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LETTER

Elemental Determination in Fuels and Biofuels: The Challenges and Opportunities for Analytical Chemistry

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While the fossil fuel industry continues to face upheavals, with discoveries of new fields, the global demand for energy and fuels drives research into alternative and renewable energies, such as biomass. This trend has been reinforced by recognizing the negative impacts of burning fossil fuels and using fossils as raw materials for industry to supply everyday demands.

In this scenario, analytical methods that are already established in laboratories worldwide must be updated to align with the trends and advances, providing new methods for the unique demands of this instigating sector, which has peculiar compositions and a broad scope of analytes. Heavy and light crude oil, coal, gas, different biomass types and their derived products are challenging samples that require experience and rigorous protocols for chemical characterization.

In terms of composition, petroleum from different reservoirs presents variations in chemical composition, both in their major hydrocarbons and in the types of elements present.[1] In contrast, biomass encompasses a diverse range, including lignocellulosic raw materials, waste, garbage, and agro-industrial residues, among others. This results in a diversity of compositions that significantly differ from hydrocarbon mixtures typical of fossil raw materials.[2]

Figure 1 summarizes the key aspects relevant to each context. When it comes to elemental composition, it is worth mentioning that the elements that most deserve attention in fossil raw materials and their fractions/products due to their presence and inherent impacts, in addition to sulfur (and nitrogen), are nickel and vanadium, alkaline and alkaline earth elements in petroleum and arsenic, cadmium, lead and mercury (in coal and natural gas).[3] In biomass raw materials and in the products and fractions derived from their conversion, the primary elements of interest are typically sodium, potassium, calcium, magnesium, aluminum, iron, copper, phosphorus, sulfur and chlorine.[4]

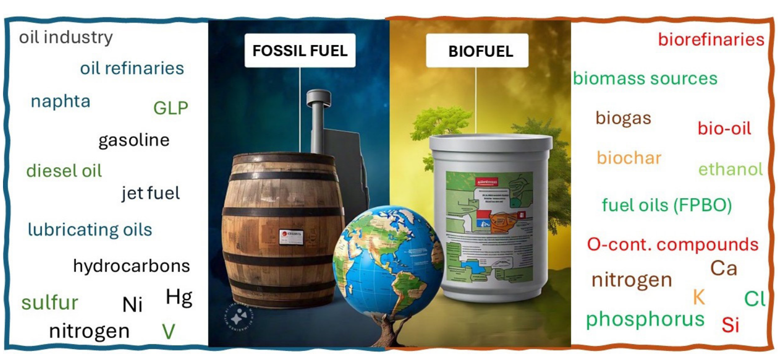

Figure 1. The key aspects of fossil fuels and biofuels covering the raw materials, main products and composition and target elements.

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A literature search covering the last 50 years indicates that some studies focused on elemental determination in fossil fuels began to be published at the beginning of the selected period (Figure 2). Conversely, it was only at the end of the last century that researchers began to focus on biofuels. More recently, there has been an increase in publications addressing both fossil and renewable fuels.

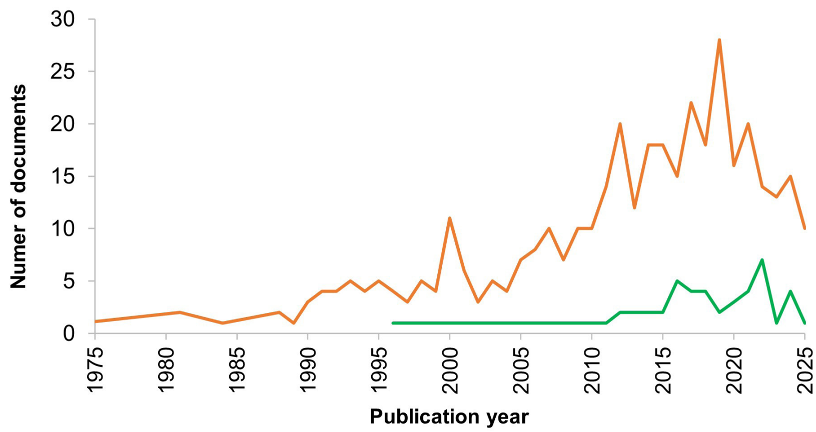

Figure 2. Number of articles published in the last decades on the topic of crude oil (orange line) or biofuels and biomass (green line) and elemental (or metal) determination. Data were obtained from Web of Science, on August 2025 (filter for document types - article or review article).

Although the industry requires methods for elemental determination, with official protocols for each type of raw material or product, the accuracy of these methods for various materials must be critically evaluated, especially due to the diversity of the matrices. Hence, while laboratories are relatively well equipped with methods to attend the requirements of petroleum industry, which has a relatively large number of standards from different entities, such as the American Society for Testing and Materials, the Institute of Petroleum, the Brazilian National Agency for Petroleum, Natural Gas and Biofuels), methods for biomass and biofuels remain relatively scarce. This scarcity is justified by technical limitations, and the recent and less widespread use of these materials, thereby justifying the smaller range of possibilities in terms of official standards. Nevertheless, the growing interest in alternatives to fossil fuels, in a way, justifies the scientific community's engagement to ensure accuracy, precision, and adequate detection and quantification limits, which is in line with the current trends in analytical chemistry and green/white chemistry.[1,5]

Despite the advances in instrumentation enabling powerful detection capabilities through techniques, such as atomic absorption, mass spectrometry or optical emission spectrometry, analyzing samples with variable compositions remains a challenge.[1,6-9] Some elements are relatively less impaired by interferences, particularly those that are not difficult to ionize in inductively coupled plasmas or microwave-induced plasmas. However, the limitations related to determining non-metals (due to the low emission wavelengths) and the low mass-to-charge ratio for mass spectrometry (e.g. Cl, Br, S, and P) hinder method development, especially at low concentrations. In this context, methods for non-metals, particularly the halogens and for the speciation analysis, seem to be the main bottlenecks, regardless of the sample type within this context.[10-12]

Equipment continues to be improved to expand applications, although for samples with oil-based compositions or solids, one remaining limitation is related to the introduction systems that work well with aqueous solutions. Some examples of successful applications are documented, although they often encounter interferences and difficulties with calibration. Moreover, direct analysis is also possible, with techniques such as X-ray fluorescence spectrometry, but limitations in the supply chain of calibration standards and matrices is not capable of covering all the range of composition. Thus, matrix-interferences continue to restrict the scope of matrices and analytes that can be measured accurately.

Sample preparation that converts samples to aqueous solutions is a common strategy that facilitates conventional calibration and fast analysis with conventional nebulization systems. Nevertheless, decomposing organic-based matrices can be a problem even with powerful systems allowing high pressure and temperature, namely high-performance microwave-assisted systems.[13] Primary challenges to circumvent include gas samples and samples from non-conventional crude oil reservoirs, in addition to the samples composed of mixtures of fossil fuels and biomass-derived fractions.

Hence, considering the task of determining the elemental composition of fossil fuels and biofuels (and general biomass-derived fractions), the application of classical and conventional methods, especially in the context of the petroleum industry, is by itself a critical aspect. These methods often involve the use of protocols based on high amounts of solvents that take hours to develop, compared to the current precepts in the development of analytical methods, despite ensuring ease of execution and assuring accuracy and reproducibility. This represents a target for analytical chemistry, which is centered on developing alternatives that address these problems. In addition, developing systematic evaluations, adjusting conditions for various types of matrices and elements, and achieving the necessary quantification limits are other points of attention. Lastly, in addition to the inherent limitations of the chosen or available method or technique, overcoming the lack of certified reference materials is another obstacle to overcome. Despite this, research in this area has continued to garner increasing attention from researchers and economic and global efforts.

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