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Characterizing plastics containing brominated flame retardants with combined LIBS and Raman spectroscopy

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Abstract. Waste electronic and electric equipment (WEEE) are collected in high amounts in the EU. However, in order to enable safe and effective recycling of their plastic fraction, harmful additives inside the plastics need to be identified. In this study, two spectroscopic methods, laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy were employed for characterizing different brominated flame retardants (BFRs) inside plastics from the actual WEEE stream, and also lab-made plastics. The results of this preliminary study indicate the ability of LIBS for accurate quantification of bromine content, and the prospective capability of Raman and combined Raman-LIBS for identifying different BFRs in plastics.

1. Introduction

As the use of plastics is steadily rising around the world, steps have been taken to drastically increase the recycling rate of these materials, particularly in the EU. The electronic and electric equipment domain constituted 6.2 % of annual plastic consumption in Europe in 2021 [1], and their collection rates are relatively high, up to 48 % [2]; thus, this fraction offers large amounts of material for recycling. In order to obtain required properties, a number of additives are compounded with their plastic components. A commonly used additive type is the brominated flame retardant (BFR), which is used for fire safety reasons. However, these chemicals are often hazardous to health and environment if migration occurs [3]; thus, recycling of the waste electronic and electric equipment (WEEE) fraction poses a challenge. In order to reprocess large quantities of plastics in this fraction, BFR-containing objects must be separated from those not containing said additives. The latter fraction, then, can be re-processed safely using regular treatment, while the former can be directed to facilities specializing in re-processing techniques for challenging materials, e.g. pyrolysis [4].

State-of-the-art methods of detecting BFRs inside plastics without using chemical analysis are few and often rely on indirect proxy measures. At the moment, X-ray fluorescence spectroscopy (XRF), which is accurate to very low concentrations, is the only verified way of reliably quantifying bromine inside plastics. Recently, near-infrared hyperspectral imaging has been attempted for classifying plastics to samples of high (over 2000 ppm) and low (below 2000 ppm) bromine concentration with reported accuracy of 90 % [5]. However, there is a need to not only detect these substances via elemental bromine, but also to identify the molecular composition, which would enable sorting chemically similar waste together, which facilitates their recycling, as re-processing chemically similar materials together provide better secondary raw material output [6]. Moreover, various novel BFRs have also been developed [7]

to replace very harmful legacy BFRs, which also speaks for the need for molecular identification. As common chemical analysis methods are slow and tedious, spectroscopic techniques have shown promise in this domain, facilitating on-line identification in sorting facilities. Thus, these methods may enable more efficient recycling of WEEE plastics.

In this paper we present our experimental research on two different spectroscopic methods, Raman spectroscopy and the quite novel laser-induced breakdown spectroscopy (LIBS), for quantifying and classifying BFR-containing plastics both from the real WEEE fraction and samples manufactured in the lab. The BFRs focused on in this study were decabromodiphenyl ether (deca-BDE), hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA).

1.1. Related work

In this section, previous studies that have utilized LIBS and Raman spectroscopy in the domain of plastics are reviewed shortly. The commonly used XRF is also reviewed, which is used to analyze the ground truth for elemental bromine concentration in plastics in this work.

Raman spectroscopy is a widely used tool for measuring complex vibrational modes of molecules, based on the wavelength changes of excitation laser light due to Raman scattering. It has been established to be an effective tool in distinguishing different plastics from each other based on their spectra [8], but is limited to measuring the sample surface. The method has been applied to quantifying flame retardants in plastics, e.g. ammonium polyphosphate and aluminium trihydrate [9], as well as BFR deca-BDE [10].

LIBS is a spectroscopic method in which a high-energy laser is focused on a sample such that a small amount of material is converted to plasma with excited atoms. As this excitation is relaxed, light characteristic of each atomic transition is emitted, which can be collected with a spectroscope. LIBS has been previously applied to plastic sorting in various works, as has been recently reviewed [8]. Detection of bromine with LIBS is challenging due to its deep ultraviolet (DUV) lying ground state transitions, and upper transitions emitting in near infrared region that requires excitation over the DUV transitions. Use of the bromine DUV emission lines has been demonstrated using a vacuum LIBS arrangement[11]; however, the vacuum is not feasible for online applications. Thus, typically bromine is detected using the atomic emission line at 827.24 nm (transition from energy level 9.36 eV to 7.86 eV). LIBS has been previously demonstrated for detection of flame retardants in plastics; however, the demonstrations have been concentrating to classification of BFR-containing plastics only made in the lab [12], or experiments with real WEEE samples employed only classification, without attempting to quantify the amount of bromine [13]. In this work, both classification and quantification is done for lab and real WEEE samples.

X-ray fluorescence (XRF) is a phenomenon in which atoms, when bombarded with X-rays, emit secondary X-rays whose energies are characteristic of each element. The elemental composition of material can be inferred from the spectra, as the secondary fluorescent X-rays are unique for each element. As X-rays are highly energetic, they penetrate materials with light elements such as plastics very easily. XRF has been applied for detecting heavy elements inside plastics, including bromine and chlorine [14], with detection limit of below 100 ppm for bromine with a modern hand-held XRF device.

2. Materials and methods

2.1. Samples

The samples used in this study included 25 samples prepared in the lab. These samples comprised of three different series: polystyrene samples with different amounts of HBCD (0, 2, 4, 6, 8, 10, and 12 wt%), and two series of ABS samples, doped with TBBPA and deca-BDE (0, 2, 4, 6, 8, 10, 12, 14, and 16 wt% in both cases). In addition to lab samples, pieces of real waste plastic samples from the WEEE stream (Category 5: small equipment of the EU WEEE Directive 2002/96/EC) were used. The pieces were selected based on their elemental bromine concentration (measured by XRF) to cover as much variation as possible. The actual BFR compound in these samples was determined with gas chromatography-mass spectrometry after concluding spectroscopic measurements, and the number of non-BFR-, deca-BDE-, TBBPA-, HBCD- and other BFR-containing samples were 2, 1, 5, 3 and 14, respectively.

2.2. Measurements

The XRF measurements were done using the Thermo Fisher Scientific Niton XL3t 900S GOLDD handheld analyzer. The device collects the XRF spectrum and automatically calculates the elemental concentration of different elements, including bromine. Plastics analysis calibration was used and thickness correction was applied to each plastic piece measurement. The total measurement time was 90 seconds, 30 seconds for each filter. The limit of detection for bromine is below 10 ppm for the analyzer.

LIBS spectra with 2048 distinct wavelengths in the range 800 - 853 nm was collected for each sample (see Figure 1a). The laser-induced plasma was ignited using laser pulse at 532 nm wavelength (Quantel Q-Smart 100) with 45 mJ of energy and temporal width of 10 ns. The pulse was focused slightly below the sample surface using a lens with 35 mm focal length. The sample was set on a transition stage that moved the sample in steps so that 5 laser pulses were shot to the same spot. The plasma emission was collected with a lens with 50 mm focal length in approximately 45° angle respective to the laser beam path. The collected plasma light was further coupled to a high-OH optical fiber bundle with 7 core fibers of $200\,\mu\mathrm{m}$ in diameter and 2 m in length (BFL200HS02, Thorlabs). The spectra were recorded with a spectrometer (Andor Kymera) equipped with an ICCD camera (Andor iStar 340T). The optimal gate delay and gate width for the signal recording with gain setting at 1800 were found to be $1\,\mu\mathrm{m}$ and $1.4\,\mu\mathrm{m}$, respectively. The obtained signals were averaged over 300 pulses.

Raman measurements were conducted using a time-gated technique, by which the collection of radiation is done in a short time window following the excitation laser pulse. As Raman scattering occurs before fluorescence, this technique enables the collection of Raman spectra with reduced fluorescence background. The spectrometer, Timegate PicoRaman, uses 532 nm excitation laser with 20 % power. 25 sub-acquisitions with 1000 detector readouts were collected over 15 pulses. The time window was set to 0.7 ns with 11 resolved time steps. Measurements employed the inverse geometry setup; the sample is measured with the Raman probe from below through an aperture on which the sample rests. The obtained Raman spectra comprised of 749 discrete data points in the range 0 - 2481 cm^{-1} (see Figure 1b).

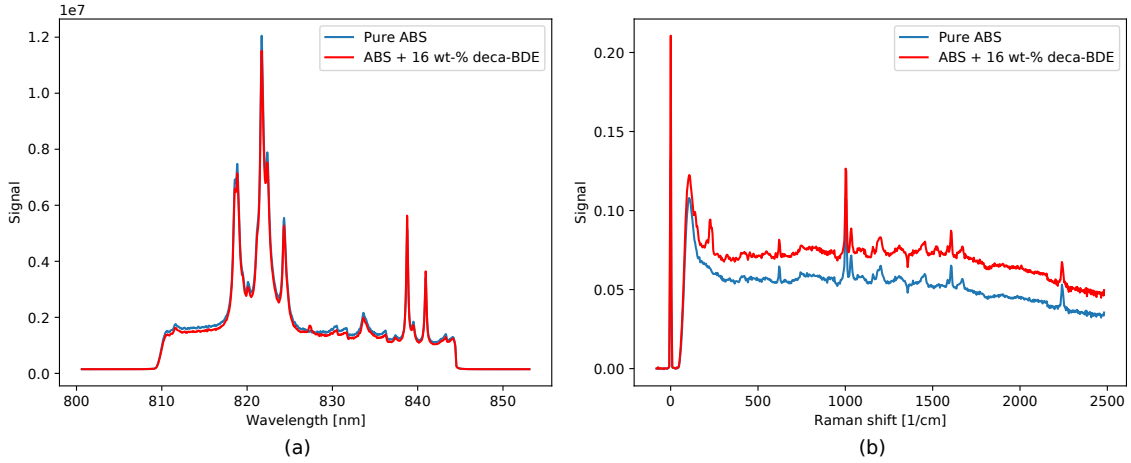

Figure 1: Raw spectra of pure ABS and ABS with 16 wt-% deca-BDE with (a) LIBS and (b) Raman spectroscopy. Elemental bromine emission is seen at 827.4 nm in LIBS spectrum. Spectral features of deca-BDE are seen at 225 cm^{-1} and 1523 cm^{-1} for Raman.

2.3. Pre-processing and data analysis

For pre-processing the LIBS spectra of the samples, the data is first de-noised with Savitzky-Golay filter (window size 11 and polynomial degree 2). Then, the spectra are standardized via the standard normal variate, i.e. the mean value of the spectral data points is subtracted from each data point, and divided

by the standard deviation of the spectrum. Finally, principal component analysis (PCA) is used for dimensionality reduction. The pre-processing of Raman spectra is identical, except baseline correction using airPLS [15] is done first prior to further steps, and the low wavenumbers (below 25 cm^{-1}) were cut to avoid interference from reflectance.

An iterative pipeline (see Figure 2) is used for finding the optimal parameters for PCA (namely, the number of components to keep) and best performing classifier/regressor. The PCA component number is iterated over from 1 to 20. For each PCA value, leave-one-out cross-validation technique is used, and a number of different machine learning models are run for each fold. Thus, a number of models are trained, for each number of principal components (PCs), on all but one sample, and tested on the left-out sample. This procedure is used for predicting each individually left-out sample.

For regression, the above pipeline is used for the WEEE and the lab samples individually for predicting the elemental bromine concentration given by XRF based on the LIBS and Raman spectra. 43 different regression models are used on each step. For classification, the pipeline is used for the combined WEEE and lab sample data, since the number of samples is relatively low. The samples are categorized into 5 classes: non-bromine containing samples, deca-BDE-containing, TBBPA-containing, HBCD-containing, and other BFR-containing samples. Three different approaches were used: LIBS and Raman spectra individually and in combination (with PCA done separately for both before combining the data). 33 different classifiers are used on each step.

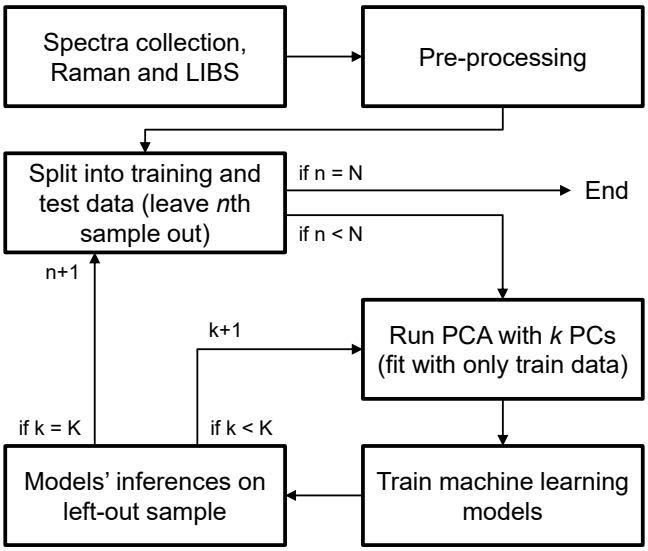

Figure 2: Visualization of the iterative pipeline. The pipeline iterates over different numbers of PCs, and runs a number of different machine learning models on each iteration step. This procedure is followed until inference is obtained for all samples that have been left out individually (leave-one-out cross-validation). In the figure, N stands for total number of samples, and K the maximum PC number.

3. Results

The cross-validation regression result plots using LIBS are shown in Figure 3. For the LIBS regression on lab and WEEE samples, the mean absolute error (MAE) was 0.0038 and 0.0578, while the maximum error was 0.0251 and 0.0578, respectively. As such, the performance on the lab samples is very good, while the WEEE case exhibits poor performance. For Raman, the regression results were very poor for both datasets; for lab and WEEE samples, the best obtained MAE were 0.0181 and 0.0183, with maximum errors of 0.072 and 0.056, respectively. The difference in MAE is negligible, so no clear correlation can be formed between the bromine concentration and the Raman spectra in either case.

For classification, selected metrics for using LIBS, Raman and their combination is shown in Table 1. As can be seen, the combined case slightly outperforms Raman, while the results of LIBS are poorer. The confusion matrix for the combined case is shown in Table 2. Out of the misclassified samples, 2 were lab-made while 9 were WEEE samples. Compared to the benchmark accuracy for 5-class classification (20 %), the results are relatively good. For LIBS, Raman and combined Raman-LIBS, the optimal PCA numbers were 18, 7, and 8 & 15, and the best models were Bagging Classifier, Logistic Regression and Extra Trees Classifier, respectively.

Table 1: Cross-validation classification results for the three datasets.

Method	F1-score	Accuracy [%]	Balanced accuracy [%]
LIBS	0.596	60.0	56.6
Raman	0.754	76.0	71.7
Combined	0.781	78.0	74.8

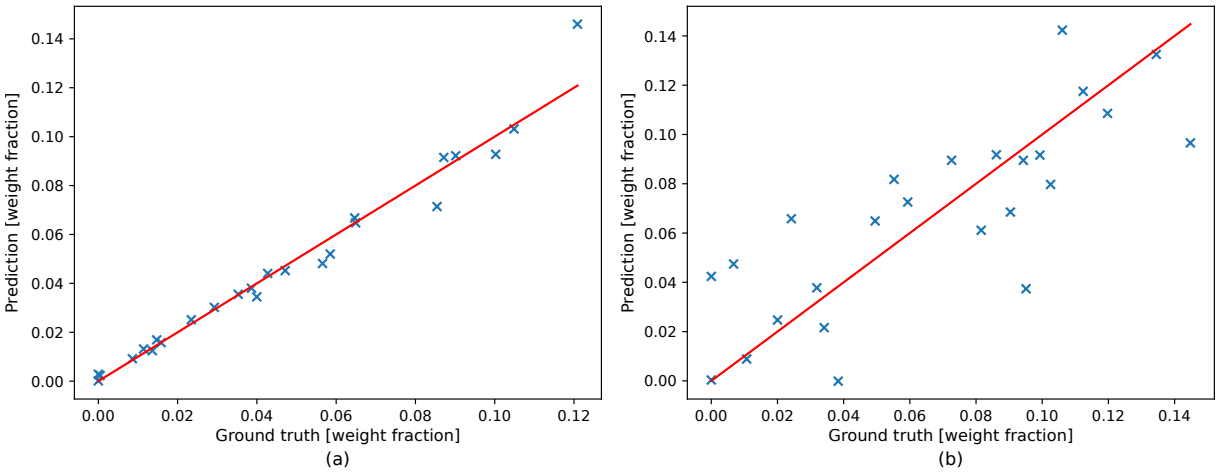

Figure 3: Cross-validated regression results for LIBS data of (a) the lab samples and (b) the WEEE samples. The optimal number of PCA components were 9 and 16, respectively, and the best model was Huber regressor in both cases. The solid red line shows perfect linear model performance, for reference.

4. Conclusion

In this paper, the use of LIBS and Raman for characterizing plastics with different BFRs was studied. According to the results, LIBS can be used to accurately predict the bromine concentration from plastics, while Raman can not. However, the differing shapes and irregularities of the WEEE samples produced poor results for LIBS, indicating the need for accurate automatized focusing. For classification, more data is needed to provide robust conclusions on the ability of the two spectroscopic methods in identifying different BFRs in plastic. However, the results with our dataset show that the capability for classification shows promise in the case of Raman and combined Raman and LIBS. These results are expected: as LIBS spectra manifest atomic excitations, it performs better in inferring bromine concentration rather than classifying BFRs; the opposite is true for Raman which probes the molecular structure. Future work includes measuring a larger set of WEEE samples with a setup allowing accurate focusing of the laser beam, as well as measuring a larger variety of samples (different polymers, different flame retardants).

Table 2: Confusion matrix of combined Raman and LIBS classification results.

		Predicted class				
		No BFR	**deca-BDE**	**TBBPA**	**HBCD**	**other**
Actual class	**No BFR**	3	0	0	1	1
	deca-BDE	0	8	0	0	1
	TBBPA	0	0	10	0	3
	HBCD	1	0	0	5	3
	other	0	0	1	0	13

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