SciAps ApNotes
April 2021

Instant Detection of Banned Fluorinated Ski Waxes Using Handheld LIBS

Introduction

Iron-on fluoro-powders and fluorinated paraffins for skis, as one vendor describes it, offer unmatched glide properties and repel dirt exceptionally well. They have been used by many national ski teams worldwide.

However, fluorinated ski waxes have been shown to have a negative environmental and health impact. They were banned by the Norwegian Ski Association in 2017, and were more recently banned by the International Ski Federation (FIS) starting with the 2020-2021 season. These waxes will also be banned from the 2022 Beijing Winter Olympics. As noted in an FIS press release: "A specialist FIS Working Group led by FIS experts Atle Skaardal (alpine skiing) and Pierre Mignerey (cross-country) and including the ski and wax industry will be formed to establish the regulations and control procedures." [1]

A major hurdle for regulation and control of the use of fluorinated waxes is the need for an easy detection method that can be used on the spot with instant results. The SciAps handheld LIBS (Laser Induced Breakdown Spectroscopy) instrument has been shown to do exactly that.

The SciAps handheld LIBS demonstrates it can measure fluorine in ski wax in less than 1 second. The Class 1 LIBS device eliminates safety concerns and regulatory burdens of handheld XRF analyzers. Moreover the LIBS device is significantly smaller, lighter, and less expensive than XRF analyzers being considered.

Experimental

Eight cross-country ski sections were sent to SciAps from Professor Paul Bierman, University of Vermont, in a blind study to determine if fluorine could be correctly identified. The skis were treated in various ways, some with and some without flourinated waxes. Figures 1a and 1b show the eight sample ski segments and the bottom surface that was analyzed.

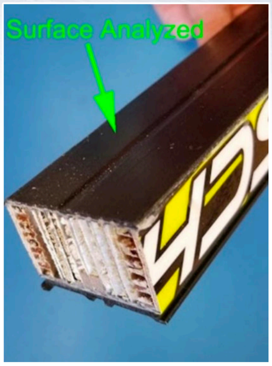

Figure 1a. Bottom surface of ski analyzed using handheld LIBS.

The various ski groups seek a fast, portable method to quickly (1-2 sec.) measure fluor content in ski wax. SciAps utilized their Z-901 analyzer. LIBS offers many advantages over handheld X-ray fluorescence (XRF) for this application.

First, SciAps LIBS is a Class 1 rated laser device in the European Union and thus is not burdened with regulatory requirements and licensing, unlike XRF.

Second, Z-901 is highly portable compared to HH XRF technology. The Z-901 is about half the size of the XRF and weighs about 1.6 kg.

Figure 1b. Eight cross-country ski segments treated with various waxes.

HH XRF requires an integrated vacuum chamber and expensive detector technology due to the low atomic number of F and resulting difficulty in measuring fluorine X-ray emissions.

High-performance LIBS is a relatively new portable analytical method. In the LIBS process, a small laser contained within the handheld instrument is fired at a sample causing a very small spark on the material under test. Light emitted from the spark is analyzed via internal spectrometers to determine the elements present in the sample. The wavelength of the light emitted identifies the element, and the intensity at that wavelength yields concentration information.

Previously, Connors and Day [2] demonstrated that fluorine in certain fast-food packaging could be detected using handheld LIBS and helium as a purge gas. While argon purging is typically used for signal enhancement during LIBS analysis, helium is known in the literature to specifically enhance fluorine emission lines. This is a result of helium's ionization potential being greater than that of fluorine and thus energy is easily transferred to the fluorine atom.[3] The helium purge is a small removable canister the user installs into the device. Each canister costs about $7 and provides about 600 tests, thus purge gas costs about 1 penny per test.

The Z-901 is a single-spectrometer unit with a range of about 200 nm. The Z can be manufactured with a variety of spectrometer designs to be optimized for a particular element or elements. In the case of fluorine, the strongest fluorine emission lines occur in the region of 620 to 780 nm as shown in Figure 3, so the analyzer is configured with a spectral range of about 600 – 800 nm. As shown in Figure 3, the LIBS device also detects the hydrogen emission about 658 nm as well as fluorine and even some helium excitation from the purge gas.

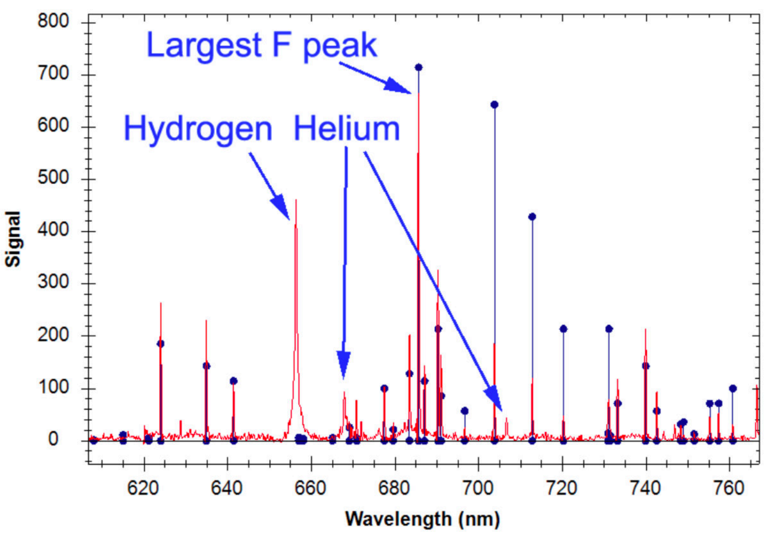

Figure 3: A Z-300 LIBS spectrum of Teflon showing the fluorine emission peaks. Blue lines and dots are NIST listed fluorine emissions lines and relative intensities.

The fluorine concentration in fluorinated packaging and waxes is much lower than Teflon (Figure 3) and is thus the challenge for detection in this work.

In order to maximize the fluorine signal, between 20 and 156 shots were averaged. The Z laser fires at 50 Hz, with 7-8 mJ/pulse laser energy, so testing times between 1-3 seconds were tried. The data were collected with zero gate delay (delay between firing the laser and opening the electronic spectrometer shutter). Zero gate delays prevent the emission signal decay that occurs with more typical microsecond delays; however, the baseline from continuum emission is increased. The effects of the increased baseline were largely removed by working with the first derivative of the spectral data.

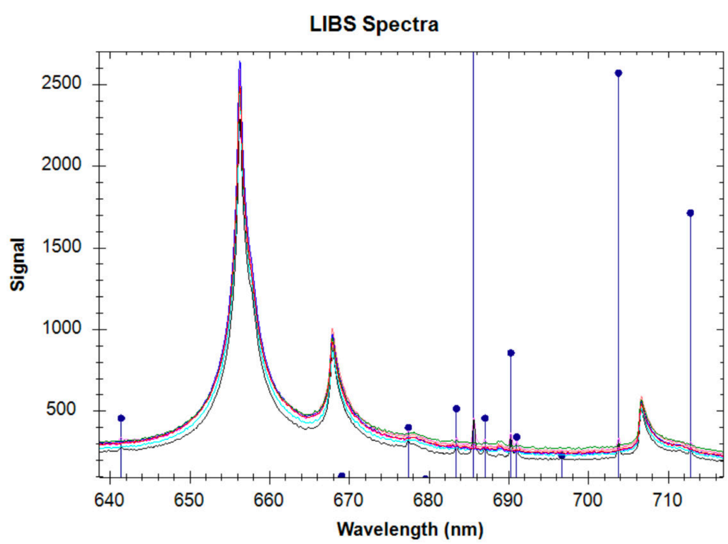

Figure 4: Spectra from the eight ski samples (each the average of 156 shots). Largest fluorine peak visible at 685.8 nm. The large peak at 656 nm is hydrogen. Helium peaks are visible at 668 and 706 nm.

Results and Discussion

Spectra from the eight ski samples are shown in Figure 4. The vertical blue lines in Figure 4 indicate where fluorine emission lines occur. The largest fluorine emission is at 685.8 nm and was observed in some of the ski samples. The data was further

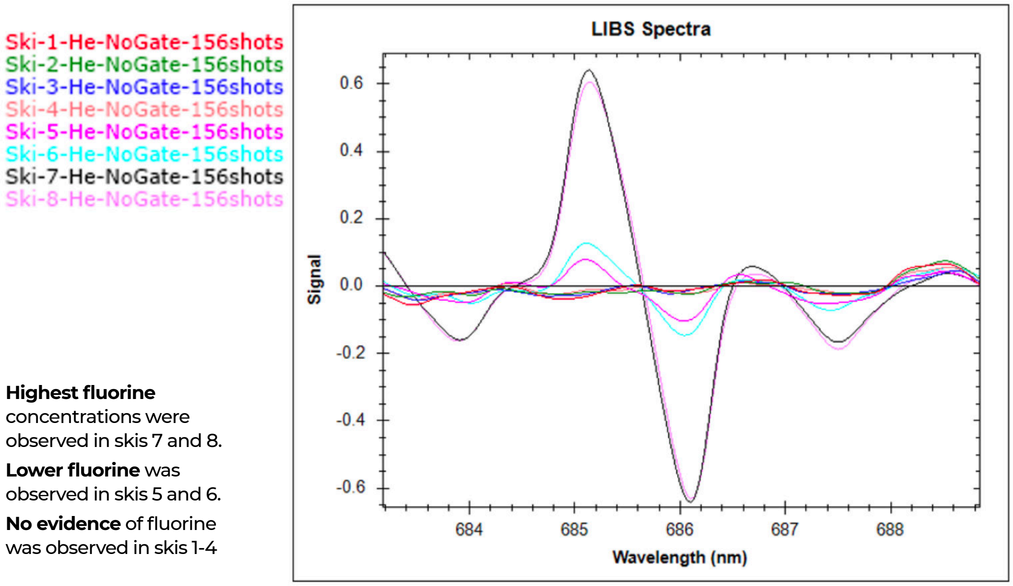

Figure 5: Normalized first derivative fluorine spectra from the eight ski samples.

processed by Savitzky-Golay first derivative filtering and normalizing to the 706 nm helium peak. The fluorine 685.8 nm emission results are summarized in Figure 5 and 6.

The results were provided to University of Vermont (UVM), after which UVM provided the treatment details back to SciAps. The integrated peak concentrations along with the ski treatments are shown in Figure 6.

The agreement between known fluorine loadings and the LIBS results was very good. Samples 7 and 8 show that the presence of fluoro wax is easily detected. Samples 1 and 3 were “blanks” with no fluoro wax added. As expected, the LIBS showed no measurable fluorine. Samples 2, 4, 5 and 6 were more interesting. The LIBS did not detect any F on samples 2 and 4. These samples had a low level of fluoro applied and ironed into the base material, then the skis were scraped and brushed to remove the wax. The LIBS did not detect fluorine in these two cases. Alternatively, samples 5 and 6 had a high level of fluoro applied and ironed into the substrate. The wax was then scraped and brushed for removal. In this case because the original fluoro loading was high, the LIBS could still detect the presence of fluorine. This means that the LIBS can also be used to determine when a ski has been appropriately cleaned of fluoro-containing wax. We also used the ratio of fluorine to hydrogen in the analysis due to the strong H line. Nearly identical results were obtained for normalization of the data to hydrogen instead of helium, showing that either one may be used as a reference signal.

One question about LIBS is the non-destructiveness of the technique. In fact, the laser ablation that occurs during the LIBS analysis removes very small amounts of material, typically tens of nano-grams. For example, Figure 7 shows the barely discernable mark left by data collection used in this study.

The resulting shot craters are approximately 200 um in diameter and about 5-10 um deep. Experimentation carried out of average signal quality vs shot count showed little difference between 25 and 150 shots. Based on this, it is believed a robust measurement could be made with a much smaller mark on the skis and in less than 1 second. Furthermore, a simple rub of the mark with a bit of wax restores the surface as shown in Figure 8.

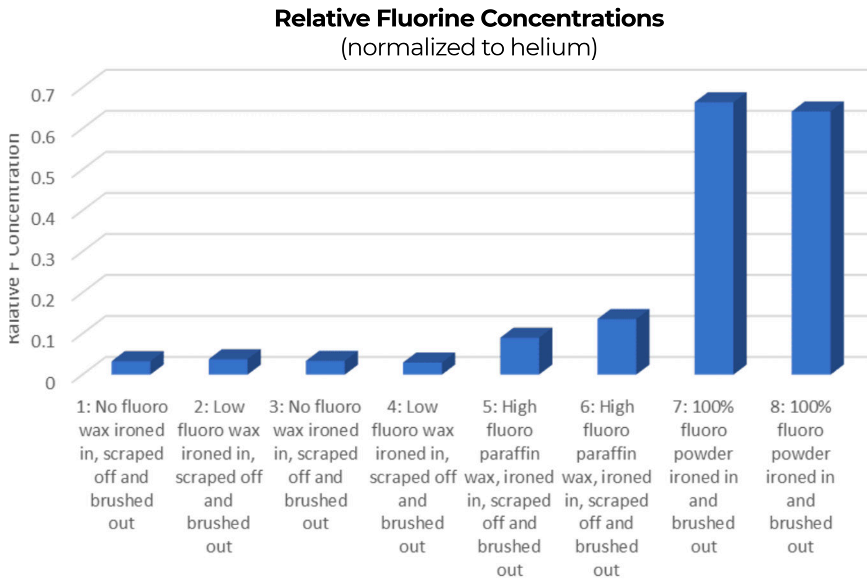

Figure 6: Relative Fluorine concentration measured with handheld LIBS versus wax type and treatment.

SciAps Z-901 LIBS

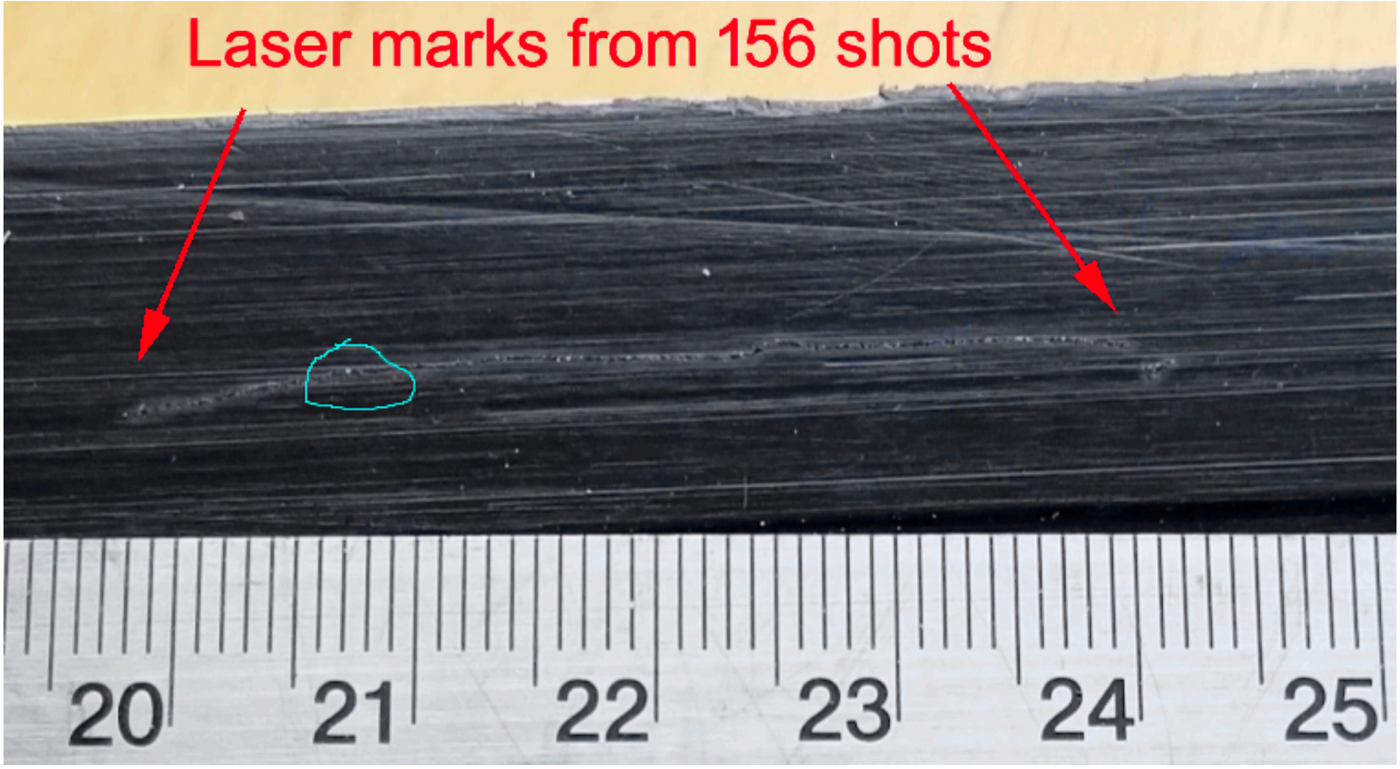

Figure 7: The handheld LIBS instrument was slowly moved during the collection of 156 LIBS laser shot data. This created the 4 cm long faint marking shown in the figure.

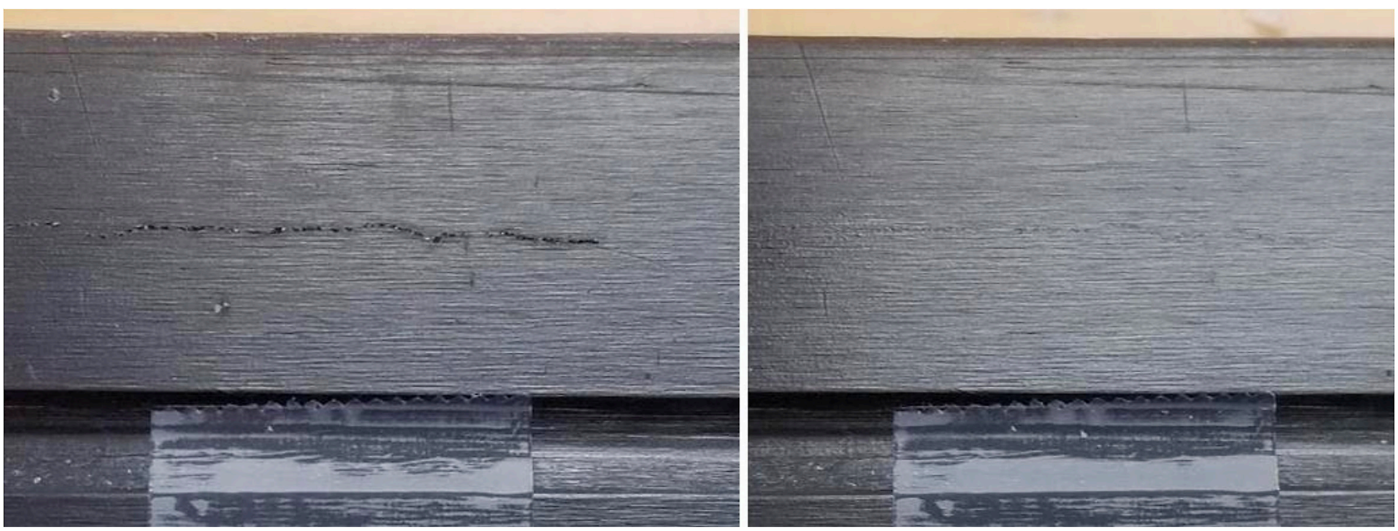

Figure 8: Left: LIBS laser ablation mark remaining on the ski bottom after data collection. Right: After rubbing the mark with a small bit of wax.

Summary

Handheld LIBS was demonstrated to effectively measure the presence of fluorinated wax on skis within seconds. Minimal damage to the wax occurs and it can be easily removed with brushing. Upon seeing the result of this blind study, Professor Bierman wrote, ***"What this means is the LIBS can see the waxes that really matter both environmentally and for health and for "cheating" now that these are being regulated for sport."***

[1] https://fasterskier.com/fsarticle/fis-moves-to-ban-fluorinated-ski-waxes-for-the-2020-2021-season/

[2] Connors, B. and Day, D (2018) Screening Food Packaging for Fluorinated Compounds using Laser-Induced Breakdown Spectroscopy. In: International LIBS Conference 2018, Atlanta, GA. 2018 October 21 – 26

[3] Cremers, D.A. and Radziemski, L.J. (1983) Detection of Chlorine and Fluorine in Air by Laser-Induced Breakdown Spectroscopy, Analytical Chemistry, https://doi.org/10.1021/ac00259a017