Challenge
Robust determination of metallic contaminants in a highly organic matrix over a wide measurement range

Solution
Exact analysis of elements from ppb to % in pyrolysis oil via long-term stable HR ICP-OES

Intended audience
Operators of pyrolysis plants, actors in the field of chemical recycling, further processors of pyrolysis oil, operators of refineries, contract labs

Metal Analysis of Waste Plastic Pyrolysis Oil via HR Array ICP-OES

Introduction

While plastics provide great benefits, plastic waste has become a global issue. In 2019, only 9% of global plastic waste was recycled.[1] Chemical recycling – a relatively new technology – can help us significantly to increase that figure, enabling us to move towards a circular economy for plastics. In contrast to traditional recycling methods, this new technology allows us to recycle mixed plastic waste as well as to turn it into new plastic products without any restrictions on purity, plastic type, or color.

Pyrolysis oil, the oil that is generated during the chemical recycling of plastics, often exceeds feedstock specifications for its next place of processing – the steam cracker – in terms of Si, Na, Fe, Pb, Hg, and other metals. The exact contaminant levels are highly variable, as no single batch of processed waste equals the next. Therefore, the analytical characterization of pyrolysis oil is crucial.

Optical emission spectrometry with inductively coupled plasma (ICP-OES) allows for a rapid and comprehensive analysis of metals in pyrolysis oil. Specifically, the PlasmaQuant 9100 Elite offers the wide measurement range (ppb to %) that is needed for pyrolysis oil. The optical resolution of 2 pm @ 200 nm helps to correctly differentiate the analyte line from the complex spectral interferences of the organic matrix. At the same time, the high-frequency generator delivers a plasma with superior robustness even for a highly organic sample such as pyrolysis oil.

This application note presents measurement results for two pyrolysis oil samples along with outstanding method detection limits. Additionally, the samples were spiked with a known analyte concentration to determine recovery rates. To demonstrate the unique long-term stability of the instrument, one pyrolysis oil sample was measured for six hours.

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Materials and Methods

Samples and reagents

The following chemicals were employed for standards and sample preparation:

- CONOSTAN® Standard S21+Be+K+Li+Sb multielement organometallic standard at 100 mg/kg (CONOSTAN®)
- 5000 mg/kg sulfur oil-based standard (CONOSTAN®)
- 100 mg/kg arsenic oil-based standard (CONOSTAN®)
- 100 mg/kg mercury oil-based standard (CONOSTAN®)
- 1000 mg/kg yttrium oil-based standard (CONOSTAN®)
- Blank oil (CONOSTAN®, 75 cSt) and Xylol (Roth, ≥ 99 %, p.a.)

Two different pyrolysis oil samples (Pyrolysis oil 1 and Pyrolysis oil 2) were investigated.

Sample preparation

The sample preparation was designed to reduce the viscosity of the sample and minimize potential interferences. Yttrium was utilized as an internal standard. The yttrium standard was diluted with xylene to achieve a final concentration of 2 mg/kg. This yttrium solution served as the diluent for each sample and standard. To mitigate viscosity differences between samples and standards, blank oil was added as needed, resulting in a final solution containing 10% w/w oil. Prior to sample dilution, samples were homogenized in an ultrasonic bath for 15 minutes and subsequently centrifuged (1125xg, 5 min). The supernatant was then diluted with the Yttrium solution (dilution factor: 10).

Instrument settings

A PlasmaQuant 9100 Elite ICP-OES combined with a Teledyne Cetac Oils 7400 autosampler was used for the analysis. The instrument was equipped with an organic sample introduction kit. The instrument parameters can be seen in Table 2.

Calibration

The calibration blank value was prepared by diluting blank oil in the yttrium solution. Calibration standards were generated through gravimetric dilution of stock solutions to achieve the required concentrations. The organometallic multi-element standard comprises metal sulfonates, hence separate calibration standards for sulfur were derived from the respective single-element oil-based standard (refer to Table 1).

Table 1: Concentration of calibration standards

Standard	Concentration [mg/kg]			
	Ag, Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Si, Sn, Ti, V, Zn	As	Hg	S
Cal 0	0	0	0	0
Std. 1	0.298	0.305	0.293	-
Std. 2	2.56	1.09	0.992	-
Std. 3	-		-	125
Std. 4	-		-	500

Table 2: Instrument settings

Parameter	Setting
RF power	1.450 W
Plasma gas flow	15 L/min
Auxilliary gas flow	1.75 L/min
Nebulizer gas flow	0.30 L/min
Nebulizer	Micromist, borosilicate nebulizer, 0.4 L/min
Spray chamber	Borosilicate cyclonic spray chamber with dip tube, 50 mL
Outer tube / inner tube	Quartz / quartz
Injector	Quartz, inner diameter 1 mm
Pump tubing	Viton
Sample pump rate	0.40 mL/min
Fast mode	0.80 mL/min
Read delay	90 s
Torch position[1]	-3 mm

* Spacing between injector and coil further suppresses carbon deposits on the injector tip

Method and evaluation parameters

Analytical wavelengths were selected based on the exceptional spectral resolution of the Analytik Jena PlasmaQuant 9100 Elite, which enables interference-free measurements of the most sensitive emission lines. The Analytik Jena ASpect PQ software utilized automatic background correction (ABC) for data evaluation.

The ABC function dynamically adjusts a global baseline to the entire spectral background throughout the entire sample analysis. Additionally, the CSI software tool (Correction of Spectral Interferences) was employed for specific element lines to eliminate background signals originating from the organic matrix. Evaluation parameters are detailed in Table 3.
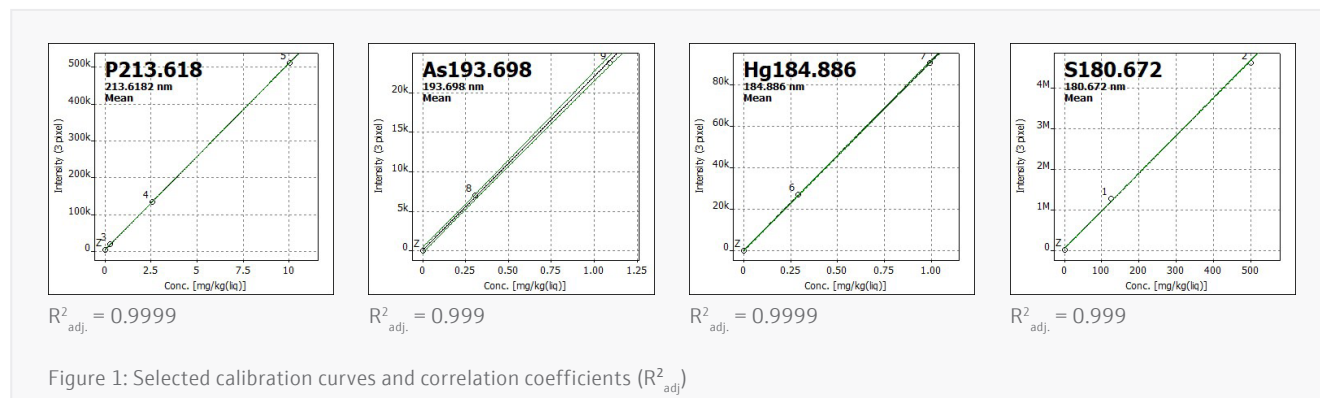
Table 3: Method parameters

Element	Line [nm]	Plasma observation	Integration	Meas. time [s]	Evaluation			
					Pixel	Baseline correction	Polynom	Correction model
Ag	328.068	axial	Peak	3	3	ABC	auto	-
Al	396.152	axial	Peak	3	3	ABC	auto	CSI
As	193.698	axial	Peak	3	3	ABC	auto	CSI
Ba	455.403	radial	Peak	3	3	ABC	auto	CSI
Ca	315.887	axial	Peak	3	3	ABC	auto	CSI
Cd	214.441	axial	Peak	3	3	ABC	auto	-
Cr	267.716	axial	Peak	3	3	ABC	auto	CSI
Cu	324.754	axial	Peak	3	3	ABC	auto	CSI
Fe	259.940	axial	Peak	3	3	ABC	auto	-
Hg	184.886	axial	Peak	3	3	ABC	auto	-
K	766.491	axial	Peak	3	3	ABC	auto	-
Li	670.791	axial	Peak	5	3	ABC	auto	CSI
Mg	280.271	axial	Peak	3	3	ABC	auto	CSI
Mn	257.610	axial	Peak	3	3	ABC	auto	CSI
Mo	202.030	axial	Peak	3	3	ABC	auto	-
Na	589.592	axial	Peak	3	3	ABC	auto	CSI
Ni	221.648	axial	Peak	3	3	ABC	auto	-
P	213.618	axial	Peak	3	3	ABC	auto	-
Pb	220.353	axial	Peak	3	3	ABC	auto	-
S	180.672	axial	Peak	3	3	ABC	auto	-
Sb	217.581	axial	Peak	3	3	ABC	auto	-
Si	251.611	axial	Peak	3	3	ABC	auto	-
Sn	189.927	axial	Peak	3	3	ABC	auto	CSI
Ti	334.941	axial	Peak	3	3	ABC	auto	-
V	309.311	axial	Peak	3	3	ABC	auto	-
Zn	213.856	axial	Peak	3	3	ABC	auto	CSI

ABC: Automatic Baseline Correction; CSI: correction of spectral interferences

Results and Discussion

A linear calibration function was achieved for all elements with a correlation coefficient of >0.999, which indicates an excellent linearity in the complete calibration range. Selected calibration curves as well as the adjusted correlation coefficients of this method are shown in figure 1.

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Figure 1: Selected calibration curves and correlation coefficients (R^2_{adj})

The measurement results for the samples are listed in the following Table 4. Additionally, the samples were spiked with a known analyte concentration to assess potential matrix effects. The recovery rates and the method detection limits (MDL), considering all dilution factors of the analytes are listed in Table 4.

Table 4: Concentration of samples, recovery rates and method specific detection limits (MDL)

Element	MDL [µg/kg]	Pyrolysis oil 1			Pyrolysis oil 1		
		Concentration measured [mg/kg]	Spike [mg/kg]	Recovery [%]	Concentration measured [mg/kg]	Spike [mg/kg]	Recovery [%]
Ag	2.2	0.776	1.14	103	0.626	0.962	106
Al	42.5	<MDL	1.14	104	<MDL	0.962	102
As	47.3	0.095	1.12	100	<MDL	1.02	95
Ba	12.3	0.107	1.14	105	0.120	0.962	100
Ca	8.0	<MDL	1.14	99	0.099	0.962	95
Cd	1.1	0.052	1.14	99	0.367	0.962	98
Cr	1.2	<MDL	1.14	104	<MDL	0.962	98
Cu	2.3	0.079	1.14	105	0.151	0.962	95
Fe	1.0	0.955	1.14	103	0.467	0.962	92
Hg	15.5	0.042	0.94	93	<MDL	1.03	109
K	66.2	<MDL	1.14	96	<MDL	0.962	90
Li	4.3	<MDL	1.14	106	<MDL	0.962	91
Mg	1.2	<MDL	1.14	103	0.034	0.962	96
Mn	1.5	0.028	1.14	104	0.012	0.962	103
Mo	4.3	0.231	1.14	101	0.285	0.962	105
Na	319	<MDL	1.14	99	<MDL	0.962	84

Continuation of Table 4: Concentration of samples, recovery rates and method specific detection limits (MDL)

Element	MDL	Pyrolysis oil 1			Pyrolysis oil 1		
		Concentration measured [mg/kg]	Spike [mg/kg]	Recovery [%]	Concentration measured [mg/kg]	Spike [mg/kg]	Recovery [%]
Ni	3.6	<MDL	1.14	102	0.928	0.962	94
P	30.5	10.05	1.14	102	6.43	0.962	94
Pb	33.6	<MDL	1.14	102	<MDL	0.962	106
S	116	26.33	-	-	47.5	68.7	100
Sb	22.5	0.070	1.14	101	<MDL	0.962	105
Si	6.9	2615	-	-	10.2	0.962	97
Sn	11.4	<MDL	1.14	101	<MDL	0.962	104
Ti	1.0	0.007	1.14	101	<MDL	0.962	102
V	2.9	0.061	1.14	104	<MDL	0.962	101
Zn	1.6	0.063	1.14	103	0.214	0.962	102

The recoveries of almost all analytes were within ±6%, which illustrates the excellent applicability of the analytical method for the determination of impurities in pyrolysis oils.

The robustness of the instrument is crucial for laboratories that want to directly analyze organic matrices such as pyrolysis oils. The PlasmaQuant 9100 Elite's high-frequency generator delivers a plasma with superior robustness, providing a strong and consistent signal intensity even for highly organic matrices. To demonstrate the outstanding performance and long-term stability of the instrument, pyrolysis oil 1 was spiked with an analyte concentration of 1 mg/kg and measured for six hours. Recoveries in the range of 95-106 % were obtained (see Figure 2). Relative standard deviations below 1.6% indicate an extremely stable performance of the instrument throughout the long-term measurement.
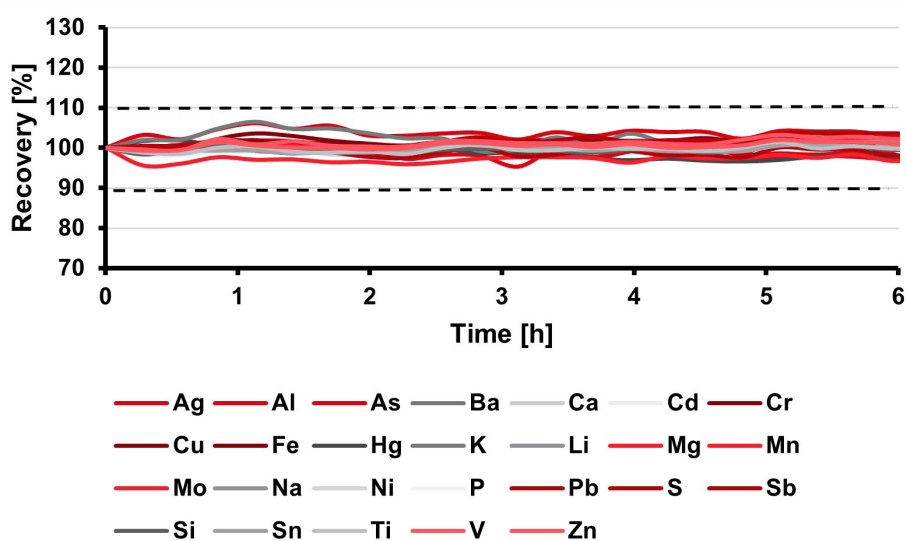

Figure 2: Percentage recoveries of spiked analytes (1 mg/kg) in pyrolysis oil during a 6-hour sequence. The relative standard deviation (RSD) values for all elements were below 1.6%.

By using the CSI tool, interfering background signals can be precisely removed from the recorded sample spectrum. This results in a clean and easy to evaluate analyte peak, which usually contributes to an improved signal-to-noise ratio and consequently improved measurement accuracy and precision. Figure 3 shows the effectiveness of the CSI tool using tin (Sn) as an example. On the left side, a recorded spectrum with significant background signals is shown. The evaluation of such a peak with a low-resolution instrument leads to an erroneous quantification of the analyte in question. The CSI-corrected spectrum, shown on the right side in Figure 3, shows an analyte peak that can be easily and reliably evaluated due to the significantly improved signal-to-noise ratio. Furthermore, a lower detection limit can be achieved.
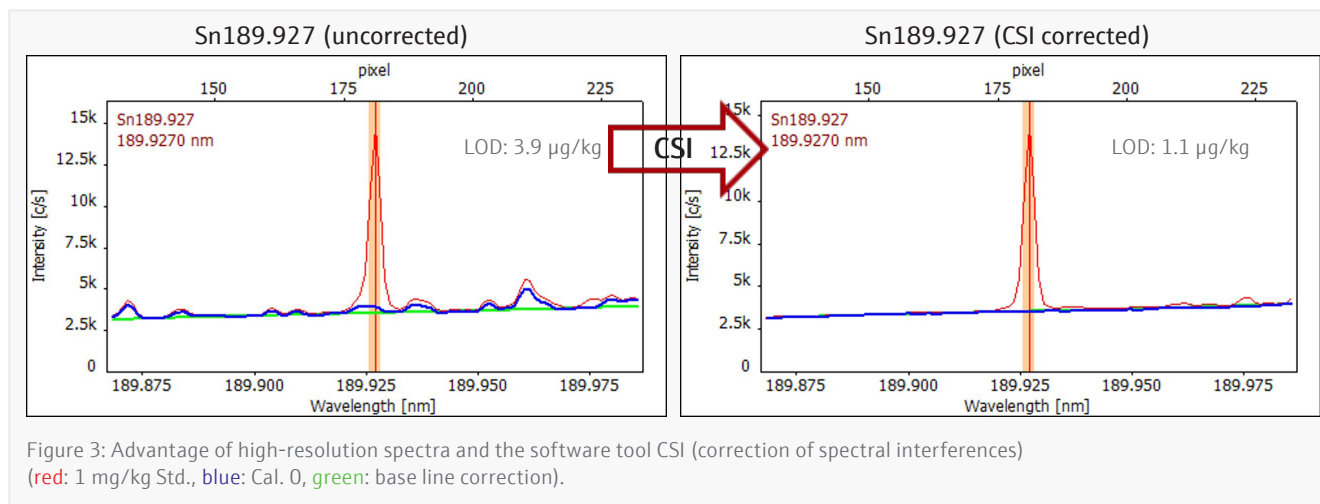
Figure 3: Advantage of high-resolution spectra and the software tool CSI (correction of spectral interferences) (red: 1 mg/kg Std., blue: Cal. 0, green: base line correction).

Summary

The presented methodology enables a simple routine analysis of trace impurities in pyrolysis oils. Typical challenges in the analysis of organic samples (e.g., the instability of the plasma, signal fluctuations due to carbon deposits and matrix-related spectral interferences) are successfully overcome.

High accuracy and precision of results are achieved by consistent excitation of the organic samples with the high-frequency generator of the PlasmaQuant 9100 Elite. Carbon deposits on the glass components are suppressed by using a vertical torch, the unique V-Shuttle Torch. In addition, an optimized torch position guarantees minimal soot formation and thus excellent long-term stability of the measurements. The high spectral resolution of the PlasmaQuant 9100 Elite of 2 pm @ 200 nm in combination with the CSI software tool ensures the separation of analyte and background signals. Thus, the non-specific background resulting from the high carbon content in the pyrolysis oil is efficiently separated from the analyte emission lines and spectral interferences are eliminated. It allows the use of the most sensitive emission lines and thus guarantees highest sensitivity for all i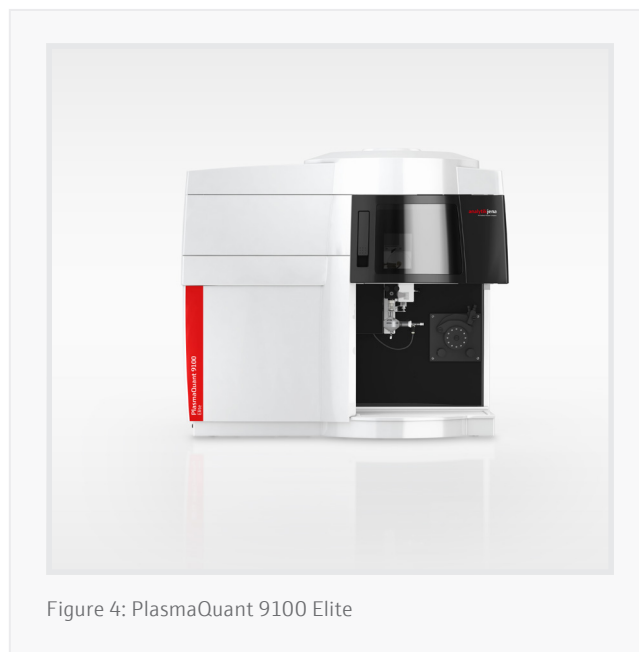nvestigated elements. In addition, data evaluation is supported by automatic baseline and spectral corrections using software tools such as ABC and CSI. This achieves detection limits in the lower µg/kg range, ensuring precise and accurate determination of the required analytes.

Figure 4: PlasmaQuant 9100 Elite

Recommended device configuration

Table 5: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant 9100 Elite	818-09101-2	High-resolution ICP-OES
Teledyne Cetac Oils 7400	810-88122-0	Sampler for analysing oils and coolants with stirring function and double rinsing station
ORGANIC KIT	810-88008-0	Sample introduction system recommended for petrochemical samples and organic solvents
Consumables Set Organic Kit	810-88044-0	Recommended consumables for approx. 1000 analyses

References

[1] OECD (2022), Global Plastics Outlook: Economic Drivers, Environmental Impacts and Policy Options, OECD Publishing, Paris, https://doi.org/10.1787/de747aef-en