Challenge
The determination of total fluorine (TF) in pyrolysis oil requires combustion at high temperatures under pyrohydrolytic conditions and thus a special digestion system with a water dosing unit.

Solution
The ICprep pyrohydrolytic digestion system ensures complete conversion of all fluorine compounds.

Intended audience
Research and routine laboratories for plastic waste recycling and pyrolysis oil production and further processing, and independent contract analysis center

Sample digestion and determination of fluorine in pyrolysis oil

Introduction

The production and utilization of pyrolysis oil is becoming increasingly important in times of raw material shortages and energy transition. A wide variety of materials can be used as feedstock to produce pyrolysis oil, with biomass and plastic waste currently being the most common raw materials. In terms of utilization, pyrolysis oil is very similar to the fossil raw material petroleum. Synthetically produced pyrolysis oil can be used both, for thermal utilization to generate energy and heat and as an important feedstock material for the production of a wide range of chemicals and industrial intermediate products.

However, there are also important differences between petroleum and pyrolysis oil, which are largely due to the highly variable chemical composition of pyrolysis oil. For example, while the element fluorine is virtually absent in petroleum, pyrolysis oil from plastic waste can contain significant concentrations of fluorine. These are undesirable because fluorine, due to its corrosive nature, can damage technical equipment in further use or processing. There are only a few established analytical methods for determining the fluorine content in organic matrices, which are usually preceded by sample digestion. Sample digestion is often carried out by combustion. The special feature here is, that water must be added during combustion to ensure complete conversion of all fluorine compounds during the oxidation or mineralization process and loss-free transfer of the hydrogen fluoride formed into an absorption solution. Water is added in a constant amount to the carrier gas oxygen. The ICprep sample preparation system is ideal for this purpose. Ion-sensitive electrodes (ISE), ion chromatography (IC), and molecular absorption spectrometry (MAS) are suitable detection methods for detecting fluoride ions formed during pyrohydrolytic digestion.

The measurements presented below were performed using an ICprep automatic for sample digestion, detection was carried out by means of a MAS-capable AAS device of the type contrAA 800 and an ion chromatograph.

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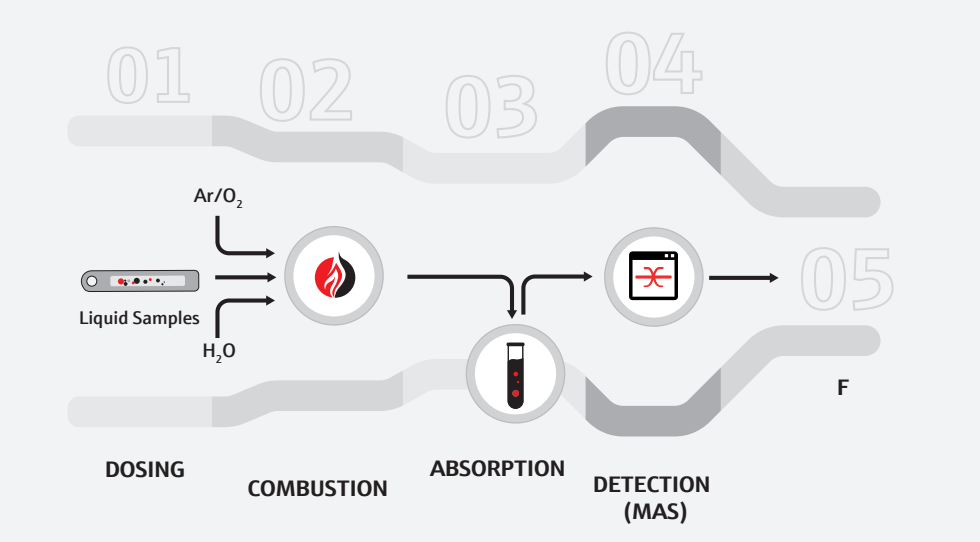

Figure 1: Schematic diagram of sample digestion for fluorine determination in pyrolysis oil with molecular absorption spectrometry

Materials and Methods

Three systems were used to determine the fluorine content in pyrolysis oil samples.

- ICprep automatic high-temperature digestion system for combustion of the samples under pyrohydrolytic conditions and for absorption of the measuring gas and the analyte (HF) in the integrated fraction collector
- Ion chromatograph with conductivity detector for the detection of fluoride ions
- High-resolution continuum source atomic absorption spectrometer contrAA 800 for the detection of fluoride ions using molecular absorption spectrometry (MAS)

Thanks to the decoupling of combustion (ICprep) and detection, the respective determination steps could be carried out flexibly in terms of waiting times or downtimes.

Samples and reagents

- 5 pyrolysis oil samples with known fluorine contents (determined in an independent laboratory, using combustion ion chromatography, CIC)
- Solvent for diluting the samples: o-xylene
- Perfluorohexane sulfonic acid (PFHxS) solution in toluene for spiking samples
- Calibration standards for IC and MAS: aqueous solutions of sodium fluoride (NaF) in water
- Gallium as a molecular formative agent and palladium/zirconium/sodium acetate modifiers for MAS

Sample preparation

Two of the five samples were diluted with o-xylene prior to combustion due to their state of aggregation or high viscosity.

The undiluted and diluted samples were filled into 2 mL sample vials and placed on the tray of the MMS sampler. The samples were then injected automatically onto a quartz glass boat, which was fed into the combustion furnace by means of the automatic boat drive (ABD).

Instrument and method settings

The combustion process took place in two phases. In the first phase, the volatile sample components were vaporized in an argon stream, followed by combustion of the gaseous products formed in an oxygen-rich atmosphere. In the second phase of the process, all remaining sample components were quantitatively mineralized in pure oxygen and converted to hydrogen fluoride (HF). The integrated flame sensor ensured safe and complete combustion of the samples. The flame sensor eliminates the need for time-consuming method development and the creation of sample feed parameters. Throughout the combustion process, a high-resolution syringe pump ensured controlled and constant water dosing. The gaseous analyte hydrogen fluoride (HF) formed was absorbed in an aqueous solution. The absorption solution was also fed into a collection vessel (15 mL centrifuge tube) of the integrated fraction collector using a syringe pump before the start of the measurement. Integrated rinsing processes ensured complete transfer of the analyte and contamination-free operation.

Table 1: Process parameters, ICprep automatic

Parameter	Settings
Furnace temperature	1050 °C
O_2 main flow	300 mL/min
Ar flow (1st phase)	100 mL/min
O_2 flow (2nd combustion, 2nd phase)	100 mL/min
2nd combustion time	100 s
Water dosage	0.2 mL/min
Absorber volume (vessel)	2 mL
Post rinse volume	1 mL

At the end of the fully automated digestion process, the individual absorption solutions enriched with analytes were filled up to a defined volume with ultrapure water in the centrifuge tubes of the fraction collector and fed into the two different detection systems. For this purpose, an aliquot of the absorber solution was injected onto an anion separation column of an ion chromatograph, while a high-resolution continuum source AAS device of the type contrAA 800 was used to determine the fluoride content in another aliquot of the same solution. Three independent digestions were performed for all samples.

Results and Discussion

Since no certified reference materials were available for the pyrolysis oil sample matrix, samples whose fluorine content had already been determined in an independent laboratory using combustion IC (CIC) were used to verify the suitability of the digestion system and the two detection methods used. Both detection systems, IC and MAS, were calibrated using standard solutions (sodium fluoride in water). For molecular absorption spectrometry (MAS) with the contrAA 800, calibration solutions in the concentration range from 2 µg/L to 100 µg/L fluoride were used. The calibration curve is shown in Figure 2. The calibration is linear over a large dynamic range, with a correlation coefficient of 0.9996.

Based on the overall procedure (digestion + MAS) for determining fluorine in pyrolysis oil, a detection limit of 85 µg/kg F was determined. This represents an improvement in detection sensitivity of approximately a factor of 10 compared to the methods previously established (e.g., CIC) for determining fluorine in this matrix.
The analysis results of all samples examined are compared with the values reported by the independent laboratory in Table 2.

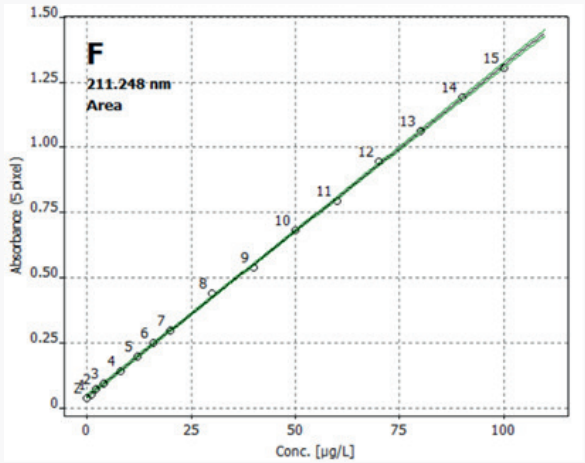

Figure 2: Fluoride calibration curve on the contrAA 800 D (MAS) spectrometry

Table 2: Results of fluorine determination (average values of a triple determination) using different detection method

Sample ID	c_F ± SD [mg/kg] Digestion with ICprep Detection with IC	Recovery rate [%] in relation to the transmitted value	c_F ± SD [mg/kg] Digestion with ICprep Detection with MAS (contrAA 800)	Recovery rate [%] in relation to the transmitted value	c_F [mg/kg] Value transmitted by external laboratory (CIC)
Pyrolysis oil 1	1.43 ± 0.18	143	1.44 ± 0.05	144	1
Pyrolysis oil 2	4.79 ±0.28	106	4.21 ± 0.13	94	4.5
Pyrolysis oil 3	6.20 ±0.38	88	6.38 ± 0.06	91	7
Pyrolysis oil 4	10.4 ± 2.0	104	10.9 ± 0.5	109	10
Pyrolysis oil 5	24.3 ± 1.0	106	24.8 ± 0.2	108	23

The results show both a very good match between the two detection methods used, and good match with the values provided by the independent laboratory. The reproducibility of all measured values can also be rated as very good for this concentration range. It is noteworthy that the standard deviations of the measured values obtained using MAS are significantly lower than the standard deviations determined using IC.

In the pyrolysis oil sample with the expected fluorine concentration of 1 mg/kg, consistent but higher fluorine concentrations than expected were found on both detection systems after digestion with ICprep. In order to rule out systematic errors, and to verify the basic suitability of the digestion and the selected detection methods for fluorine determination, three pyrolysis oil samples were spiked with a PFAS standard solution, perfluoro hexane sulfonic acid in toluene. Due to the poor solubility of the PFAS standard solution in the original samples, these were diluted with o-xylene and spiked with PFHxS in toluene. The contribution of the PFAS standard to the fluorine concentration in the samples was 6.3 mg/kg. One set of non-spiked diluted samples and one set of spiked diluted samples were measured. The results of these measurements are summarized in table 3.

Both, the good match of the results of the diluted samples with the expected value and the high recovery rates for the spikes in the range of 94% to 101% of the spiked samples confirm the suitability of the ICprep digestion system and the selected detection methods for fluorine determination in pyrolysis oil.

Table 3: Results of fluorine determination (average values of a triplicate analysis) with diluted and spiked samples

Sample ID	c_F [mg/kg] Expected value after sample dilution and spiking	c_F ± SD [mg/kg] Digestion with ICprep Detection with IC	Recovery rate [%] of the spike solution	c_F ± SD [mg/kg] Digestion with ICprep Detection with MAS (contrAA 800)	Recovery rate [%] of the spike solution
Pyrolysis oil 3	3.5	3.07 ± 0.04		3.60 ± 0.33	
Pyrolysis oil 3, spiked	9.8	9.01 ± 0.15	94	9.70 ± 0.30	97
Pyrolysis oil 4	5.0	4.95 ± 0.03		5.32 ± 0.05	
Pyrolysis oil 4, spiked	11.3	11.3 ± 0.2	101	11.4 ± 0.5	97
Pyrolysis oil 5	11.5	11.1 ± 0.1		11.7 ± 0.6	
Pyrolysis oil 5, spiked	17.8	17.2 ± 1.1	97	17.7 ± 1.4	95

Summary

With the help of ICprep, digestion for fluorine determination in pyrolysis oil can be carried out quickly and easily. In combination with an ion chromatograph as a separate detection system, results equivalent to those obtained with the online CIC method can be achieved at any time. Another very suitable fluorine detection method is molecular absorption spectrometry (MAS), which can be performed with a suitable AAS device (e.g., contrAA 800). In addition to equivalent results, this technique offers further decisive advantages: higher sensitivity and thus improved detection limits, as well as a very high analysis speed (about three times higher than with IC). In addition to fluorine determination using MAS, the contrAA 800 can quantify metal and metalloid concentrations like classic AAS.

An independent pyrohydrolytic digestion system can be advantageous, especially for smaller sample numbers that do not justify the purchase of a costly coupled CIC (combustion ion chromatography) system. An AAS device of the contrAA type or an existing ion chromatograph already available in the laboratory can then be loaded with the digested samples (absorption solutions) at any time, thereby increasing utilization for these systems can be ensured.

In addition to the ICprep, the described digestion can also be performed with the AOX analyzer multi X 2500 or the elemental analyzer multi EA 5X00 if these are equipped with a corresponding kit for pyrohydrolytic sample digestion. This means that these systems can also be used in fluorine determination, thereby utilization of hardware can be increased.

ICprep can also be operated with a ceramic combustion tube, which can be particularly advantageous when analyzing samples rich in alkaline and earth alkaline metals.

Figure 3: ICprep automatic

Figure 4: contrAA 800

Recommended device configuration

Table 4.1: Overview of required devices, accessories and consumables – fully automated solution and detection

Article	Article number	Description
ICprep automatic	450-300.102	Flexible system for sample digestion using pyrohydrolytic high-temperature combustion
multiWin software	450-011.803	Control software
contrAA 800 D - HR-CS AAS	815-08002-2	For flame and graphite furnace AAS as well as molecular absorption spectrometry (MAS)

Table 4.2: Overview of required devices, accessories, and consumables - upgrading an existing multi X 2500 or multi EA 5X00 device

Article	Article number	Description
Extension kit ICprep basic	450-300.110	Kit for extension of a multi X 2500 or multi EA 5X00 for sample preparation for solid, liquid, EOF, and AOF samples according to pyrohydrolytic high-temperature combustion, absorption, and collection of the reaction gases formed for further analysis steps
Extension kit ICprep automatic	450-300.111	Kit for extension of a multi X 2500 or multi EA 5X00 for fully automated sample preparation for solid, liquid, EOF, and AOF samples according to pyrohydrolytic high-temperature combustion, absorption, and collection of the reaction gases formed for further analysis steps, including fraction collector
multiWin 5 upgrade	450-011.804	Upgrade of an existing multiWin version for use of the ICprep function

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