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Wladimir Ruiz, Julie Guillemant, Lucie Coniglio, Ryan Rodgers, Jan Christensen, et al.. Bio-oil Inorganic Analysis: A Minireview of Current Trends, Challenges, and Future Perspectives. *Energy & Fuels*, 2023, 37 (16), pp.11608-11621. 10.1021/acs.energyfuels.3c01462 . hal-04196123

HAL Id: hal-04196123

<https://univ-pau.hal.science/hal-04196123v1>

Submitted on 5 Sep 2023

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

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KEYWORDS. " Bio-oils ", "inorganic speciation ", " chromatography ", " ICP ", " FT-ICR MS ".

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 ICP-OES (inductively coupled plasma optical emission spectrometry) and ICP-MS (inductively coupled plasma mass spectrometry) techniques, however, other quantitation techniques are compiled and discussed in this review. Additionally, the few studies that have been recently reported on the inorganic speciation of bio-oils by SFC-ICP-MS (supercritical fluid chromatography inductively coupled plasma mass spectrometry), GPC-ICP-HRMS (gel permeation chromatography inductively coupled plasma high-resolution mass spectrometry), and ESI FT-ICR MS (electrospray ionization fourier transform ion cyclotron resonance mass spectrometry) are also addressed. Cumulatively, the reports suggest that the lack of standard analytical methods in 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 towards 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 RED II (Renewable Energy Directive for 2021–2030), 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 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 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 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-oil, in order to ensure its 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 feedstock (vegetable oils, animal fat, 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, followed by quantification using 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 HTL products from sewage sludge.¹⁵ The study of inorganic content in bio-oils started before 2010, but it gain 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.

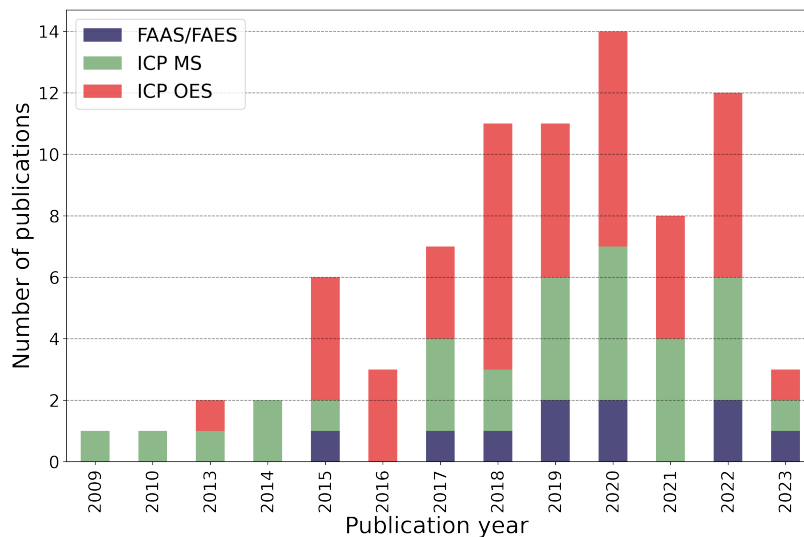


Figure 1. Publications record count given on Scopus citation database with the keywords: bio-oils, biocrude, metal determination, inorganic analysis, inorganic speciation, trace metal, inorganic determination, flame atomic absorption spectrometry, flame atomic emission spectrometry, inductively coupled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

The aim of this work is to critically review the current advances and challenges in inorganic analysis of bio-oils. It is presented, an exhaustive compilation of analytical techniques reported for total inorganic analysis of bio-oil, including examples of commonly used ICP-OES. Furthermore, the bio-oils inorganic speciation examples reported so 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 like fermentation, transesterification, hydrodeoxygenation (HDO), pyrolysis, and hydrothermal liquefaction. 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 European Commission's terminology for consistency (see Figure 2). The European Commission defines biofuels as follows: First-generation biofuels are derived from edible biomass feedstocks, which encompass sugar, starch crops such as sugar cane, corn, wheat, and vegetable oils like soybean, oil 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 into 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 crop other than corn).¹⁹ Furthermore, Haldor Topsoe, 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 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 energy transition.

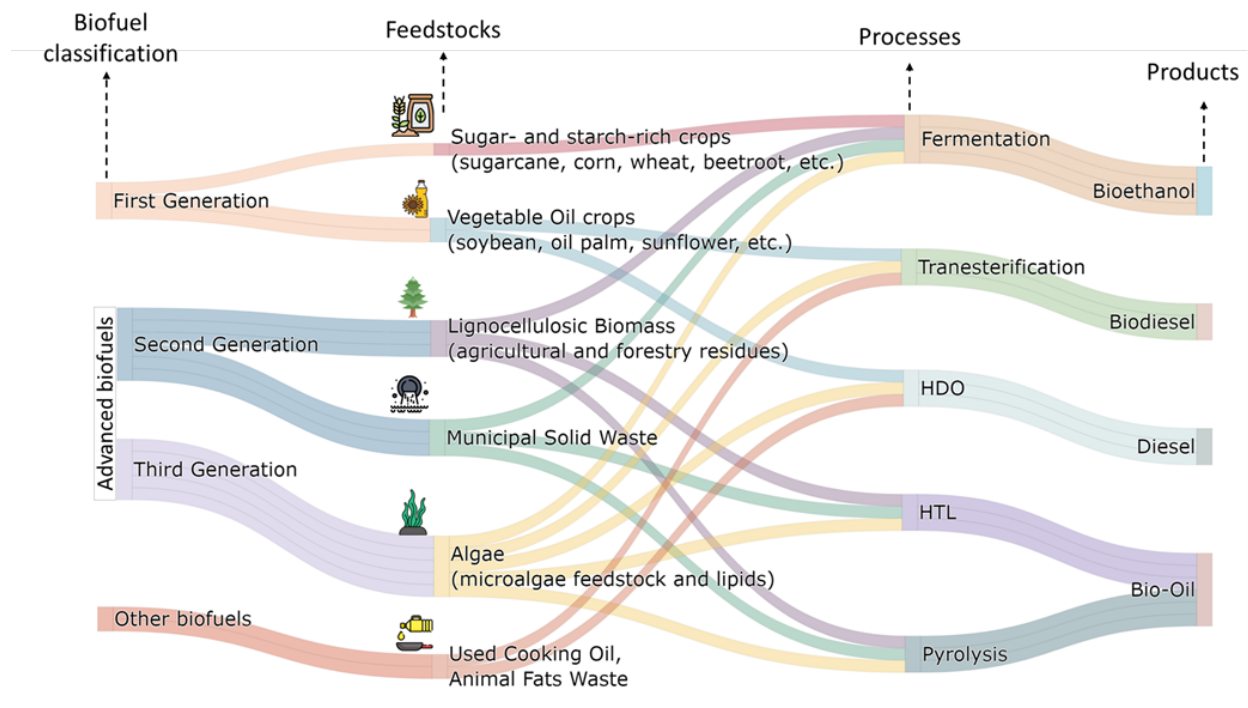


Figure 2. General scheme of the different sorts of liquid biofuels according to European Commission.^{1,17,18}

The three main liquid biofuels are bioethanol, biodiesel, and bio-oils. Current global biofuel production is approximately two million barrels per day (BPD),²² with the following breakdown: 65.7% ethanol, 27.8% FAME/biodiesel, and 6.5% renewable diesel/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 fatty acid methyl esters (FAME) 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 AAMEs (alkali/alkaline earth metals, e.g. Na, K, Mg, Ca) and other inorganic

species in bioethanol and biodiesel primarily depends on 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 and phosphorus (10 ppm) in biodiesel.²⁹ Similarly, ASTM and CEN prescribe allowable limits for trace elements in ethanol and diesel.³⁰⁻³² Bioethanol and biodiesel, being first-generation biofuels, benefit from validated analytical methods for inorganic content determination, with applicable standards from organizations like ISO, CEN, and ASTM.³³⁻⁴¹ The efficacy and drawbacks of the several analytical techniques for the inorganic analysis of these biofuels have been extensively researched and discussed elsewhere.⁴² However, this minireview paper 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 hydrothermal liquefaction (HTL). Pyrolysis can be divided into several types, including slow, fast, catalytic, and hydro-pyrolysis. 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 high pressure and temperature with a solvent for several minutes (10 - 60 minutes), 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 comprised 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 x GC),⁵¹ flash chromatography,⁵² high-performance liquid chromatography (HPLC),^{53,54} gel permeation chromatography (GPC),⁵⁵ and detection systems such as ultraviolet-visible detection (UV-visible),⁵⁴ refractive index detector (RID),⁵³ Fourier transform infrared spectroscopy (FTIR),⁵⁶ nuclear magnetic resonance (NMR),^{52,56} mass spectrometry system (MS)⁵¹, and high-resolution mass spectrometry (HRMS).^{52,57-60}

The metal and metalloid contents of bio-oils corresponds to 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 a catalyst, 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 oligomers products with 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, 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 functional density theory (DFT).⁶⁴ A comprehensive summary of the effect of metals on pyrolysis bio-oils has been provided by Giudicianni *et al.*⁶⁵

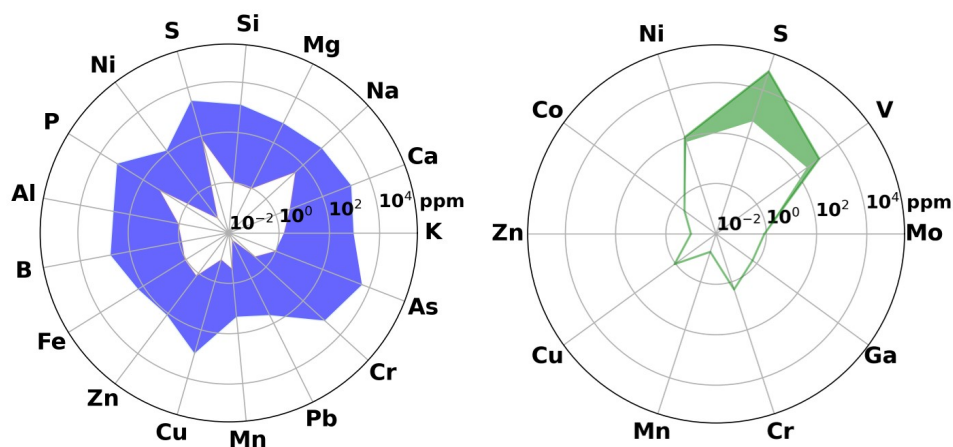


Figure 3. Representation of inorganic content of bio-oils^{13,55,66-72} (left, blue) and crude oil⁷³⁻⁷⁵ (right, green).

During pyrolysis or HTL processes, inorganic nutrients in biomass are distributed among 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 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 sulfur content expected for crude oils.⁷³ Given the inherent complexity of inorganic content in bio-oil, dedicated analytical methods are required. To begin addressing this demand, an exploration of the most recent analytical methods for 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 content. Table 1 summarizes 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 multi-element analysis capabilities are provided by plasma-based methods, such as Inductively Coupled Plasma Mass

Spectrometry (ICP-MS) and 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 multi-element analysis, although being limited to surface analysis. Ion Chromatography (IC) is a moderately complex method, primarily dedicated to ionic species. All 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 multi-element 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 the 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 multi-element analysis. Furthermore, when compared to its counterpart, 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 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 matrixes and releasing

soluble metal nitrates. In several cases, nitric acid has been employed alongside other digestion agents like hydrochloric acid (HCl), perchloric acid (HClO₄), hydrofluoric acid (HF), and hydrogen peroxide (H₂O₂).^{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, such as 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.

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

| Technique | Principles | Complexity | Sample Volume | Advantages | Disadvantages | Usual Limit of Detection (LOD) |
|---|---|-------------|---------------|---|---|--------------------------------|
| FAAS (Flame Atomic Absorption Spectroscopy) | 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 |
| GF AAS (Graphite Furnace Atomic Absorption Spectroscopy) | 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 |
| HR-CS GF AAS (High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry) | Measures the absorption of light by atoms in a graphite furnace | High | < 1 mL | High sensitivity, small sample volume, multi-element analysis | Requires complex optimization, expensive equipment | ppb level |
| ICP-MS (Inductively Coupled Plasma Mass Spectrometry) | Uses ionized atoms and mass spectrometry for element analysis | High | 1-10 mL | High sensitivity, multi-element analysis, isotopic analysis | Requires sample digestion, expensive equipment | ppt level |
| ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) | Uses ionized atoms and optical emission for element analysis | High | 1-10 mL | Multi-element analysis, wide dynamic range | Requires sample digestion, expensive equipment | ppm to ppb level |
| TXRF (Total Reflection X-Ray Fluorescence) | Measures the fluorescent X-rays emitted by a sample | Medium | < 10 μ L | Small sample volume, non-destructive, multi-element analysis | Limited to surface analysis, may require specific standards | ppb level |
| IC (Ion Chromatography) | 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 |

Flame Atomic Absorption Spectrometry (FAAS) is a straightforward technique enabling the analysis of one inorganic element at a time, as opposed to multi-element 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. As Cd was present at lower concentrations than Zn and Pb in both studies, it was determined using graphite furnace atomic absorption spectrometry (GF AAS), as it provides lower detection limits.^{69,81} As an improved version of the GF AAS technique, the analytical technique high-resolution continuum source graphite furnace atomic absorption spectrometry (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, and Nakadi *et al.* for Si.^{72,80} In the HR-CS GF AAS, the use of a high-intensity xenon short-arc lamp, a high-resolution double monochromator, and charge coupled device (CCD) as a detector, represents an important improvement in the limits of detection (LOD).⁸⁰

Table 2. Total analysis methods for 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 US EPA 3051A standard method. | ICP-MS | Cr, Mn, Co, Ni, Fe, Cu, Zn, As, Cd, and Pb | He <i>et al.</i> ¹³ |

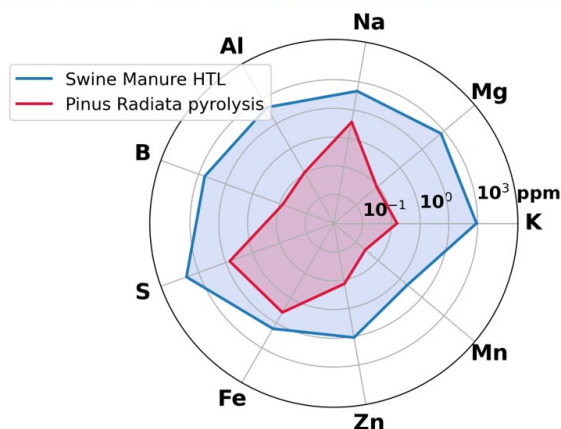
| | | | | | |
|-----------|---|---|----------------|---|------------------------------------|
| | | | TXRF | K, and Ca | |
| | Miscanthus grass | Microwave digestion of sample in HNO ₃ + HCl (3:1), following US EPA 3050B standard method. | ICP-MS | As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni, Se, Sb, Ag, Tl, U, V, and Zn | Arnold <i>et al.</i> ⁸² |
| | Avicennia marina (phyto remediation) | Microwave digestion of sample in HNO ₃ + HCl (3:1), following US EPA 3051A standard method. | ICP-MS | Cr, Cd, As, Pb, Ni, and Fe | He <i>et al.</i> ⁸³ |
| Pyrolysis | Water hyacinth (phyto remediation) | Microwave digestion 200 mg of sample in 5.00 mL of HNO ₃ , then diluted to 50 mL in water | FAAS | Pb | Jiu <i>et al.</i> ⁷⁷ |
| | Water hyacinth (phyto remediation) | Microwave digestion 200 mg of sample in 5.00 mL of HNO ₃ , then diluted to 50 mL in water | FAAS | Cr | Lin <i>et al.</i> ⁷⁸ |
| | Peach pit, Rice husk, Sugar cane straw | Direct weighing of the sample on graphite platform (5 and 10 mg) | HR-CS GF AAS | Pb | Duarte <i>et al.</i> 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) onto graphite platform. | HR-CS GF AAS | Si | Nakadi <i>et al.</i> ⁷² |
| | Pine and Cottonwood | Microwave digestion 500 mg of sample in 10.00 mL of HNO ₃ and 2.00 mL of H ₂ O ₂ | ICP-OES | Ca, K, Mg, Na, P, and S | Naske <i>et al.</i> ⁶⁷ |
| | Municipal solid waste | Wet digestion of samples in a solution of HNO ₃ , HClO ₄ , and HF (3:2:1 by volume) | FAAS GF AAS | Zn, and Pb Cd | Ding <i>et al.</i> ⁶⁹ |
| | Sedum plumbizincicola (phyto remediation) | Wet digestion of samples in a solution of HNO ₃ , HClO ₄ , and HF (3:2:1 by volume) | FAAS GF AAS | Zn, and Pb Cd | Zhong <i>et al.</i> ⁸¹ |

| | | | | | |
|-----------------|--|---|-------------------------|---|------------------------------------|
| | Biosludge | Wet digestion of the samples in 20 mL of HNO ₃ :HClO ₄ :HF (3:5:2) in a Teflon-lined closed vessel and placed in a high-pressure digestion oven (170 °C for 5 h). 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 <hr/> ICP-MS | Al, Ca, Fe, K, Mg, Na, S, Co and Zn <hr/> As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Sb, Se, Sr, Ag and V | Chiang <i>et al.</i> ⁸⁴ |
| Flash Pyrolysis | Willow plant stems and leaves (phytoremediation) | Microwave digestion 250 mg of sample in 4.00 mL of HNO ₃ and 2.00 mL of H ₂ O ₂ , then diluted to 25 mL in water | ICP-OES | Zn, Cd, and Pb | Stals <i>et al.</i> ⁷⁹ |
| | Chromated copper arsenate-treated wood (CCA-W) and Alkaline copper quaternary compounds-treated wood (ACQ-W) | Microwave digestion 500mg of sample in (10 ml) of HNO ₃ :HCl:H ₂ O ₂ (8:1:1, v/v), then diluted to 50 mL in water, followed by filtration | ICP-OES | As, Cu, Cr, Al, Ca, K, Mg, Na, P, and Si. | Kim <i>et al.</i> ⁵⁵ |
| Fast pyrolysis | Pinus radiata | Microwave digestion 300 mg of sample in 2.50 mL of HNO ₃ and 2.50 mL of H ₂ O ₂ , 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 <i>et al.</i> ⁷¹ |
| | Commercial bio-oils | Microwave digestion 200vmg of sample in 20.00 mL of HNO ₃ , HCl, and H ₂ O (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 <i>et al.</i> ⁸⁵ |

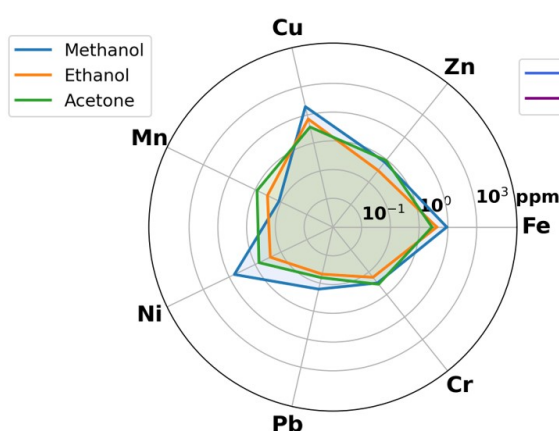
| | | Evaporation–ashing–digestion–IC method | IC | | |
|--|------------------------|--|---------|---|-----------------------------------|
| Thermochemical liquefaction (supercritical conditions) | Camellia oleifera cake | Wet digestion 0.5 g of sample in 10 mL of HNO ₃ + H ₂ O ₂ (2:1, v/v) for 10 min at rt. Then, heated at 80 °C until clear solutions. Then, evaporated and dissolved in 5 mL 0.2 M HNO ₃ , filtered through 0.22 µm filter paper, and made up to 10 mL with water. | ICP-OES | Zn, Pb, Cd, Ni, Fe, Mn, Cr and Cu | Chen <i>et al.</i> 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 <i>et al.</i> ⁷⁰ |
| Liquefaction | Swine manure | Microwave digestion of sample (200 C, 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 <i>et al.</i> 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 <i>et al.</i> ⁶² |

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 multi-elemental analysis of this type of samples. 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 multi-element total inorganic analysis of pyrolysis bio-oils. In the case of He *et al.*, total reflection X-ray fluorescence (TXRF) was used for the determination of the elements K and Ca instead of ICP-MS, since the isotopes of these elements are known to be difficult to analyze under low and medium-resolution conditions due to the significant interference from polyatomic ions. The ICP-OES technique has been used for the multi-elemental 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, depending on 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 (LOQ) than the microwave-ICP-OES method.⁸⁵

(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)

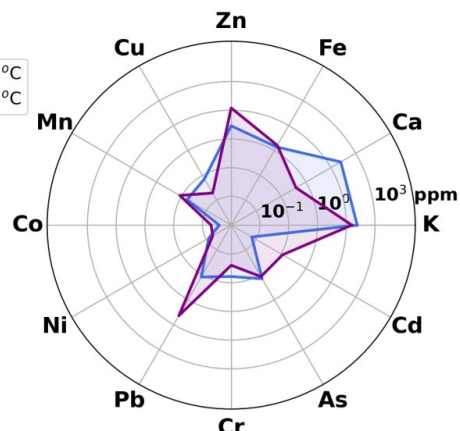


Figure 4. Inorganic finger prints of bio-oil samples with (a) different biomass and processes, (b) different solvents in HTL (hydrothermal-liquefaction) process, and (c) different temperatures in pyrolysis process.

Multielement analysis of bio-oils provides a complete overview of the behavior of the nutrients transferred to the bio-oils during the thermochemical conversion processes. In Figure 4a, it is shown the difference in the fingerprint of bio-oils obtained from different types of biomass and production processes. 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 on 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 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 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 HNO₃), F3 (oxidizable fraction, treated with H₂O₂) 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 to 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, careful consideration of sample matrix effects, and interpretation of data within the appropriate context. By adhering to these practices, it can be ensured that the data obtained is 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

Regarding 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 spearhead a fresh methodology to analyze sulfur species in bio-oils. Their

innovative approach incorporates comprehensive two-dimensional gas chromatography (GCxGC), combined with a selective sulfur chemiluminescence detector (SCD), and headspace gas chromatography coupled to a 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 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. Auersvald *et al.*'s research critically enhances the knowledge of sulfur speciation in bio-oils, providing invaluable insights for bio-oil upgrading.⁹⁴

ICP-MS alone and achieving parts-per-billion detection limits. Importantly, the methodology also revealed information about the selective affinity of inorganic species to 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 in order to get a valuable analytical tool.⁹⁵

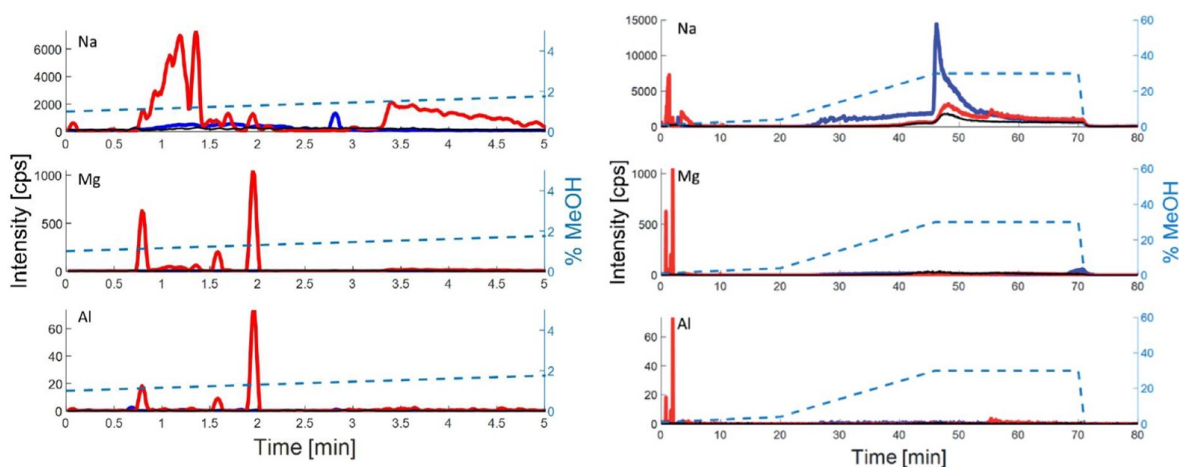


Figure 6. SFC-ICP-MS chromatograms of Na, Mg, and Al in the analysis of pyrolysis oil produced from milorganite fertilizer (blue), coal tar (red) and the THF blank (left: retention time 0 - 5 min, right: retention time 0 - 80 min). Adapted with permission from ref⁹⁵
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On 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 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 three months of aging (See Figure 7). These observations underscore the dynamic and complex nature of bio-oils, emphasizing the need for robust analytical techniques like 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 biofuel production processes' efficiency and sustainability.⁹⁷

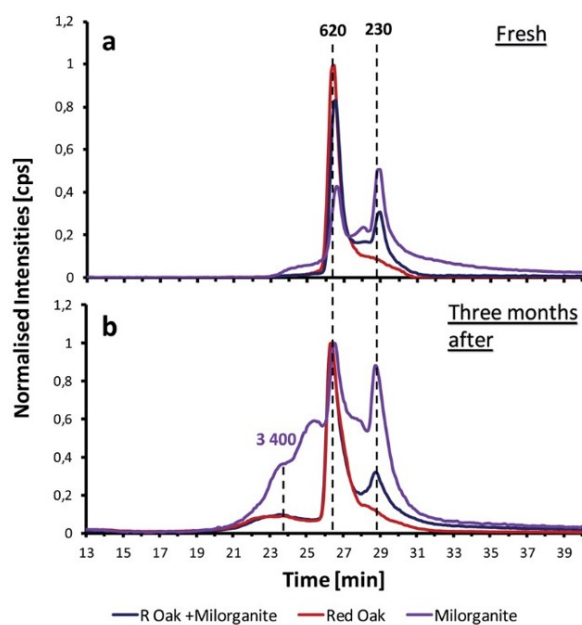


Figure 7. GPC-ICP-HRMS chromatogram corresponding to the analysis of P in the two xylene soluble extracts of three lignocellulosic feedstocks: red oak (red), milorganite (purple) and a 50:50 mixture of red oak and milorganite (blue), fresh sample (a) and three months after (b). Adapted with permission from ref⁹⁷ Copyright 2023 Royal Society of Chemistry.

When it comes to analyzing complex matrices like biofuels, it is reasonable to consider chromatographic techniques coupled with detection systems that provide better visibility of the analytes. However, high-resolution mass spectrometry (HRMS) techniques allow 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

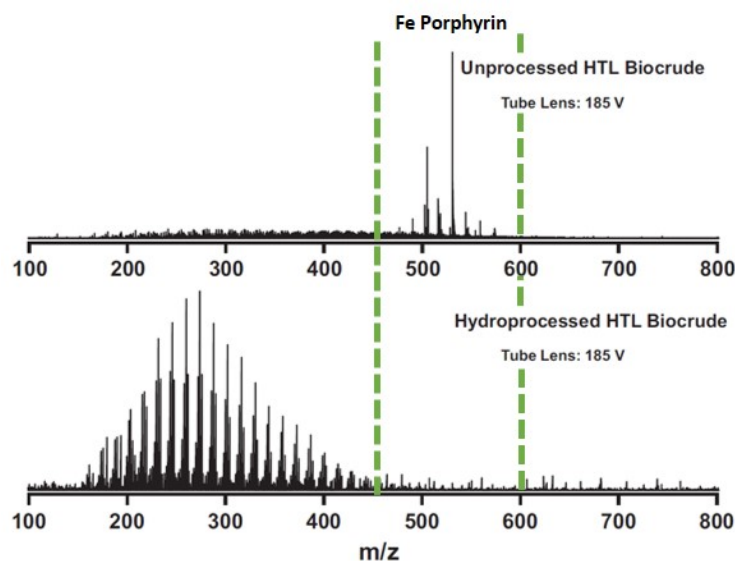


Figure 8. Positive-ion ESI FT-ICR mass spectra of cyanobacteria HTL biocrudes collected with a tube lens voltage of 185 V unprocessed (top) and hydroprocessed (bottom). Mass spectral signals for Fe porphyrins (m/z 450–600) dominate each mass spectrum and they are absent in the hydroprocessed HTL biocrude. Adapted with permission from ref⁶⁸ Copyright 2023 Elsevier.

Inorganic species in bio-oils have been analyzed using FT-ICR MS. As example, iron porphyrins from microalgae HTL bio-oil were studied by Jarvis *et al.*⁹⁸ They observed DBE (17-22) similar to previously reported for Ni and V porphyrins from heavy crude oil and bitumen DBE (17-25) by Liu *et al.*⁹⁹ Jarvis *et al.* 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.* on vanadyl porphyrins speciation in asphaltenes is an example of how the HRMS techniques can be coupled to chromatography system to get complementary information about the inorganic species in the samples.¹⁰⁰ Applying 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 ¹⁰² (2015), cater to the analysis of biofuels, specifically Trace Metals in Organics, employing techniques like ICP-MS¹⁰¹ and ICP-OES¹⁰². However, these standards aren't explicitly designed for bio-oils and may not address their unique characteristics. Similarly, ISO 16967, primarily applicable to solid

biofuels, might not be entirely suitable for liquid bio-oils. The round-robin study by the Haldor-Topsoe group exemplifies the discrepancy between labs when analyzing identical samples using ICP-OES and ICP-MS techniques, attributed to varied sample preparation methods.¹⁰³ Lieneman *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 due to 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 the one conducted by Lin *et al.*¹⁰⁴, which investigated the impact of potassium (K) on Pt-TiO₂ 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-TiO₂ interface, reducing 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 catalyst

performance and biomass conversion efficiency. The development of advanced analytical techniques, which merge chromatographic systems with ICP-MS and HRMS, is promising in 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 impacts of inorganic species on bio-oil production and processing is crucial. Utilizing high-resolution techniques like 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. CONCLUSIONS.

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 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 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 towards sustainable bio-oil technologies.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

Any funds used to support the research of the manuscript should be placed here (per journal style). [Brice: please add any funding sources];

Notes

The authors declare no competing financial interest.

ABBREVIATIONS

AAMEs, Alkali/Alkaline Earth Metals; ANP, National Agency of Petroleum, Natural Gas and Biofuels (Brazil); ASTM, American Society for Testing and Materials; 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 Esters; FAAS, Flame Atomic Absorption Spectroscopy; GC, Gas Chromatography; GC x 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-visible, Ultraviolet-Visible Detection; US EPA, United States Environmental Protection Agency.

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