The Road as Polluter?

Iron and steel slag in road building: Routine determination of the total fluorine content

Using iron and steel slag in road building can cause the fluorine compounds contained in the slag to enter the environment. Dominik Hahn, currently a PhD student in the Technical Chemistry department at the University of Koblenz-Landau, developed a method for the determination of fluorine content in slag using Combustion IC as part of his bachelor's thesis. For this, he was awarded the VDI research prize by Verein Deutscher Ingenieure Mittelrhein e. V. (the Association of German Engineers for the Middle Rhine region).

Slag: A useful byproduct

In 2016, approx. 460–600 million tonnes of iron and steel slag (blast furnace and steel mill slag) accrued in the steel industry, according to an estimate by the United States Geological Survey[1]. Slag is the non-metallic substance that is left over when ore is smelted. However, it is not a waste product: For example, slag is a basis for alternative construction materials in road engineering or for raw materials in the cement industry.

An important parameter for assessing the environmental compatibility of iron and steel slag is the leachability of fluorine. How the leaching behavior of slag products containing fluorine works is not entirely clear. Current research projects are therefore focusing on understanding the complex processes of fluorine leaching and influencing these by making changes in metallurgical work[2].

Researching fluorine leaching from slag

The amount of leached fluorine in column or batch eluates alone is not enough to assess the leaching behavior of a slag. It has to be considered in relation to the original total concentration of fluorine in the solid. Research into the leaching behavior of slag requires a quick routine method for the measurement of the total fluorine content in slag with high precision and detection limits of below 50 mg/kg.

A quick routine method for the determination of the total fluorine content in slag has not been available until now: common methods, such as the standard method in accordance with DIN 51084 («Determination of the total fluorine content in inorganic oxidic raw and basic materials»), involve work-intensive sample preparation. This is carried out to transfer the analyte to a solution and to separate it from disruptive elements such as calcium, aluminum, and iron(III) ions. Performing the sample preparation manually is not only time and cost intensive, it also represents a major source of errors.

Reduce time and errors

Ion chromatography with inline combustion digestion (Combustion IC) has until now primarily been used for organic matrices such as fuels, polymers, pharmaceuticals, and food. With its fully automated analyses, however, it is also suitable for determining the total amount of fluorine in slag. As it hasn't previously been used for slag analyses, the parameters for pyrohydrolytic digestion and transferring the analyte into the absorption solution have to be optimized to ensure reliable analysis of inorganic oxidic samples such as slag.

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Figure 1. The Combustion IC system comprising 930 Compact IC Flex, 920 Absorber Module, and Combustion Module from Analytik Jena

Sample preparation in Combustion IC

Pyrohydrolytic digestion, which is also described in DIN 51084, is fully automated in Combustion IC and is connected inline to the IC analysis system. Firstly, thermal digestion of the sample takes place under argon atmosphere. The pyrolysis gases that arise are then combusted in a stream of oxygen and with the continual addition of small amounts of ultrapure water. The addition of ultrapure water prevents deposits and glass corrosion from occurring and ensures that the fluorine is fully transformed into hydrogen fluoride.

The gases produced by combustion digestion are dissolved in an absorption solution and transferred to the analysis module. The solution is then degassed and, before chromatographic separation takes place, Inline Ultrafiltration is used to release the particles and protect the separation column. The subsequent sequential suppression ensures stable, low background conductivity and therefore precise and correct determination of the fluorine concentration by means of conductivity detection. Figure 2 illustrates a diagram of the Combustion Module.

Optimization of Combustion IC for slag

To optimize Combustion IC for the determination of fluorine in slag, the sample weight, post-combustion time, ultrapure water rate, and the volumes and concentrations of the elution and absorption solutions were considered.

> *The longer post-combustion time allows the fluorine to be separated more effectively from strong bonds.*

Post-combustion time

Trials with various post-combustion times have shown that extended post-combustion times enabled more effective digestion (Figure 3). The longer post-combustion time allows the fluorine to be separated more effectively from strong bonds, as are found in slag. The flattening of the curve with post-combustion times exceeding 300 s marks the optimum that can be achieved by adapting the post-combustion time.

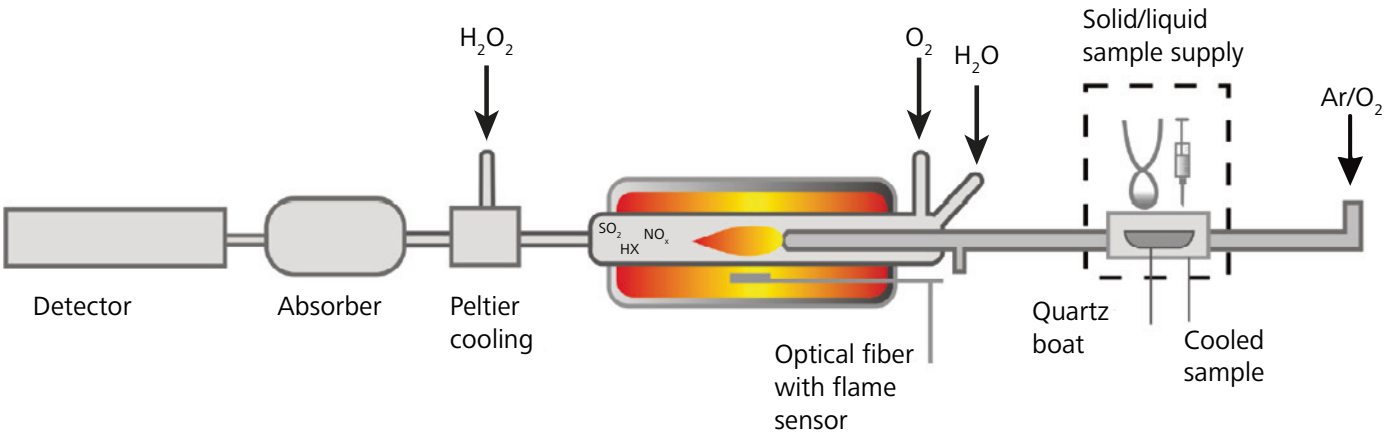


Figure 2. Operating principle of the Combustion Module

Sample weight

Attempts to optimize the sample weight revealed that digestion is most effective with a sample size of approx. 10 mg (Figure 4). Using smaller sample weights impacts on measurement precision, as the analyte concentration in the eluent is too small. A large sample weight results in an unfavorable relationship between sample surface and sample mass: the small area on which energy can be transferred leads to a temperature gradient in the sample during combustion digestion, causing aggregates to form. The digestive effect of the combustion is compromised by this. A maximum sample surface is achieved by distributing the sample delicately on quartz wool felt.

Ultrapure water flow rate

By adapting the ultrapure water flow rate, the absorption of the combustion gases by water vapor can be improved (Figure 5). Doubling the ultrapure water flow rate to 0.2 mL/min resulted in the analyte being absorbed more effectively. In addition, a higher flow rate counteracts glass corrosion and deposits in the combustion tube.

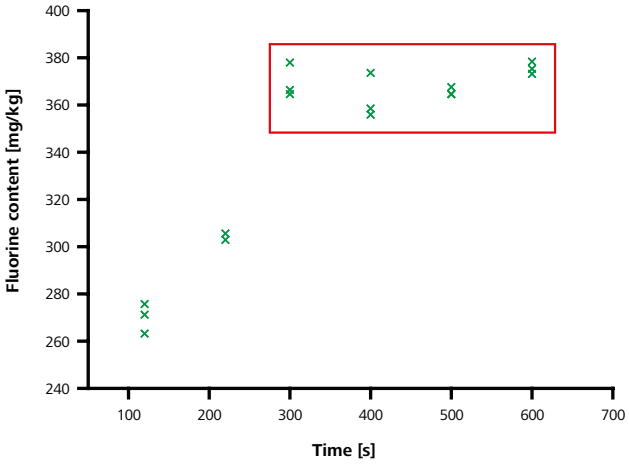


Figure 3. Optimization of the post-combustion time

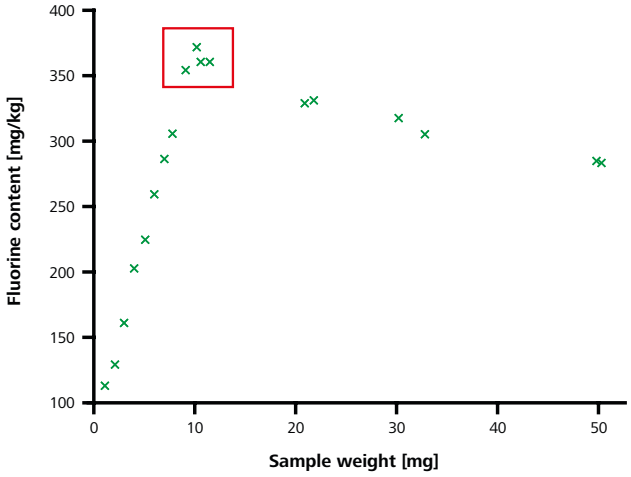


Figure 4. Optimization of the sample weight

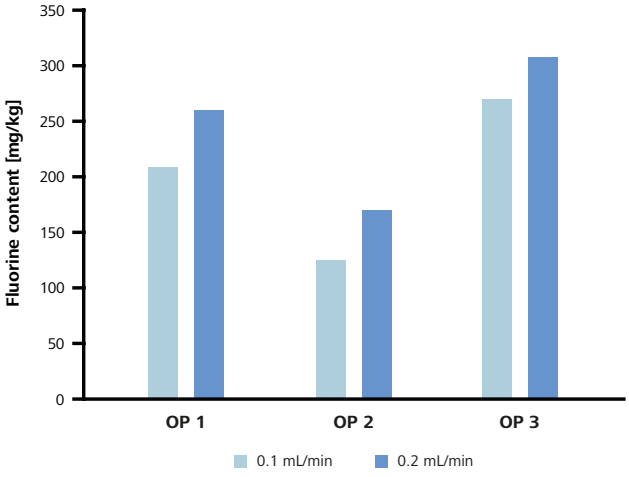


Figure 5. Optimization of the ultrapure water flow rate

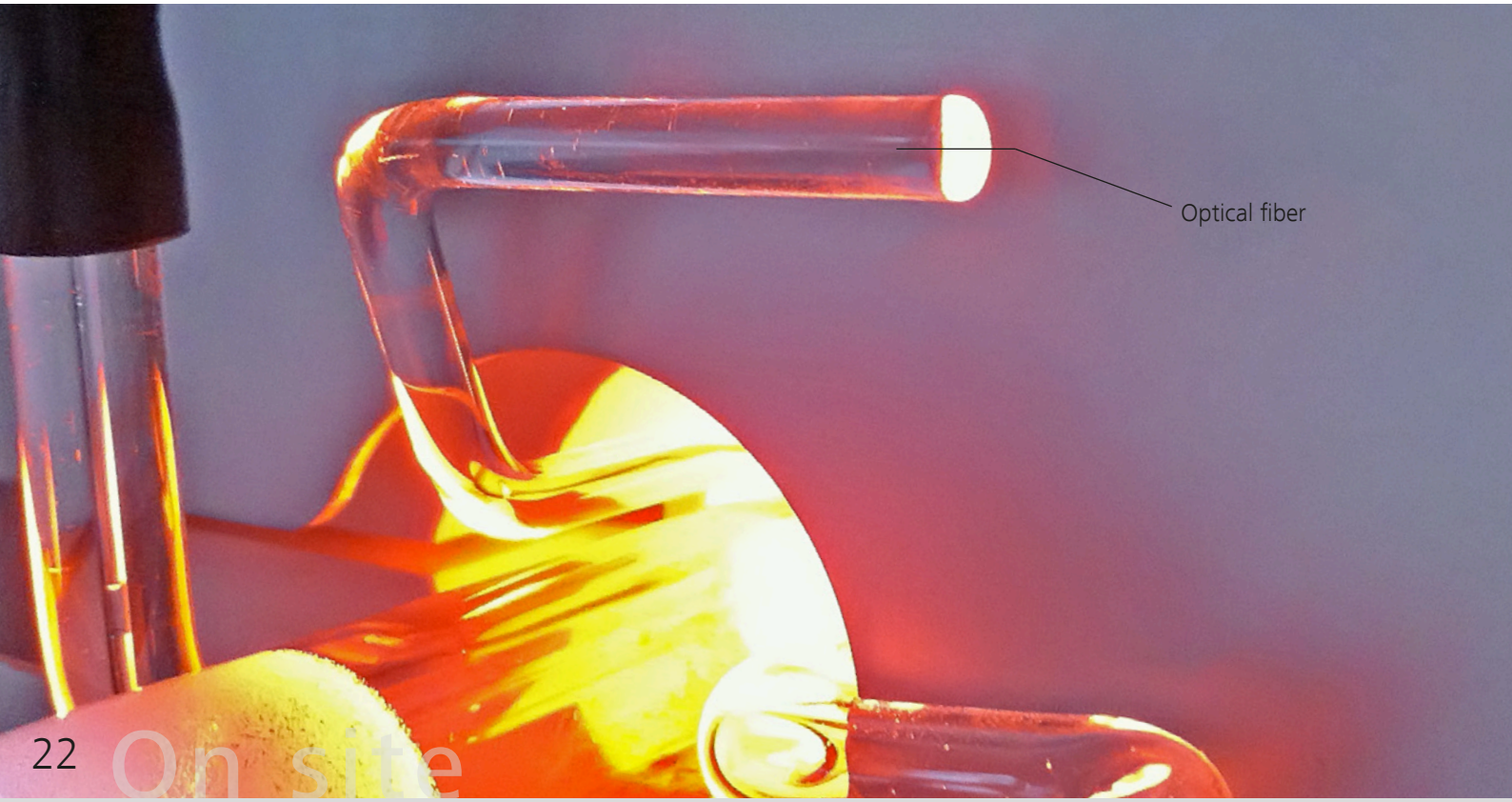
As a result of the optimization measures, the amount of fluorine able to be detected selectively was increased by an average of 55%.

Detectable fluorine volume significantly increased

In addition to the adaptations described above, the volumes and concentrations of the elution and absorption solutions were optimized in order to improve the transfer of the analyte to the IC module. As a result of the optimization measures, the amount of fluorine able to be detected selectively was increased by an average of 55%.

Figure 6 shows the measurements of three optimization samples and four real samples based on the initial method and the optimized method. In order to check the rate of optimization, the four standard reference materials STD 1 to STD 4, which covered a concentration range from 280 ± 20 mg/kg to 2712 ± 135 mg/kg, were also measured.

Close-up of part of the Combustion Module's sample injection system. Light from the pyrolysis oven is conveyed through the optical fiber to the flame sensor. To make it easier to see the optical fiber, the flame sensor has been removed from this image.



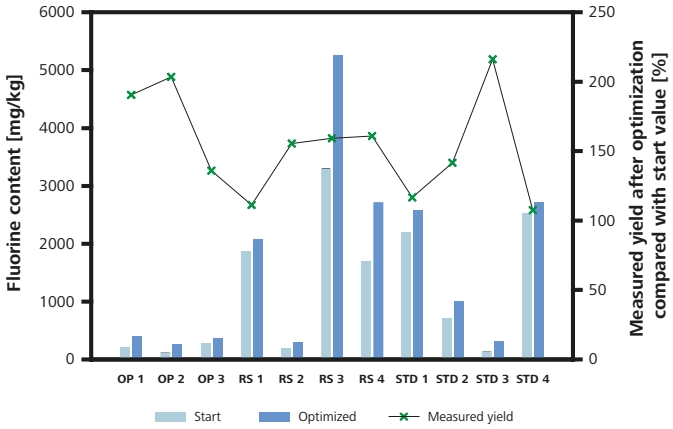


Figure 6. Optimization results: The detected fluorine volume increases by at least 7.5% and a maximum of 116.3%. It increases by 55% on average.

Fluorine determination as the basis for environmentally responsible slag management

When validating the method, detection and determination limits of 2 mg/kg and 6 mg/kg respectively were determined for fluorine in slag. Over a range from < 10 mg/kg to 5,000 mg/kg, a standard deviation of < 2% was achieved. Thanks to their precision and reliability, fluorine concentrations measured by Combustion IC are suitable for assessing the environmental compatibility and usage potential of steel production slag.

References

[1] *Mineral Commodity Summaries 2017;* U.S. Geological Survey; U.S. Government Publishing Office: Washington, DC, 2017; S. 98. DOI: 10.3133/70180197.

[2] Massnahmen zur Erhaltung des umweltgerechten Recyclings von Feuerfestreststoffen und der nachhaltigen Nutzung von Elektrolichtbogenofenschlacken unter besonderer Berücksichtigung der Herkunft und des Verhaltens von Fluorid. Mineralmahlwerk Westerwald Horn GmbH & Co. KG, Aktenzeichen 32127/01.

About the author

Dominik Hahn, 24, from Koblenz in Germany has in the past year completed a master's degree in Chemistry and Physics of Functional Materials at the University of Koblenz-Landau. At bachelor level, he studied Applied Natural Sciences, also in Koblenz. Since the end of 2017, Dominik has been a PhD student at the University of Koblenz-Landau where he is aiming to complete a doctorate in the field of high-temperature ceramic materials.