Challenge
Determination of the total fluorine (TF) and chlorine (TCl) in coal requires combustion at high temperatures under pyrohydrolytic conditions and thus a special digestion system with water dosing unit.

Solution
The ICprep pyrohydrolytic digestion system can be used to ensure a complete conversion of all fluorine and chlorine compounds contained in coal.

Intended audience
Coal and power plant laboratories, contract laboratories for solid fuel and combustibles analysis

Sample Digestion for the Determination of Fluorine and Chlorine in Coal According to ASTM D8247

Introduction

Even in times of the so-called energy transition and climate protection, a large number of coal-fired power plants (> 2400) are still operated worldwide for heat or electricity generation. Coal as a source of energy is available almost everywhere on earth.

In addition to the main element carbon, coal also contains hydrogen, nitrogen, sulfur and oxygen in the form of complex carbon compounds as well as mineral components that remain as ash after combustion. The mineral components include fluorine and chlorine, which are among the undesirable elements due to their corrosive properties. During combustion, gaseous HF and HCl are produced, which can lead to emissions and pollution for the environment on the one hand and also damage the technical installations in combination with water formed during combustion. Therefore, the concentrations of fluorine and chlorine in coals are also checked, in order to be able to initiate counter measures at an early stage. The ASTM D8247 describes a method for determining TF and TCl in coal, which combines high-temperature pyrohydrolytic combustion at > 950 °C with subsequent ion-chromatographic determination of the anions fluoride and chloride. A so-called CIC system (Combustion Ion Chromatography) can be used for this purpose, the use of separate systems for digestion (furnace) and detection (IC) is also possible. Coal combustion produces gaseous products that are collected in an aqueous absorption solution. From this solution, an aliquot is then injected on the IC separation column. For a complete conversion of all compounds during combustion and for a loss-free transfer of the hydrogen fluoride and chloride into the absorption solution, a controlled water dosage during oxidation is crucial. During this process the water is added to the carrier gas in a constant quantity. In accordance with ASTM D8247, all furnaces or digestion systems operating in the temperature range from 950 °C to 1,100 °C that allow controlled water dosing during combustion and allow the absorption of the measured gases in an aqueous solution can be used for sample digestion for fluorine and chlorine determination. For example, elemental analyzers specially upgraded for pyrohydrolysis or the ICprep system described in this paper.

The separation of digestion and detection increases the application flexibility and utilization of already existing systems. The following experiments were performed with an ICprep automatic and an independently operated ion chromatograph to demonstrate the suitability of the digestion system for the determination of TF and TCl in coal.

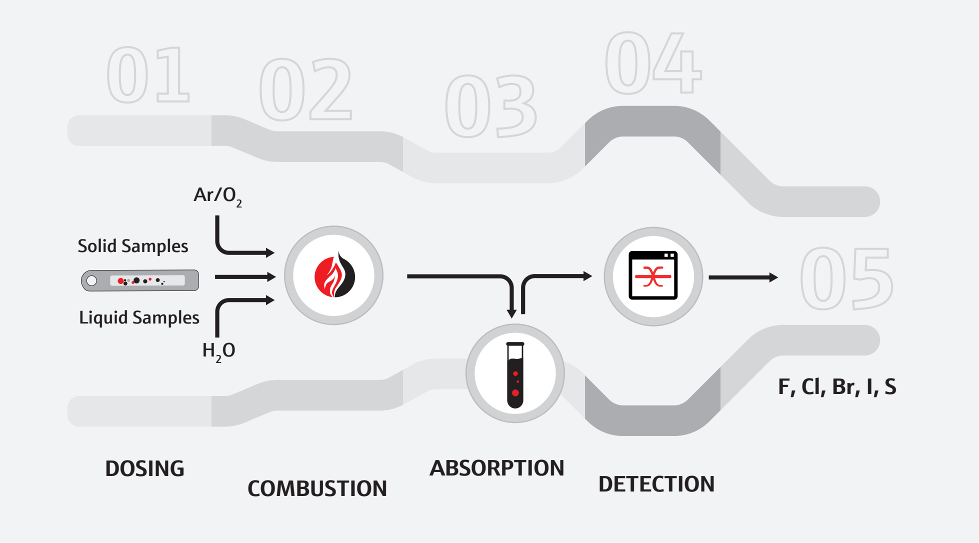

Figure 1: Schematic diagram of the procedure for determining F and Cl in coal (ICprep is used for the step of sample digestion according to pyrohydrolysis)

Materials and Methods

Two systems were used to determine the TF and TCl in two certified reference materials (CRM), one coal and one fly ash, and one coal sample:

- ICprep automatic - high-temperature digestion system for the combustion of samples under pyrohydrolytic conditions and the absorption of the reaction gases (HF and HCl) in the integrated fraction collector
- Ion chromatograph with conductivity detector - for the detection of fluoride and chloride ions

Thanks to the separation of combustion (ICprep) and detection (IC), the respective steps could be carried out flexibly in terms of time without waiting or downtimes.

Samples and reagents

- Two coal samples, of which one is a CRM BCR 460
- One fly ash sample, which is CRM BCR 038

Sample preparation

All samples were dried in a laboratory oven at 105 °C ± 3 °C for approx. four hours and then stored in the desiccator. The dried samples were weighed in quartz vessels (m: 10 - 30 mg) and placed on the tray of the autosampler MMS of the ICprep.

Instrument and method settings

The prepared samples were automatically fed into the combustion process with the help of the ABD. The combustion process was carried out in two phases, with the volatile sample components being evaporated in an argon stream in the first phase followed by the combustion of the formed gaseous products in an oxygen-rich atmosphere. In the second process phase, all remaining sample components were quantitatively mineralized in pure oxygen and converted to HF and HCl. The integrated flame sensor ensured safe and complete combustion. The flame sensor eliminates the need for time-consuming method development and the creation of sample feed parameters, and its advantages are particularly useful for more complex solid and liquid samples. During the entire combustion process, a high-resolution syringe pump ensured a defined and constant water dosage. The gaseous analytes HF and HCl were absorbed in an aqueous solution. This absorber 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 analytes and carry-over-free work ensured complete transfer of the analytes and carry-over-free work.

Table 1: Settings on ICprep automatic

Parameter	Setting
Furnace temperature	1050 °C
O_2 main flow	300 mL/min
Ar flow (1st phase)	150 mL/min
O_2 flow (2nd phase)	150 mL/min
Post-combustion time	300 s
Water dosage	0.2 mL/min
Absorber supply	2 mL
Post-purge volume	1 mL

Results and Discussion

To demonstrate the suitability of the ICprep digestion system, two suitable reference materials were digested in addition to a coal sample and analyzed with an IC. For this purpose, the individual absorption solutions from the fraction collector were filled up to a defined volume after combustion with ultrapure water.
In addition to a coal reference material BCR 460, which had a certified fluorine concentration of 225 mg/kg ± 8 mg/kg and an indicative chlorine value of 59 mg/kg ± 18 mg/kg, another reference material, coal fly ash BCR-038, was examined. This material had certified values for both chlorine (323 mg/kg ± 22 mg/kg) and fluorine (538 mg/kg ± 13 mg/kg).
The analytical results of all samples examined are summarized in Table 2.

Table 2: Results of the TF and TCl determination

Sample ID	TF [mg/kg], TCl [mg/kg], measurement 1	TF [mg/kg], TCl [mg/kg], measurement 2	TF [mg/kg], TCl [mg/kg], measurement 3	TF [mg/kg], TCl [mg/kg], mean value	RSD TF [%], RSD TCl [%]	Recovery TF [%] TCl [%]
Coal	231	215	230	**225**	4.0	**100**
(CRM BCR 460)	48	49	54	**50**	6.4	**85**
Coal sample	123	127	131	**127**	3.1	
	15	17	18	**17**	8.8	
Fly ash	531	529	534	**531**	0.5	**99**
(CRM BCR 038)	327	318	314	**320**	2.1	**99**

The measured values of the fluorine determination for the coal reference material show on average a very good match with the certified value of 225 mg/kg, the recovery is 100%. The obtained relative standard deviation is 4%. For the same reference material an indicative, non-certified chlorine concentration was given which could be confirmed with 85% recovery rate. For the second CRM (coal fly ash), the two certified element contents for fluorine and chlorine were also found very well with 99% each. The reproducibility of the measured values was also excellent with 0.5% RSD and 2.1% RSD respectively. All results confirm that ICprep can be used to fully decompose and absorb the reaction gas of coal samples and related materials in accordance with ASTM D8247. Thus, the ICprep digestion system lays the foundation for reliable and reproducible results of fluorine and chlorine determination.

Summary

With the ICprep, digestion for fluorine and chlorine determination according to ASTM D8247 is simple and cost-effective. In particular, a pyrohydrolytic digestion system can be an advantage when the sample number is low and the purchase of a cost-intensive coupled CIC (combustion ion chromatography) system does not yet justify it. An already in the laboratory existing ion chromatograph can then at any time be fed with the collected absorption solutions of the samples and thereby experience a higher utilization.
In addition to the ICprep, the described digestion can also be performed with an AOX analyzer multi X 2500 or an elemental analyzer multi EA 5X00 if they are equipped with a corresponding kit for pyrohydrolysis and absorption. Thus, these analyzers can also be used for the determination of fluorine or chlorine and the utilization rate can be increased.

Figure 2: ICprep automatic

The ICprep can also be operated with a ceramic combustion tube, which can be particularly advantageous for the analysis of alkaline and earth alkaline containing samples.

Recommended device configuration

Table 3.1: Overview of required devices, accessories and consumables – fully automated solution

Article	Article number	Description
ICprep automatic	450-300.102	Flexible system for sample digestion using pyrohydrolytic high-temperature combustion
Solids kit for MMS	450-300.034	MMS accessory for automated dosing of solids
multiWin software	450-011.803	Control software

Table 3.2: Overview of required devices, accessories and consumables – extension of a present analysis system

Article	Article number	Description
Extension kit ICprep basic	450-300.110	Kit for expanding a horizontal operated multi X 2500 or multi EA 5X00 for sample preparation for solid, liquid, EOF and AOF samples after pyrohydrolytic high-temperature combustion, absorption and collection of the reaction gases formed for further analysis steps
	or	
Extension kit ICprep automatic	450-300.111	Inclusive automatic collection of absorption solutions by fraction collector

References

[1] ASTM D8247 „Standard test Method for Determination of Total Fluorine and Total Chlorine in Coal by Oxidative Pyrohydrolytic Combustion Followed by Ion Chromatography Detection"

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