Smart note | 001624

Trace elemental analysis

Analysis of elemental contaminants in renewable fuel feedstocks

After decades of experience in processing crude oil, refiners face a new challenge of converting plant and animal-based feedstocks into fuel sources. Elemental analysis of fuels derived from plant and animal-based feedstocks is an important application for the modern renewable energy industry. It is essential for quality control, equipment condition monitoring, waste recycling, and even post-processing in the production process. This Smart Note will explain how the elemental composition of renewable fuel feedstocks samples from a major refining company can be assessed using techniques based on inductively coupled plasma and highlight some important aspects to consider in practice.

The measurement of trace metals in plant/animal-based feed feedstocks may create specific challenges related, for example, to sample nature and homogeneity so that specific solutions may need to be employed.

Why is it necessary to monitor trace metals in renewable fuel feedstocks?

Biofuels play an important role in the world's effort to reduce greenhouse gas (GHG) emissions in transport. When converting a plant or animal byproduct into a renewable hydrocarbon biofuel, a catalyst will likely be a key component of that process.

A common conversion technique currently employed is hydrotreating. Hydrotreating involves reacting the feedstock with hydrogen under elevated temperatures and pressures, in the presence of a catalyst. The catalysts utilized in this process are prone to "poisoning" or rapid deactivation by way of adsorption of impurities in the feed. Trace metal impurities are inherent in certain renewable feedstocks.

What is the business impact of understanding your renewable fuel feedstock metals composition?

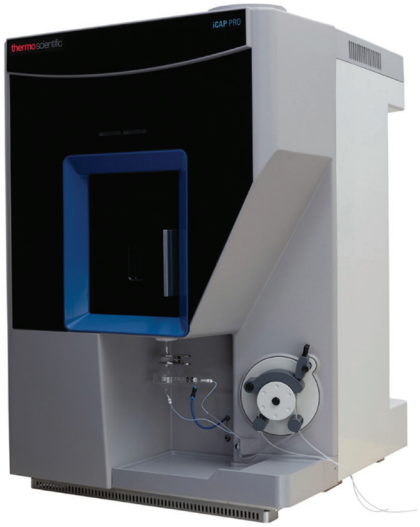
A poisoned catalyst will, at minimum, cause an interruption of plant operations, and in the worst case, create a need to replace the spent catalyst. This can create several areas of incurred cost, such as profit loss from plant downtime, purchase of fresh catalyst, and unit turnaround staffing. Identifying and quantifying the feedstock's impurities can allow you to plan an appropriate pre-treatment process to remove the unwanted impurities, and/or accurately forecast the rate at which your catalyst is deactivating and will need to be regenerated or replaced.

Who should be monitoring their renewable fuel feedstocks?

Refiners who are exclusively producing renewable/biofuels or co-processing with conventional hydrocarbon streams. The U.S. Renewable Fuel Standard, administered by the EPA, sets biofuel blending mandates for oil refiners. These mandates require that transportation fuel solid in the U.S. contain a minimum volume of renewable fuels. Refiners must comply with this mandate or buy tradeable credits (RINs) from those that comply.

Which instruments can be used for the determination of trace elements in fuel feedstocks?

The analysis of trace elements as impurities in renewable fuel feedstocks can be conducted with different techniques. Inductively coupled plasma-optical emission spectroscopy (ICP-OES), performed with an instrument such as the Thermo Scientific™ iCAP™ PRO Series ICP-OES, is often the primary choice, as it provides significant advantages, including simplicity, speed, and robustness. It is also a highly sensitive technique with a large dynamic range, enabling the detection of impurities in concentration ranges between sub $\mu g \cdot L^{-1}$ and % levels.



iCAP PRO ICP-OES system

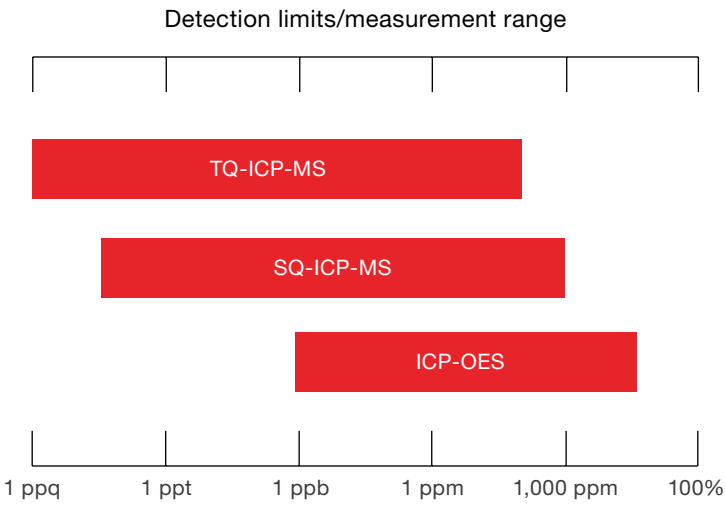
- Excellent matrix tolerance and flexibility for different sample types
- Detection limits generally suffice for many applications
- Good dynamic range of typically 6 orders
- Reduced analysis time due to simultaneous measurement of the full spectrum in iFR Mode

iCAP TQ ICP-MS system

- Some sample matrices may require accessories for efficient analysis
- Excellent detection limits for challenging applications
- Higher dynamic range (~10 orders)
- Very short analysis time possible due to single Kinetic Energy Discrimination Mode
- Isotopic information available if required

Another strong tool is inductively coupled plasma mass spectrometry (ICP-MS), performed with a system such as the Thermo Scientific™ iCAP™ Qnova Series ICP-MS. ICP-MS provides superior detection limits, which can be several orders of magnitude lower than those obtained with ICP-OES. However, this technique is more difficult to apply in laboratories that are seeking to analyze different sample types, such as alternating between renewable fuel feedstocks and produced waters.

Both techniques allow for simultaneous analysis of a large number of elements in the periodic table. Because of that, full elemental determination can be performed within a maximum measurement time of 5 minutes by an ICP-OES system and within 2–3 minutes by an ICP-MS system. Further acceleration of sample turnover time can be achieved when using valve-based systems for integrated sample delivery.



Technique	Analysis time	TDS tolerance
ICP-OES	All in 1–5 min	Up to 25%
SQ-ICP-MS	All in 2–3 min	Typically below 0.5%, but can be expanded using Argon Gas Dilution (AGD)
TQ-ICP-MS		

What are the benefits of using ICP-OES?

The iCAP PRO XPS Duo ICP-OES system is the ideal choice for laboratories looking for a fast, flexible, and highly productive instrument for renewable fuel feedstock sample analysis. The instrument allows the user to develop and apply methods with greatest flexibility, i.e., optimized analysis conditions for both organic as well as aqueous sample types. With minimum integration time, and the ability to read out the entire optical spectrum (UV and visible range) in a single exposure using intelligent Full Range (iFR), the system provides unmatched sample turnover time with excellent stability. The enhanced Ultra Violet (eUV) analysis mode can be used to further enhance sensitivity for elements that fall in the wavelength range of 167.021–240.063 nm, including critical analytes such as mercury, sulfur, lead, and cadmium. The dual view configuration with the vertical torch design allows for axial and radial viewing for samples requiring the measurement of low and high concentrations in the same run. The unique design featuring a vertical torch orientation in iCAP PRO Series ICP-OES instruments increases robustness for challenging samples and enables high-matrix and direct measurement on organic samples. Table 1 shows typical iCAP PRO XPS Duo ICP-OES system configuration parameters for analyzing fuel feedstock samples.

Table 1. iCAP PRO XPS Duo ICP-OES system configuration parameters

Nebulizer	MiraMist
Spray chamber	Baffled cyclic
Nebulizer flow	0.40 L/min
Aux flow	1.50 L/min
Coolant flow	12.5 L/min
Pump tubing	Sample: white-orange
	Waste: white-white
Pump speed	30 rpm
RF power	1150W
Integration time	15 s
Radial view height	11 mm
Uptake time	45 s
Rinse time	45 s

With the above instrument settings, excellent DLs for a wide range of analytes with multiple wavelengths have been achieved, as shown in Figure 1 (Axial) and Figure 2 (Radial).

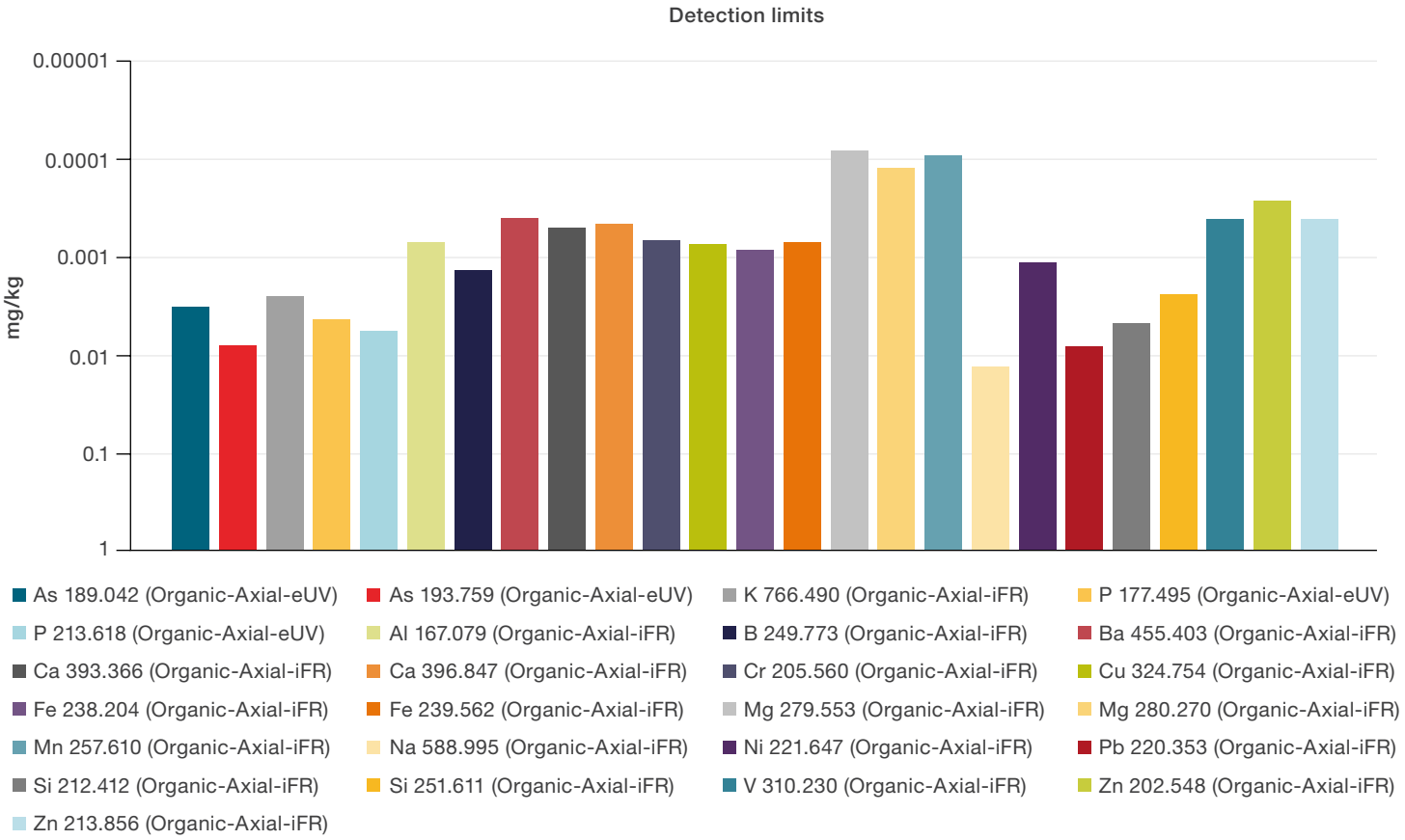
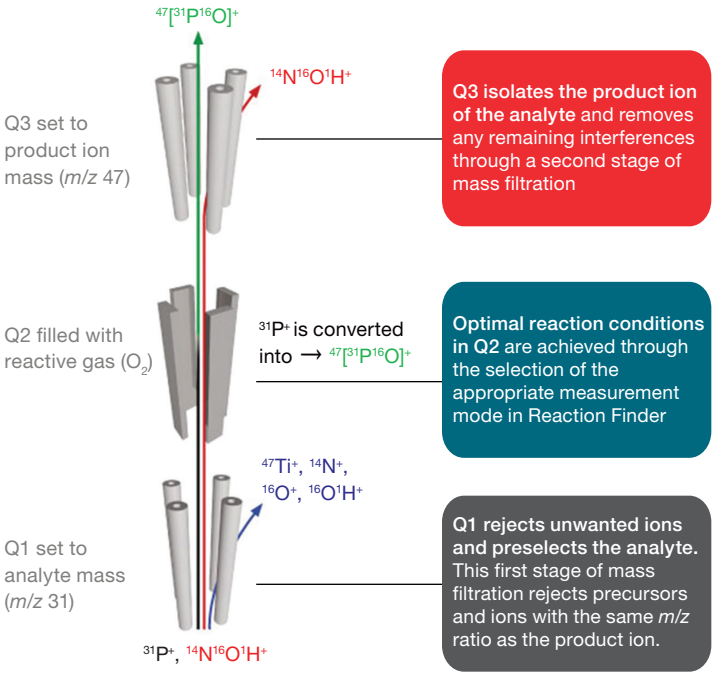


Figure 1. Detection limits of the elements with different wavelengths (Axial)

Figure 2. Detection limits of the elements with different wavelengths (Radial)

What are the benefits of using ICP-MS?

Single quadrupole ICP-MS instruments, such as the Thermo Scientific™ iCAP™ RQ ICP-MS, are the perfect choice for laboratories testing for trace elements in different kinds of sample matrices. These instruments have become workhorses in many analytical laboratories due to their straightforward interference removal, which allows simple operation and high sample turnaround. Triple quadrupole ICP-MS systems are more often found in research laboratories but have become increasingly accepted in applied analytical testing laboratories, as their advanced capabilities to remove interferences allow access to difficult elements more easily and provide higher confidence in the data produced. The process of interference removal using O_2 as a reactive gas is highlighted using ^{31}P analysis as an example.



The selected target analyte $^{31}P^+$ enters Q1 together with all interferences, here mostly polyatomic interferences formed from other components of the sample matrix and the ambient air surrounding the plasma. In the first quadrupole (Q1) all ions apart from the target analyte are rejected, so that possible side reactions and contributions of other interferences at the intended product ion mass are eliminated.

In Q2, the target analyte is reacting to form $^{47}[^{31}P^{16}O]^+$ using the reactive gas, whereas the interference is not reacting in the same way.

The third quadrupole (Q3) performs a final mass filtration step and isolates the product ion once again from other ions with different *m/z* ratios. The target analyte can therefore be detected free from interference and hence any unwanted bias.

An iCAP-TQ ICP-MS was used to analyze selected fuel feedstock samples for a major refining company. Table 2 summarizes the operating configuration and parameters used during the data acquisitions for the samples. Please note that the results displayed in the following will only focus on a fraction of the analytes typically analyzed in renewable fuel feedstocks.

Table 2. System components/hardware setup of the iCAP TQ ICP-MS system

System components/hardware setup	
Component	**Name/description**
Acquisition modes	TQ-O_2, SQ-KED
Torch	Quartz – organics
Torch center tube/Injector	Quartz - 1.0 mm i.d.
Spray chamber	Quartz cyclonic
Nebulizer	PFA-ST concentric
Sample cone	Pt sample cone
Skimmer cone	Pt skimmer cone – insert version
Skimmer cone insert	2.8 mm – high sensitivity
Peristaltic pump tubing – sample	Free aspirated
Peristaltic pump tubing – waste	Santoprene™ – gray/gray – 1.295 mm i.d.
Peristaltic pump speed	20 rpm

Table 3 shows the analytical figures of merit obtained using the parameters mentioned above. Direct comparison to the detection limits obtained previously using ICP-OES demonstrates the superior sensitivity of ICP-MS.

Table 3. Calibrations figures of merit

Isotope	Range (µg/L)	IDL (µg/L)	BEC (µg/L)	R^2
^{31}P ($^{31}P^{16}O$)	0–200	0.308	11.28	>0.9999
^{39}K	0–200	0.138	2.097	0.9996
^{75}As ($^{75}As^{16}O$)	0–200	0.006	0.048	0.9999

To verify the accuracy of the results obtained, ideally a certified reference material closely matching the sample type is recommended, but if this is not available, spike recovery study can be performed as an alternative. Here, this test was done using soy, previously spiked with the analytes of interest at a concentration of approximately 20 µg·L^{-1}. The results are summarized in Table 4. Quantitative recovery was obtained for all elements investigated here.

Table 4. Spike recovery study on a fuel feedstock sample

Element	Soy 1 (µg/L)	Spike level (µg/L)	Soy 1 spike (µg/L)	Spike recovery (%)
^{31}P ($^{31}P^{16}O$)	N.D.	20.29	20.114	106
^{39}K	0.261	20.29	18.538	90
^{75}As ($^{75}As^{16}O$)	0.037	19.67	21.322	108

Do I need special devices or accessories for the analysis of oil samples?

In comparison to the analysis of samples in aqueous solutions, the difference in vapor pressure and viscosity is a challenge when analyzing organic matrices. This leads to the need for a dedicated configuration of the sample introduction system. Whereas samples with high viscosity, such as crude oil or fuel oil, require heating of the sample introduction system components to remain fluid, samples with a lower boiling point need cooling of the spray chamber to avoid overloading the plasma and sudden extinction. In many cases, samples can be diluted using a suitable solvent to alleviate some of the issues. Examples of suitable diluents, available in sufficiently high purity, are kerosene, xylene, or PremiSOLV™. Another critical point is often the dilution of the original sample prior to analysis. Due to the different density and viscosity, preparation of dilutions is ideally done gravimetrically, as opposed to volumetric dilutions often applied for aqueous solutions.

Organic resistant tubing should be used for analyzing fuel samples, for example phthalate-free Solvent Flex tubing, available with different diameters for sample uptake or drain. Another dedicated device for oil analysis is the Teledyne CETAC™ ASX-7400 stirring autosampler (Figure 3), here connected with an iCAP PRO XPS Duo ICP-OES system. This autosampler provides a dedicated and integrated solution for the testing of oil-based samples. It contains a stirrer, which assures that samples can be homogenized prior to analysis in a precise and repeatable manner. For laboratories performing the analysis of both aqueous and organic matrices, it provides a dual rinse station, so that switching between two sample types is simplified. The ASX-7400 Oil autosampler is included in the plug-in for Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution Software, so that it is fully embedded and controlled from within the same user interface as the main instrument used for analysis.

Figure 3. Teledyne CETAC ASX-7400 stirring autosampler connected with an iCAP PRO XPS Duo system

A ceramic torch (D-Torch for the iCAP PRO Series ICP-OES; PLUS-Torch for the iCAP Qnova Series ICP-MS) is recommended for laboratories running a higher number of such samples. Conventional torches can devitrify when exposed to the higher temperatures and intense UV emission of a plasma running organic solvents, leading to increased maintenance requirements and higher cost due to potentially premature failure. Ceramic torches are well-known to withstand such demanding conditions and can be used for decreasing the background signals for some analytes, in particular silicon. They offer improved lifetime and reduced maintenance for high matrix samples, especially for organic samples such as fuel feedstock.[1]

D-Torch for iCAP PRO Series ICP-OES

PLUS-Torch for iCAP Qnova Series ICP-MS

Reference:

1. Product Spotlight 44485: Thermo Scientific iCAP Qnova Series ICP-MS – PLUS Torch for improved ICP-MS analysis of challenging samples.

Learn more at **thermofisher.com/tea**