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Screening Food Packaging for Fluorinated Compounds Using Laser-Induced Breakdown Spectroscopy

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Background

Perfluorinated alkylated substances (PFAS) are a family of fluorosurfactants. They have been used in packaging of foods, particularly fried fast food, because their lipophobicity inhibits oils leaking through packaging layers.

PFAS are known to bioaccumulate and have been connected to adverse health outcomes in humans. Long chain PFAS known as C8 compounds (with 8 or more carbon atoms per chain) have longer biological half-lives and have been voluntarily discontinued in food packaging in the United States. Shorter chain PFAS and other fluorinated hydrocarbons continue to be used. However, individual states, as well as some countries, are considering limits on total organofluorine compounds used in food packaging.

Field-portable handheld LIBS analyzers have expanded potential applications for in situ elemental analysis. They allow for rapid screening and quantification of any element in almost any matrix type. The ability of LIBS to test light elements such as fluorine make it particularly well suited to applications where other field-portable elemental analysis techniques such as X-ray fluorescence spectroscopy (XRF) are insensitive to the lightest elements.

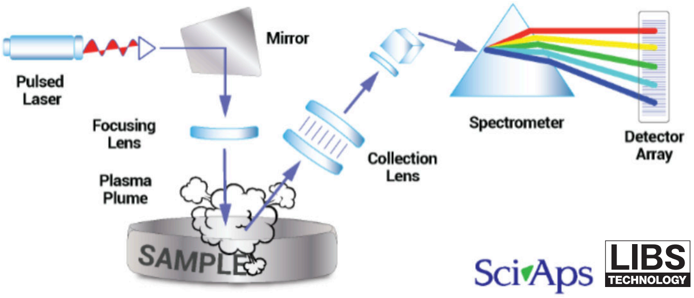

Fig. 1. Illustration of the LIBS process.

Experimental

Figure 1 shows an illustration of the LIBS process. A SciAps Z-300 handheld LIBS analyzer was used for measurements (this instrument is superseded by Z-901 Fluorine, shown in Fig. 2).

SciAps LIBS analyzers make use of of several advanced features:

- Wide spectrometer range covering 185-950nm
- Time gating of CCD detector to minimize bremsstrahlung background
- Helium purge gas (enhances F signal)
- X/Y rastering of laser across sample
- Integrated camera for sample positioning

Fig. 2. New for 2021: SciAps Z-901 handheld LIBS analyzer. Internal purge gas cartridge shown on left.

Detection of fluorine is taken as a marker for the potential presence of PFAS, though LIBS will not speciate the fluorine-containing compound.

Samples of food packaging were obtained from several fast-food restaurants and stores in the Boston area. Samples were presented to the analyzer and tested as-is with no preparation. Time gating of the CCD was used with 250ns gate delay. For each sample, LIBS spectra were acquired for 150 consecutive pulses, with the sample manually rastered across the laser focus. Each sample was tested in replicates of 10, with spectra averaged together.

Samples included:

- Paper wrappers for sandwiches and baked goods
- Paper bags to hold oily foods
- Corrugated cardboard sandwich boxes
- Compressed cardboard boxes for French fries
- Microwave popcorn bag

Results and Discussion

Spectra were inspected for the F (I) peak at 685.60nm, which is the most prominent overlap-free peak in most matrix types. A secondary F (I) peak at 690.25nm exists, but it is weaker and overlaps with another unidentified peak at 690.40nm that was present in many blank samples.

Spectra plotted below have had Savitzky-Golay smoothing applied to reduce noise levels and have been corrected to remove any baseline offsets.

Paper wrappers (Fig. 3) for sandwiches varied in their levels of F detected.

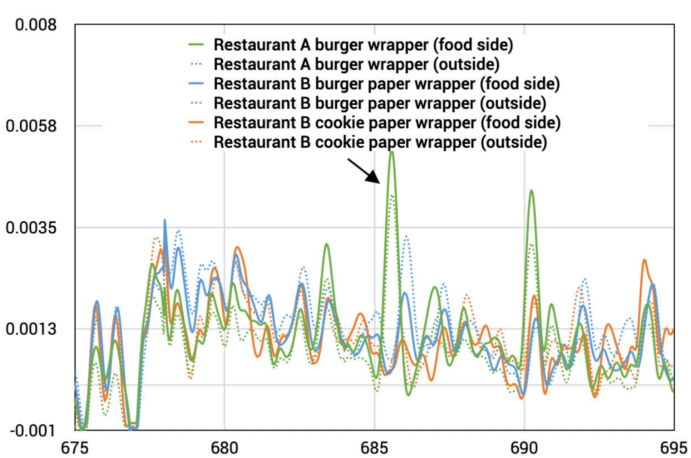

Fig. 3. F 685.60nm signal from various paper wrappers.

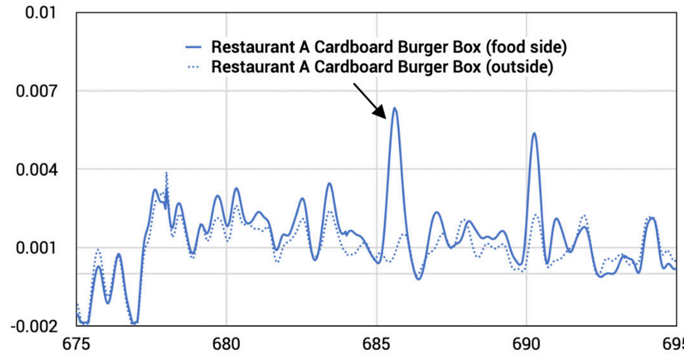

Fig. 4. Hamburger clamshell cardboard box. F was present on the food-facing side (solid) but not outside of the box (dashed).

Some samples like cardboard hamburger boxes (Fig. 4) showed F only on the food side. French fry cardboard boxes from three separate fast-food chains were tested, but none had detectable levels of F.

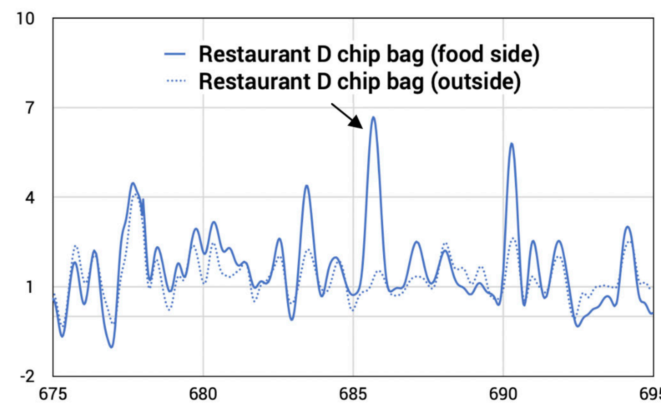

Fig. 5. F signal on food side (solid) of tortilla chip bag, but not outside (dashed).

A tortilla chip bag showed weak LIBS signal overall but showed some F signal on the food side of the bag. No F was seen on the outside (Fig. 5).

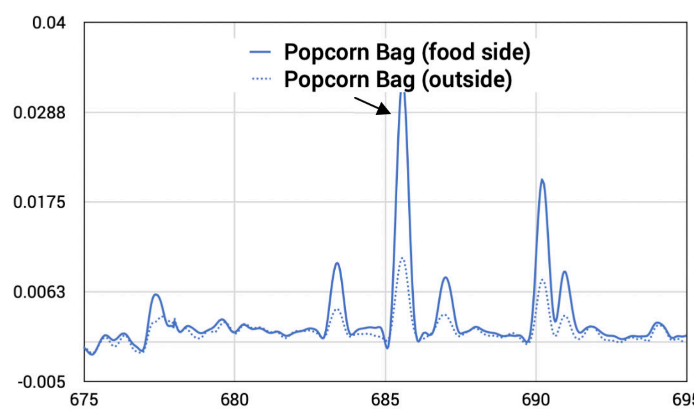

Fig. 6. Microwave popcorn bag. F is present on both sides, but higher levels on food side.

The highest levels of F were seen in a store-brand microwave popcorn bag. F was seen on both sides, though with higher levels on the food side (Fig. 6).

Detection of fluorine was determined by integrating the F 685.60nm peak in each of the 10 replicates and calculating

Summary of Integrated F Signal for Select Samples

Sample	Avg F685.60nm signal	StDev	Sigma Confidence
Restaurant C burger paper wrapper (food side)	-0.15	0.5	-0.3
Restaurant C burger paper wrapper (outside)	0.19	1.0	0.2
Restaurant D tortilla chip bag (food side)	2.1	0.9	2.4
Restaurant D tortilla chip bag (outside)	0.14	0.4	0.3
Restaurant A Cardboard Burger Box (food facing)	2.6	0.5	5.0
Restaurant A Cardboard Burger Box (outside facing)	-0.22	0.6	-0.4
Restaurant A Burger Wrapper (food facing)	2.7	0.5	5.1
Restaurant A Burger Wrapper (outside facing)	2.8	0.7	3.8
Restaurant B burger paper wrapper (food side)	-1.29	0.6	-2.0
Restaurant B burger paper wrapper (outside)	-2.12	0.5	-4.5
Popcorn Bag (food side)	24	3	7.1
Popcorn Bag (outside)	5	1	4.2

Table 1. Samples highlighted in blue meet 95% confidence detection threshold.

the average and standard deviation of signal. Samples with average signal greater than twice the standard deviation (2σ, or 95% confidence) were treated as positive detection.

As LIBS is an elemental analysis technique, it cannot determine whether detected F is from PFAS or other F-based compounds, nor whether the F was intentionally added. A quantitative detection limit for F was not determined, so some samples marked as non-detect may contain lower levels of F, may have F inhomogeneously distributed on the surface, or may have poor laser-sample coupling, producing weak LIBS plasma.

Conclusions

Portable handheld LIBS analyzers have been demonstrated to screen food packaging effectively for the presence of fluorine, which may be indicative of the presence of PFAS or other organofluorine compounds.

Further work could quantitatively calibrate a LIBS analyzer for F levels in packaging should elemental action levels be established. Lack of matrix-matched certified reference materials is a concern for any further quantitative work. Further work may also include correlating quantitative LIBS F concentrations with content of PFAS determined by other techniques like LC/MS.

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