

Im folgenden Beitrag geht es nicht um das von der FIS eingesetzte ALPHA II der Firma Bruker (<https://www.opticsblog.bruker.com/fluoro-wax-ban-ft-ir-analyzer/>), sondern um den mit dem Lothar-Späth-Award ausgezeichneten Fluortracker der Firma Kompass.

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in Wissenschaft & Wirtschaft



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WAS MAN WILL.“

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# Detection of fluorine in skibases and skiwaxes

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## Abstract

The Fluorine Tracker (FT) is a novel measuring device for the detection of fluorine in ski waxes and ski soles, which is based on Selective Broadband Reflection and Absorption Spectroscopy (SBRAS) and realizes the surface analysis with visible light, infrared and ultraviolet radiation. The instrument can detect fluorine concentrations in the single-digit atomic percent range. Furthermore, the method allows measurements at different depths of wax or ski sole, from a few nanometers to several 100 micrometers.

## Introduction

Per- and polyfluoroalkyl substances (PFAS) comprise several thousand fluorinated compounds with the unique tribological property of water repellency, thereby reducing the negative effect of capillary attraction which slows down the ski [1, 2]. Because of the strong carbon-fluorine bonds the degradation of PFAS in nature is highly retarded and some substances persist indefinitely [3]. Some PFAS are toxic and have been linked to negative health impacts. The environmental and health impacts of fluorinated ski waxes have also been scientifically confirmed [4, 5]. Regulations have been established in the USA that are already in place and were implemented in the EU from July 2020.

At the FIS Council Meeting, 23rd November 2019, in Konstanz "Council Member Martti Uusitalo as chairman of Vauhti ski wax provided a detailed insight into the current situation concerning the specific elements which are subject to produc-

tion prohibition. He stated that the only way to develop a practical test to be used for FIS competitions will be to ban all fluor products and not only the specific molecules which are banned from production. The Council thereafter decided that the use of fluorinated ski waxes, which have been shown to have a negative environmental and health impact were banned for all FIS disciplines from the 2020/2021 season" [6].

## State of the art

Methods based on different physical principles exist for the detection of fluorine. These methods are partly quantitative and obtain the information from different depths of the material (information depth). What all methods have in common is that their use in competitions is only possible to a very limited extent. The restriction results from the construction and the way of handling of the device. As a rule, the devices are designed for broad laboratory use. In terms of price, the devices range between 20 T€ and more than 1 million €.

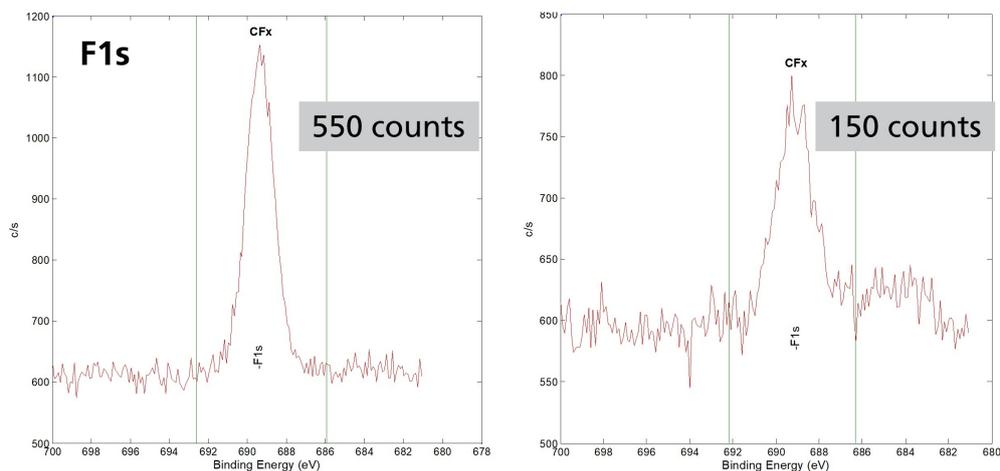


Figure 1: Left: Fluorinated ski base. Right: Ski base after removal of material with a thickness of 100 nm.

### X-Ray Photoelectron Spectroscopy (XPS)

XPS can be used to determine the concentration of fluorine in wax and ski base as well as the penetration of wax into the ski base. The surface of the base is irradiated with an x-ray beam, causing binding electrons to leave the surface. Due to the very precise measurement of the electron energy, i.e., the binding energy, the atom that emitted this electron can be identified. XPS is highly surface-sensitive with an information depth of less than 3 nm. In addition, after calibration using an inbuilt gold sample, XPS is quantitative and gives reliable

results down to concentrations of less than 1 atomic percent.

As an example the analysis of a fluorinated ski base is presented in Fig. 1. With 550 counts the fluorine F1s core level peak was clearly identified. When by a material removal procedure (sputtering with Argon ions) 100 nm were stripped off, the signal dropped to 150 counts. When it is assumed that fluorine is equally distributed inside the ski base, then fluorine must have migrated from the inside to the surface, causing the higher concentration at the very surface.

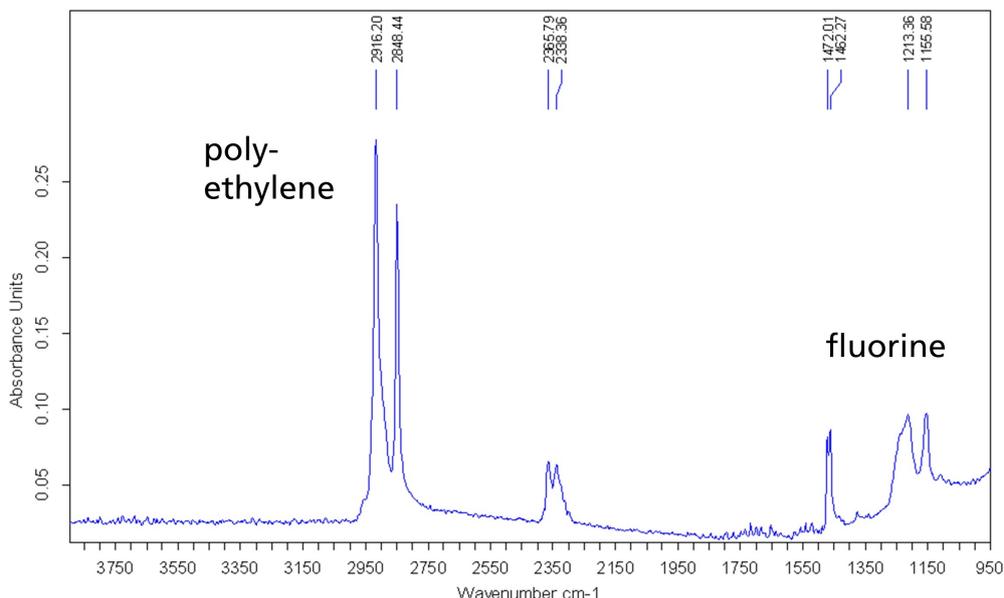


Figure 2: Absorbance FTIR spectrum of a waxed ski base.

### FTIR-ATR Spectroscopy

Another measurement method for the detection of fluorine on the ski base is infrared spectroscopy and here especially the Fourier-Transformed Infrared Spectroscopy

(FTIR-ATR) method. FTIR means that the raw signal, i.e., the light intensity, is not measured as a function of wavelength, but as a function of the position of a mirror inside the interferometer. Therefore, this signal

must first be Fourier-transformed to obtain the usual IR representation of light intensity as a function of energy in terms of wavenumbers, see Fig. 2.

ATR means attenuated total reflection. This principle has become the standard technique for measuring FT-IR spectra. Here, infrared light passes through a crystal of an IR-transparent material (diamond, ZnSe, or germanium) and then interacts with a sample that has previously been pressed onto the crystal. The resulting spectrum contains information about all substance-specific properties.

One of the first IR measurements to identify the C-F valence vibration in waxes is described in [7] and proved the presence of the symmetric and an asymmetric valence vibration at 1050 and 1300  $\text{cm}^{-1}$ .

The detectable species are molecular groups, the detection limit is approx. 0.1 - 1% and the information depth is 1 to 10  $\mu\text{m}$ , depending on the angle of impinging light.

In order to keep the device functioning, the ATR crystal has to be cleaned regularly. The measuring time per spot is between 30 s and 1 minute. For interpretation, the spectra have to be normalized using for instance the polyethylene peak. The method is not quantitative.

#### *X-ray fluorescence analysis (XRF)*

A third method, which is currently used for the field detection of fluorine, is X-ray fluorescence analysis. XRF uses the effect of fluorescence following excitation with an X-ray. Electrons close to the nucleus are freed, which then leave the surface and are detected by a radiation detector. The samples are not destroyed. The detection limit of XRF is about one microgram per gram (ppm). The measurement takes place in a vacuum chamber. It enables the identification and concentration determination of elements with an atomic number of 5 or more. The heavier the elements, the better the method works. Since fluorine with an atomic number of 9 is quite light, the detection is sometimes complicated, so the method had to be optimized for the detection of fluorinated waxes [8]. However, XRF is not yet

able to detect trace amounts, but requires a certain number of wax particles. The use of this method for competition is very limited. Wax samples taken from a ski have to be sent to a laboratory for analysis.

#### *Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)*

With TGA and DSC further methods exist that allow conclusions to be drawn about the composition of ski waxes.

In TGA, the change in mass of the wax sample is measured as a function of temperature. The sample is heated in an inert, temperature-stable crucible in an oven. A microbalance is used to record the mass change. A loss of mass may result from a decomposition reaction or from a volatile component evaporating. An increase in mass can result from chemical reactions, such as oxidation. The method can be used, for example, to detect whether the fluorine component is present as a di- or tri-block copolymer.

In DSC, sample and reference sample are heated simultaneously so that both crucibles always have the same temperature. The two crucibles are subjected to a temperature-time program and the heat flow difference between the two samples is recorded. In the spectrum, physical and chemical reactions can be read off in the form of endothermic or exothermic peaks. By comparing the peak areas, a statement can be made about the proportion of the fluorine component. Both methods are not suitable for field use.

#### *Gas chromatography (GC)*

GC is an analytical method for separating mixtures into individual chemical compounds. GC is only applicable to components that are vaporizable in gaseous or undecomposed form. A gas chromatography-mass spectrometry coupling succeeds in determining the composition of the vapor space above the sample. This method was used by [9, 10] to analyze 50 commercially available ski waxes. Perfluorocarbons and perfluoroalkanes compounds were reli-

ably detected. The measurements are time consuming because the gas species must diffuse through a column to become analyzed.

## How the FT works

### General function

The detection of fluorine in ski waxes is based on SBRAS. SBRAS exposes the ski base to electromagnetic irradiation with a wide spectral distribution. The sensors detect direct and diffuse reflection for background signal treatment. For fluorine tracking absorption measurements in the ultraviolet and infrared regime are performed. The received signal is proportional to the content of fluorine and the thickness of the wax layer. Thus, thin layers with high fluorine content may result in the same signal as thick layer with low fluorine con-

centration. The influence of reflectivity of the ski surface was addressed by adapted algorithms combining the signals of visible (VIS), infrared (IR) and ultraviolet (UV) light channels. In addition, the impact of colored bases was treated in this way. The device combines the input of 3 VIS sensors, 2 UV sensors and 4 IR sensors. Both in UV and IR range along the source-sensor axis (inline) and perpendicular to it measurements are performed. Inline sensing is used for the evaluation of direct absorption. The setup in perpendicular direction considers the diffuse contributions of absorption, see Fig. 3. The algorithm of the FT is constantly improved by machine learning (ML) routines. The arrangement of the multi-sensor setup requires multidimensional optimization to sharpen its performance [11].

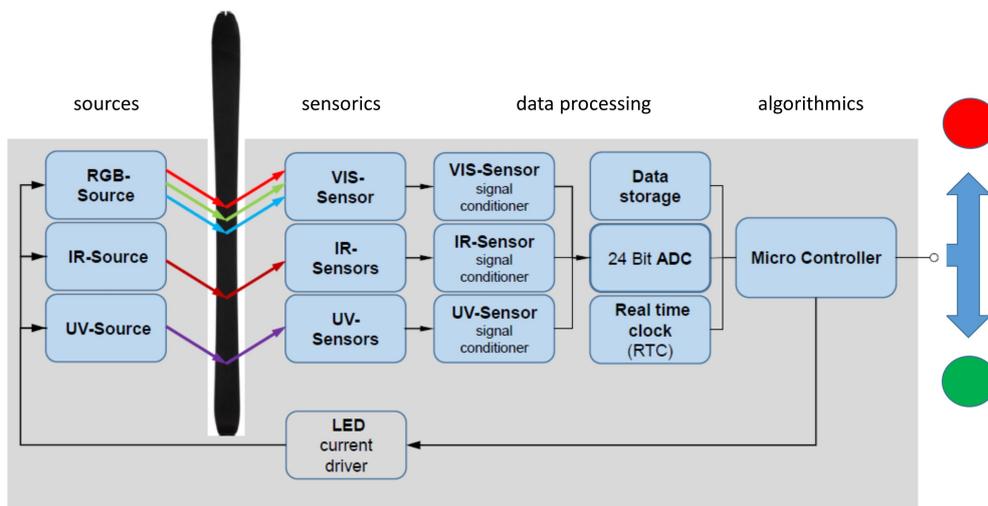


Figure 3: Setup of the sensing device.

### Influences on the optical signal

The quality of the optical signal is largely determined by the reflectivity of the surface. This is influenced by the ski base peeling, grinding as well as waxing, brushing and polishing. Hand structures have an influence as well [12]. In addition to the directional reflection, there is also a diffuse component caused by the peeling and grinding ridges as well as by introduced structures. Furthermore, the quality of the ski base polymer as well as its color and transparency have a significant influence. In some cases, color pigments fluoresce, which can lead to overlaps with the measured values.

In the worst case, the fluorescence phenomena are in the range of the UV absorption. Since the ski base is usually filled with carbon black or nanoparticles, the optical influences of these additives also play a role. By proper ski preparation an intimate bond between polymer and wax is formed [13] which interacts with light and sometimes generates a fatty look of the base. Finally, the influence of scattered light should be mentioned, which may lead to the general reduction of signal intensities and to a significant decrease of the signal-to-noise-ratio. Thus, a complex parameter space is created which can only be addressed with the multi-

sensor approach demonstrated and the self-improving algorithm mentioned above.

### *Information depth*

Both the fluorine tracker and FTIR instruments have an information depth of approx. 0.1 to several 10  $\mu\text{m}$ . This means that the excitation with infrared light excites absorbing vibrations down to this depth. Thus, an FTIR instrument measures both the wax layer and the underlying ski base, which can lead to distortions in the case of a fluorinated ski base. When excited with ultraviolet radiation, the depth of information is significantly less. With ultraviolet light, valence electrons are excited. Their return to the ground state can occur without radiation, via fluorescence or via phosphorescence. Due to the very high absorption coefficients of most polymers in this spectral range, the penetration depth is less than 100 nm [14]. Since the FT uses wavelengths greater than 250 nm, even shallower penetration depths can be expected. Thus, this channel is only open to near-surface layers.

## Calibration

Since optical methods provide limited quantitative information only, the FT must be connected to a standard. The method used is XPS, which in turn provides accurate, energy-resolved spectra by using the built-in gold sample for spectra calibration. Wax samples with low fluorine concentrations and samples of fluorinated polymers are used to calibrate the FT. XPS measurements are performed on these samples, outputting concentrations as atomic or mass percent. A calibration curve is obtained, which is then stored in the FT. Since the physical principles of the two methods are fundamentally different, systematic errors are avoided.

To address the issue that for all optical methods – i.e., the FTIR and FT – besides concentration of the observed species the signal also depends on the thickness of the measured layer, calibration samples were

prepared using the common steps of ski preparation. If the last step of preparation, that means brushing, was performed properly, wax and polymer form an indistinguishable compound with a thickness between 1 and 2  $\mu\text{m}$  [15]. Therefore, for calibration, the wax layer thickness was considered constant. Improper preparation results in thicker wax layers.

## Results

Field tests have so far been carried out in Falun, Östersund and Lenzerheide. For this purpose, 3 devices were in use. For the tests, ski technicians from several national teams were asked to prepare skis and make them available for the FT measurements. The tests served to optimize the evaluation algorithm. During the first tests in Falun, a non-optimized version was used, which still unsatisfactorily reflected the condition of the skis. Based on the information provided by the ski technicians, the algorithm was refined and a much improved version was used in Östersund and Lenzerheide. The quality of fluorine detection is thus dependent on the quality of the information provided by the ski technicians. Laboratory tests were performed in parallel to improve the correlation between preparation condition and FT measurement results.

### *Alpine World Cup in Lenzerheide*

Figure 4 clearly shows that waxes with different fluorine content can be differentiated. The diagram is based on 53 individual measurements. The error bars underline that the best differentiation is possible for highly-fluorinated waxes with respect to low-fluorine waxes. The difference between low-fluorine waxes and waxes containing no fluorine is not as pronounced, thus the error bars nearly overlap. However, it has to be mentioned, that at a certain fluorine concentration the tribological effect of suppressed capillary action vanishes. This threshold is located in the lower border of the low-fluorine box.

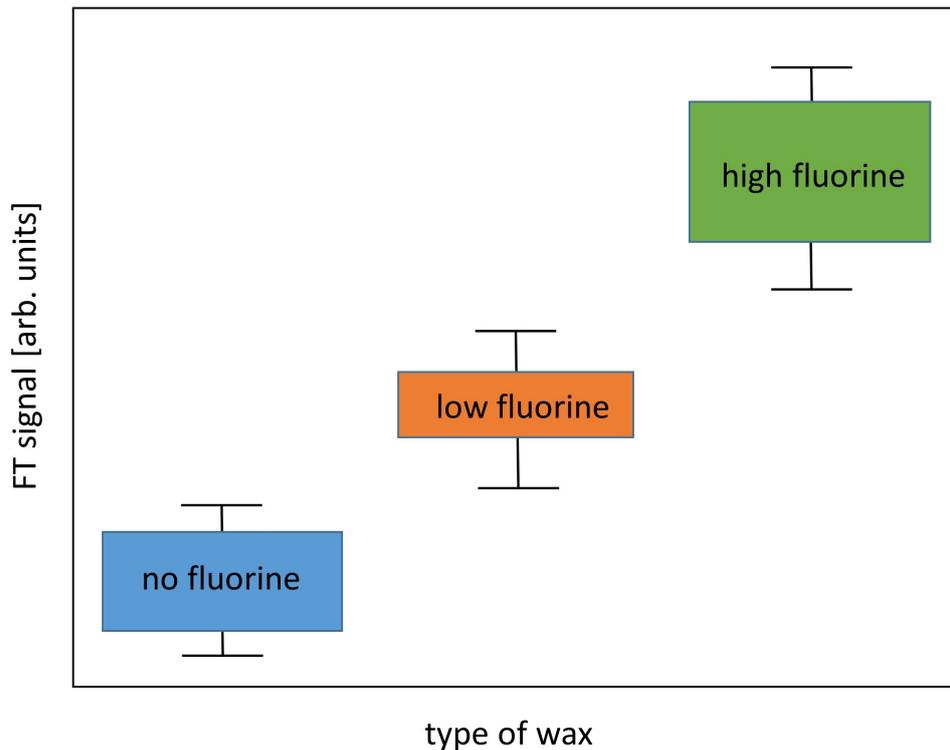


Figure 4: FT signals of 53 pairs of alpine skis during the Lenz-erheide worldcup in March 2021.

## Summary

The FT is an instrument based on the latest physical measurement technology and data processing. The device is self-learning, i.e., the detection of fluorine improves with increasing number of measurements. The handling is easy and the light-exposure time per ski is in the range of seconds. By connecting the FT to the XPS method, absolute measurements are possible with atomic concentrations. However, these results are not published during the tests at

the competition, but an indication per red/green signal is used for decision making.

## Acknowledgment

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## About the Author



Matthias Scherge is a professor of tribology. This is the science of friction, wear and lubrication. Prof. Scherge heads the Fraunhofer MikroTribologie Centrum, teaches at the Karlsruhe Institute of Technology and manages Team Snowstorm. He also advises the Nordic Paraski Team Germany and several national and international athletes on scientific and technical issues.

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