waste (different solvents)

(c) Pyrolysis bio-oil from phytoremediation waste (different temperatures)

Figure 4. Inorganic fingerprints of bio-oil samples with (a) different biomass and processes, (b) different solvents in the HTL process, and (c) different temperatures in the pyrolysis process.

the other papers representing alternative methods. The majority of studies in total inorganic analysis of bio-oils have employed acid microwave-assisted mineralization as the sample preparation technique, with nitric acid (HNO_3) frequently being the digestion agent of choice.[77,78] This could be attributed to the strong oxidizing nature of HNO_3, making it effective at breaking down organic matrices and releasing soluble metal nitrates. In several cases, nitric acid has been employed alongside other digestion agents, like hydrochloric acid (HCl), perchloric acid ($HClO_4$), hydrofluoric acid (HF), and hydrogen peroxide (H_2O_2).[13,69,79] This strategy is typically adopted to enhance the overall digestion process and ensure the stability of certain elements during analysis. Alternative sample preparation methods have also emerged, such as dilution in organic solvents, e.g., acetone,[70] ethylene glycol butyl ether,[62] and ethanol.[67] Similarly, Duarte et al. adopted a direct solid analysis approach by directly weighing the sample onto a graphite platform, eliminating the need for potentially complex and time-consuming digestion processes.[80] These alternative methods, while advantageous in certain contexts, also come with limitations. Direct analysis methods, while reducing sample preparation time, may not be suitable for all types of bio-oil samples, particularly those with high organic content or complex matrices. On the other hand, dilution in organic solvents is relatively simple but may not effectively solubilize all inorganic constituents, potentially leading to incomplete or biased analytical results.

FAAS is a straightforward technique enabling the analysis of one inorganic element at a time, as opposed to multielement analysis. This methodology has been applied in the work of Jiu et al.[77] and Lin et al.,[78] who studied the impact of impregnating water hyacinth with Pb and Cr, respectively, on the yield and composition of pyrolysis products. Ding et al.[69] and Zhong et al.[81] used FAAS to investigate the distribution of Zn and Pb metals in the pyrolysis products of municipal solid waste and *Sedum plumbizincicola* (phytoremediation plant) biomass, respectively. Because Cd was present at lower concentrations than Zn and Pb in both studies, it was determined using graphite furnace atomic absorption spectrometry (GF AAS), because it provides lower detection limits.[69,81] As an improved version of the GF AAS technique, the analytical technique HR-CS GF AAS has been developed for the analysis of biomass, bio-oils, and other pyrolysis products as earlier noted in the direct analysis work of Duarte et al. for Pb (ref 80) and Nakadi et al. for Si (ref 72). In HR-CS GF AAS, the use of a high-intensity xenon short-arc lamp, a high-resolution double monochromator, and a charge-coupled device (CCD) as a detector represent an important improvement in the limits of detection (LODs).[80]

ICP−MS can be considered as the second most widely used technique in the total inorganic analysis of bio-oils after ICP−OES. The low LOD of ICP−MS makes it an ideal technique for multielemental analysis of this type of sample. However, certain considerations must be made to avoid possible interferences in the target isotopes. The studies of Zhang et al.,[70] Arnold et al.,[82] and He et al.[13,83] are some examples of the use of ICP−MS for the multielement total inorganic analysis of pyrolysis bio-oils. In the case of He et al.,[13,83] total reflection X-ray fluorescence (TXRF) was used for the determination of the elements K and Ca instead of ICP−MS, because the isotopes of these elements are known to be difficult to analyze under low- and medium-

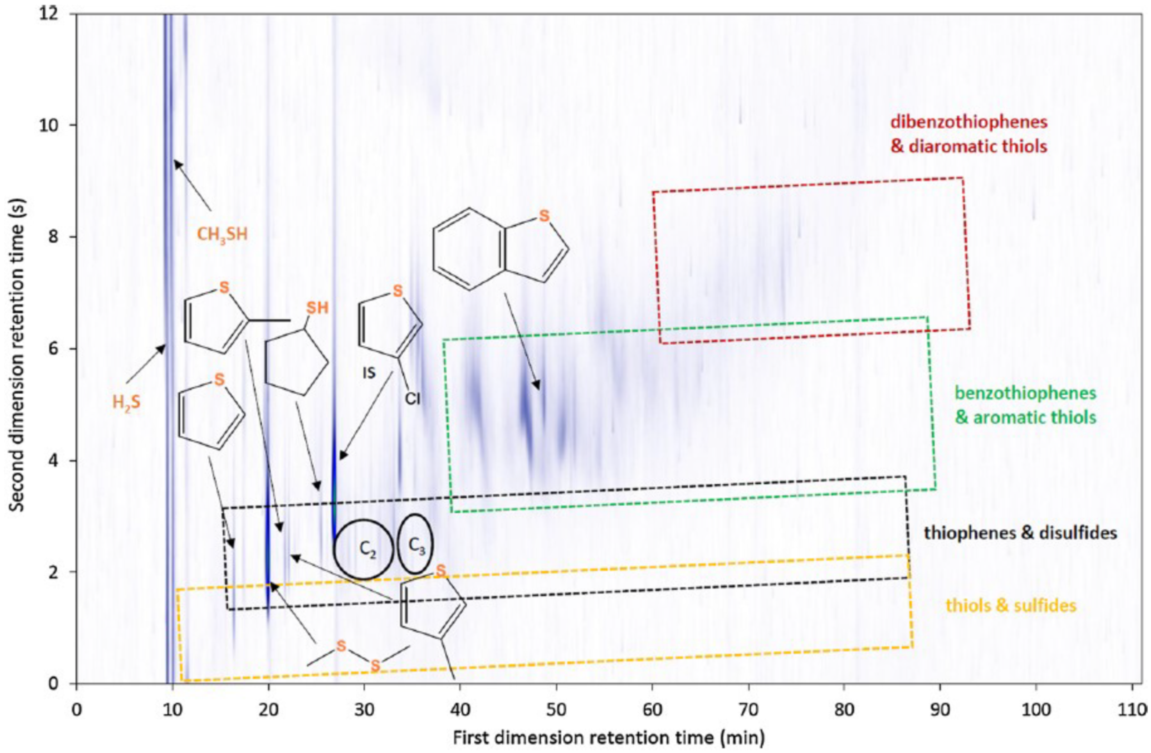


Figure 5. GC × GC−SCD chromatogram of the straw bio-oil organic phase. Circled groups: C_2, C_2-thiophenes; C_3, C_3-thiophenes. This figure was adapted with permission from ref 94. Copyright 2021 Elsevier.

resolution conditions as a result of the significant interference from polyatomic ions. The ICP−OES technique has been used for the multielemental analysis of the inorganic content of bio-oils from all types of biomass: phytoremediation,[79] animal manure,[66] municipal waste,[69] microalgae,[62,86] among others. However, dependent upon the metals of interest, the choice of the preferred technique may vary, as each metal has its own peculiarities in terms of interferences, as shown by Chiang et al.[84] On the other hand, Zhang et al. developed a multistep method for the analysis of AAMEs consisting of evaporation of the bio-oils, followed by ashing, and then the digestion of the resulting ash, followed by IC. This method gave lower limits of quantification (LOQas) than the microwave−ICP−OES method.[85]

Multielement analysis of bio-oils provides a complete overview of the behavior of nutrients transferred to the bio-oils during the thermochemical conversion processes. In Figure 4a, the difference in the fingerprint of bio-oils obtained from different types of biomass and production processes is shown. It can be observed that the general content of analyzed metals in the bio-oil from pyrolysis of *Pinus radiata* (phytoremediation plant)[71] was lower than in the bio-oil obtained from HTL of swine manure.[66] This type of inorganic fingerprint is an interesting tool to study the effect that production process variables can have on the distribution of minerals, as shown in Figure 4b, where it is observed that, depending upon the solvent used in the HTL of *Camelia oleifera* cake, the amount of metal content in the bio-oil does not change for some metals, like Cr, but has an important effect for some other metals, like Ni and Mn.[68] Another example is presented by He et al. (see Figure 4c), where variation in the temperature significantly affects certain metals, such as Ca, Pb, and Cd, but is inconsequential for other metals, such as Fe, Mn, and As.[13]

5. INORGANIC SPECIATION OF BIO-OILS

Speciation consists of the identification and/or quantification of one or more analytes in the sample, which provides insight into how the analyte(s) may be distributed in the sample. On the other hand, fractionation consists of the classification and separation of an analyte or group of analytes according to their physical or chemical properties.[87] Unfortunately, there is a dearth of literature on the speciation and fractionation studies of inorganic elements and compounds in biofuels, such as bioethanol, biodiesel, and bio-oils. This section aims to explore the limited examples found in the literature concerning the examination of inorganics in bio-oils.

An example of fractionation analysis is the Community Bureau of Reference (BCR) sequential extraction procedure, which is commonly used in contaminated soils and has been widely reported for the analysis of sewage sludge biomass and its respective biochar produced from the HTL process.[15,88,89] The original BCR sequential extraction method involves fractionation by solubility and reactivity of the samples into four fractions: F1 (acid-soluble fraction, treated with acetic acid), F2 (reducible fraction, treated with hydroxylamine hydrochloride and HNO_3), F3 (oxidizable fraction, treated with H_2O_2) and F4 (residual fraction, treated with aqua regia). These fractions are considered in decreasing order of toxicity, and they are analyzed for heavy metals, such as Cu, Zn, Cr, Ni, Pb, and Cd.[88,89] Moreover, the use of a variation of this method has been reported for HTL bio-oil from sewage sludge in the works of Leng et al.[90] and Yuan et al.[91] In this variation, the bio-oils were fractionated into only two fractions, the acid-soluble exchangeable fraction (F1) and the non-exchangeable fraction (F2−F4), to evaluate the risk assessment of these samples. The dependability of these analyses must include rigorous method validation, strict quality control protocols, experienced analysts,

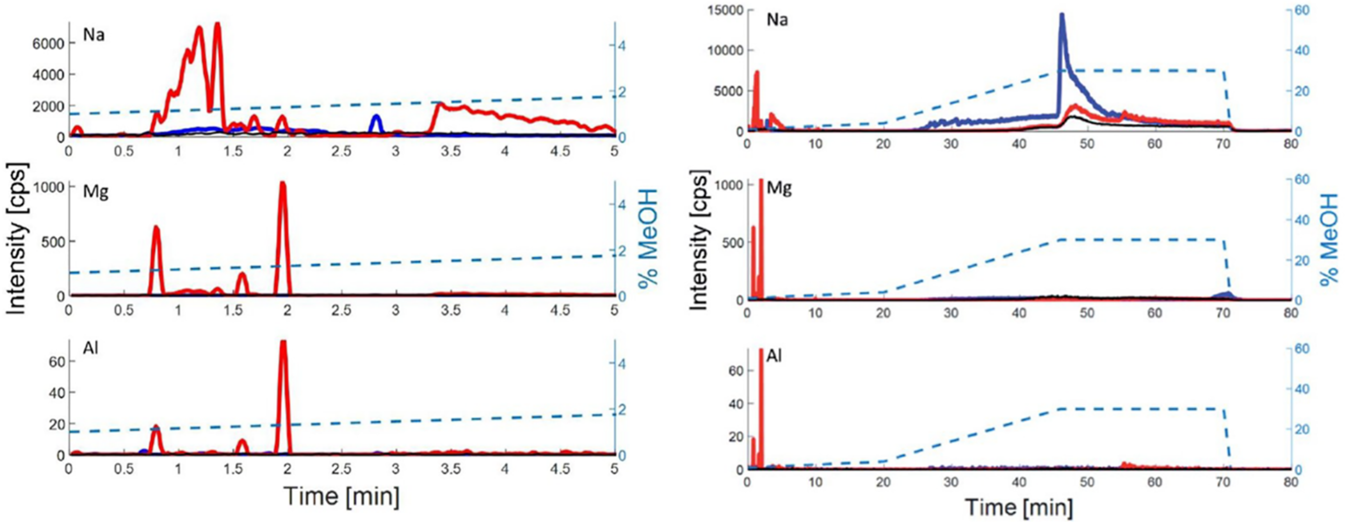


Figure 6. SFC−ICP−MS chromatograms of Na, Mg, and Al in the analysis of pyrolysis oil produced from Milorganite fertilizer (blue), coal tar (red), and the tetrahydrofuran (THF) blank (left, retention time of 0−5 min; right, retention time of 0−80 min). This figure was adapted with permission from ref 95. Copyright 2020 Royal Society of Chemistry.

careful consideration of sample matrix effects, and interpretation of the data within the appropriate context. With adherence to these practices, it can be ensured that the data obtained are reliable and accurate. Additionally, Zhang et al. investigated the distribution of sulfur species in the bio-oil derived from hydrothermal carbonization of *Spirulina* (a type of microalgae) at different temperatures. The researchers employed special colorimetric methods using LIANHUA test kits for the analysis of inorganic components (sulfide and sulfate detection), while the molecular organic sulfur-containing components were analyzed using gas chromatography−mass spectrometry (GC−MS) for compounds such as aromatics, thiophene, and thiazole.[92]

With regard to the inorganic speciation of biofuels, the bibliography is not as abundant as in the case of crude oil.[93] Nonetheless, a few noteworthy contributions have been made. For instance, Auersvald et al.[94] spearheaded a fresh methodology to analyze sulfur species in bio-oils. Their innovative approach incorporates comprehensive GC × GC, combined with a selective sulfur chemiluminescence detector (SCD), and headspace gas chromatography coupled to quadrupole mass spectrometry (GC−MS). The team applied this novel analysis to bio-oils produced from the ablative fast pyrolysis of beech wood, *Miscanthus*, wheat/barley straw, and straw hydrotreated bio-oil. Their in-depth examination uncovered a substantial variety in the sulfur content across the tested bio-oils, with 18−62% of total sulfur stemming from GC-detectable compounds, chiefly hydrogen sulfide, methanethiol, dimethyl disulfide, and several thiophenes, as illustrated in Figure 5. This sulfur speciation was amplified under more severe hydrotreatment conditions (360 °C and 8 MPa), resulting in significant desulfurization of these bio-oils, leaving only traces of thiophenes detectable. The research of Auersvald et al. critically enhances the knowledge of sulfur speciation in bio-oils, providing invaluable insights for bio-oil upgrading.[94]

In a proof-of-concept study, Garcia-Montoto et al.[95] developed an interface coupling a supercritical fluid chromatography (SFC) system akin to HPLC with ICP−MS detection. The authors employed this novel approach for the quantitative analysis of bio-oils derived from pyrolysis of Milorganite fertilizer and coal tar, quantifying the distribution of metal species, such as Na, Mg, Al, Mn, Fe, and Cu, as a function of the retention time. One of the key strengths of SFC lies in its efficiency and versatility. SFC operates under conditions where the mobile phase is a substance at its critical point, where it exhibits both gas- and liquid-like properties. This gives it an advantage over traditional HPLC, because SFC can separate and analyze compounds that are challenging for HPLC, including thermally labile compounds and nonpolar analytes.[96] The SFC technique was found to be effective, producing results comparable to ICP−MS alone and achieving parts per billion (ppb) detection limits. Importantly, the methodology also revealed information about the selective affinity of inorganic species for different molecular groups present in the samples (see Figure 6). This novel SFC−ICP−MS approach is emerging as a potential powerful tool for speciation analysis. However, as suggested by the authors, future efforts should focus on improving plasma stability and chromatographic separation to obtain a valuable analytical tool.[95]

On the other hand, Garcia-Montoto et al.[97] applied the gel permeation chromatography−inductively coupled plasma high-resolution mass spectrometry (GPC−ICP−HRMS) methodology, typically employed for crude oils and their fractions, to explore phosphorus speciation in fast pyrolysis bio-oils. This innovative approach facilitated the detection of specific phosphorus-containing species, providing insights into the molecular weight distribution changes over time. The study revealed that red-oak-derived biocrudes usually exhibit phosphorus species with an average molecular weight of 620 Da, while biocrudes containing Milorganite show a more complex molecular weight distribution with maximums in 620 and 230 Da. Additionally, the researchers detected a noteworthy increase in the molecular weight of phosphorus species in Milorganite-containing biocrudes after 3 months of aging (see Figure 7). These observations underscore the dynamic and complex nature of bio-oils, emphasizing the need for robust analytical techniques, such as GPC−ICP−HRMS. The ability to monitor molecular weight shifts over time can inform improved storage methods and shed light on bio-oil aging. The valuable insights obtained through this research pave the way for refining

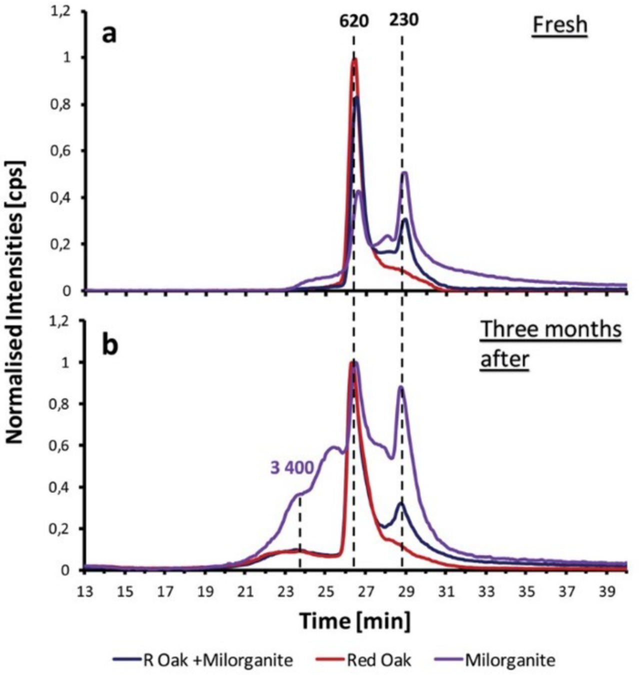


Figure 7. GPC−ICP−HRMS chromatogram corresponding to the analysis of P in the two xylene-soluble extracts of three lignocellulosic feedstocks: red oak (red), Milorganite (purple), and a 50:50 mixture of red oak and Milorganite (blue), of the (a) fresh sample and (b) after 3 months. This figure was adapted with permission from ref 97. Copyright 2021 Royal Society of Chemistry.

the efficiency and sustainability of biofuel production processes.[97]

When it comes to analyzing complex matrices, such as biofuels, it is reasonable to consider chromatographic techniques coupled with detection systems that provide better visibility of the analytes. However, HRMS techniques allow for speciation screening of high-molecular-weight compounds in bio-oils that cannot be analyzed by widely used GC−MS methods.[57] An example of HRMS techniques is Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), which has been used for the molecular speciation of oxygenated molecules present in the bio-oil matrix in various studies (composition of bio-oils of different origins, upgrading processes, selectivity, and efficiency of separation procedures, among others) as resumed by Stas et al.[57]

Inorganic species in bio-oils have been analyzed using FT-ICR MS. As an example, iron porphyrins from microalgae HTL bio-oil were studied by Jarvis et al.[98] They observed double bond equivalent (DBE) (17−22) similar to that previously reported for Ni and V porphyrins from heavy crude oil and bitumen DBE (17−25) by Liu et al.[99] Jarvis et al.[98] investigated the problem of clogging of the bed reactor for catalytic hydrotreatment of bio-oil (for removal of polar species). They related the sharp decrease in iron content upon hydrotreatment of bio-oil (determined by ICP−OES) and the disappearance of the porphyrin signal in the mass spectrum (shown in Figure 8) to iron deposits in the catalyst bed, which leads to catalyst deactivation and clogging of the bed reactor.[98] The work of Chacon-Patiño et al.[100] on vanadyl porphyrin speciation in asphaltenes is an example of how the HRMS techniques can be coupled to the chromatography system to obtain complementary information about the inorganic species in the samples.[100]

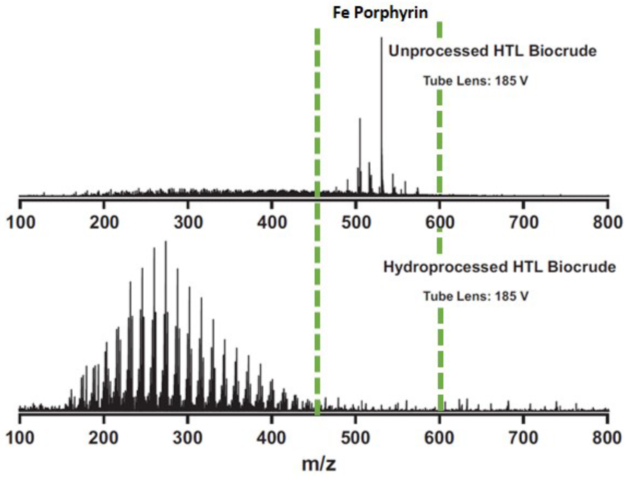


Figure 8. Positive-ion ESI FT-ICR mass spectra of cyanobacteria HTL biocrudes collected with a tube lens voltage of 185 V (top) unprocessed and (bottom) hydroprocessed. Mass spectral signals for Fe porphyrins (*m*/*z* 450−600) dominate each mass spectrum, and they are absent in the hydroprocessed HTL biocrude. This figure was adapted with permission from ref 98. Copyright 2016 Elsevier.

Appling this philosophy of thinking to the new generation of fuels will bring important contributions regarding the inorganic chemical nature of bio-oils.

6. CHALLENGES AND PERSPECTIVES

In biofuel research, particularly bio-oils, challenges persist despite extensive studies, especially regarding the standardization of analytical methods for accurately determining inorganic constituents. Few standards, such as ASTM UOP1005 (2014)[101] and ASTM UOP1005 (2015),[102] cater to the analysis of biofuels, specifically trace metals in organics, employing techniques like ICP−MS[101] and ICP−OES.[102] However, these standards are not explicitly designed for bio-oils and may not address their unique characteristics. Similarly, ISO 16967, which is primarily applicable to solid biofuels, might not be entirely suitable for liquid bio-oils. The round-robin study by the Haldor Topsøe group exemplifies the discrepancy between laboratories when analyzing identical samples using ICP−OES and ICP−MS techniques, attributed to varied sample preparation methods.[103] Lienemann et al.[16] took a significant step to resolve this by comparing several sample preparation methodologies for analyzing inorganic elements in fast pyrolysis bio-oils, using ICP−OES. The notable discrepancies, particularly between ISO 16967 and the methanol dilution method, put the reliability of existing techniques into question. ISO 16967 demonstrated higher inorganic content results compared to simple dilution and ICP−OES analysis. This finding suggested that dilution-based methods might underestimate alkali contents as a result of partial solubilization of the oil in methanol and the inability to account for methanol-insoluble inorganics.

Therefore, a refined standard incorporating a rigorous homogenization step and avoiding heating steps that induce aging and loss of volatile species is necessary. Studies like that conducted by Lin et al.,[104] which investigated the impact of potassium (K) on Pt−TiO_2 catalyst deactivation in biomass catalytic fast pyrolysis, exemplify the need for a comprehensive understanding of the effects of inorganic species on bio-oil production and processing. They demonstrate that low K loadings deactivate the catalyst by poisoning strong Lewis acid sites, inhibiting acid-catalyzed alcohol dehydration. High K loadings lead to K accumulation at the Pt−TiO_2 interface, reducing the performance in *m*-cresol hydrodeoxygenation and CO oxidation. Importantly, the deactivation caused by K is reversible through water washing, facilitating catalyst regeneration. These findings offer valuable insights for optimizing the catalyst performance and biomass conversion efficiency. The development of advanced analytical techniques, which merge chromatographic systems with ICP−MS and HRMS, is promising for elucidating the nature and behavior of inorganic species in bio-oils.

Lastly, with the challenges, such as reactor clogging and bio-oil aging, highlighted by Jarvis et al.[98] and Garcia Montoto et al.,[97] an evolution in analytical methodologies is required. Techniques need to be adapted and optimized for each specific type of bio-oil, paying special attention to sample preparation for accurate results. Studying the impact of inorganic species on bio-oil production and processing is crucial. Utilizing high-resolution techniques, such as FT-ICR MS can aid in the detailed analysis of complex bio-oils. Through a focused and comprehensive approach, sustainable and efficient bio-oil technologies can be developed.

7. CONCLUSION

In conclusion, navigating the complexities of bio-oil as an energy source presents distinct challenges, primarily the lack of standardized methods for accurately quantifying inorganic constituents. Evidence from comparative studies has highlighted notable discrepancies in results, thus underscoring the critical need for method standardization in the analytical chemistry community. It is envisioned that the development and implementation of advanced analytical techniques, combining chromatographic systems with ICP−MS and HRMS, may provide a viable solution, offering a detailed and comprehensive characterization of inorganic species in bio-oils.

Given the inherent variability in bio-oil properties, it is recognized that these novel methods should exhibit adaptability to accommodate distinct bio-oil types, emphasizing the importance of a tailored sample preparation to ensure accurate and reproducible results. Additionally, the impact of inorganic species on bio-oil production and processing should be meticulously studied. Comprehensive investigations into their effects on catalyst performance, reactor operation, bio-oil stability, and aging are paramount to unveiling new insights. Despite the existing challenges, the fusion of advanced analytical techniques with a comprehensive approach to studying inorganic species in bio-oils could be pivotal in moving toward sustainable bio-oil technologies.

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Ryan P. Rodgers is a professor, international chair leader (UPPA), and member of IC2MC, who specializes in elemental and molecular analysis of complex matrices at the National High Magnetic Field Laboratory (Florida State University). He received his Ph.D. degree in analytical chemistry from Florida State University in 1999. After a postdoctoral appointment at Oak Ridge National Laboratory, he returned to the Ion Cyclotron Resonance Program at the National High Magnetic Field Laboratory as an assistant scholar−scientist and courtesy faculty member in the Chemistry Department. Currently, he serves as the Director of the Future Fuels Institute, FSU Distinguished Scholar, Research Faculty III, and is a past associate editor of *Energy & Fuels*.

Jan H. Christensen is a professor in environmental analytical chemistry. He is leader of the Analytical Chemistry Group, Department of Plant and Environmental Sciences, University of Copenhagen, Denmark, and heads the Research Centre for Advanced Analytical Chemistry (RAACE). He has authored and co-authored more than 150 peer-reviewed papers and book chapters on these topics. His current research focus is on development and application of multidimensional chromatography platforms in combination with chemometric data analysis.

Victor Garcia-Montoto earned his Ph.D. degree in analytical chemistry from the University of Pau and Adour Countries in 2020, where he focused on inorganic speciation analysis in renewable feedstocks and petroleum heavy oil fractions through liquid chromatography and other separation techniques hyphenated with ICP−MS. Currently, he works as a customer support engineer at Agilent Technologies.

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NOMENCLATURE

AAME = alkali and alkaline earth metal
ANP = National Agency of Petroleum, Natural Gas and Biofuels (Brazil)
BCR = Community Bureau of Reference
CEN = European Committee for Standardization
DBE = double bond equivalent
DFT = density functional theory
ESI FT-ICR MS = electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry
FAME = fatty acid methyl ester
FAAS = flame atomic absorption spectroscopy
GC = gas chromatography
GC × GC = comprehensive two-dimensional gas chromatography
GF AAS = graphite furnace atomic absorption spectrometry
GPC = gel permeation chromatography
GPC−ICP−HRMS = gel permeation chromatography−inductively coupled plasma high-resolution mass spectrometry
GHG = greenhouse gas
HDO = hydrodeoxygenation
HPLC = high-performance liquid chromatography
HR-CS GF AAS = high-resolution continuum source graphite furnace atomic absorption spectrometry
HRMS = high-resolution mass spectrometry
HTL = hydrothermal liquefaction
HVO = hydrotreated vegetable oil
IC = ion chromatography
ICP−MS = inductively coupled plasma mass spectrometry
ICP−OES = inductively coupled plasma optical emission spectroscopy
ISO = International Organization for Standardization
LOD = limit of detection
LOQ = limit of quantification
MS = mass spectrometry
NMR = nuclear magnetic resonance
RED II = Renewable Energy Directive for 2021−2030
RFS2 = Revised Renewable Fuel Standard
RID = refractive index detector
SFC−ICP−MS = supercritical fluid chromatography−inductively coupled plasma mass spectrometry
SCD = sulfur chemiluminescence detector
TXRF = total reflection X-ray fluorescence
UV−vis = ultraviolet−visible
U.S. EPA = United States Environmental Protection Agency

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