

In-line measurements of chlorine containing polymers in an industrial waste sorting plant by laser-induced breakdown spectroscopy



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ABSTRACT

We report on laser-induced breakdown spectroscopy (LIBS) of chlorine containing waste polymers in-line of an industrial materials sorting plant. Material from municipal waste plastic collection containing different types of plastic pieces and impurities is measured without pre-treatment directly on the conveyor belt (conveyor speed 2 m/s). The encapsulated LIBS system mounted to the conveyor comprises a fast Nd:YAG laser and spectrometer with charge-coupled device (CCD) detector, a distance sensor, and a software for quasi real-time evaluation of measured LIBS spectra. Approximately 800,000 spectra are collected during the in-line measurement series using one laser pulse per spectrum. The optical plasma emission of Cl I at 837.6 nm is detected to identify waste polymers with high Cl content such as polyvinylchloride (PVC). The LIBS spectra are evaluated employing a fast linear correlation algorithm. The correlation histogram for more than 20,000 spectra shows three distinct peaks that are associated to different materials containing high amount of Chlorine (>20 wt %), Titanium, and low amount of Cl (<20 wt%). Signals of the LIBS sensor and a commercial near-infrared (NIR) optical reflection sensor were found to deviate for some samples. Such deviations might be caused by dark PVC samples that are detected by LIBS but missed by NIR reflection. Our results show that fast in-line identification of Cl containing waste polymer by LIBS is feasible under industrial conditions.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a versatile technique easy to apply for chemical analysis of multi-component materials. Measurements can be performed under ambient conditions and without pre-treatment of sample materials and element concentrations are determined with typical limits of detection (LOD) in the range 1–30 ppm, except for halogens [1–3]. The unique strength of LIBS is fast multi-element analysis out of the laboratory using portable or transportable measurement systems. Various groups have demonstrated field applications of LIBS under harsh conditions and in industrial environment, e.g., for on-site or in-line analysis of coal ash [4,5], metal melts [6–9], metal scrap [10], minerals [11], slag in steel production [12], and oil spill residues [13]. The LIBS has been employed also for the inspection of polymer waste [14–16] and the discrimination of different types of technical polymers [17,18].

Halogen elements like fluorine, chlorine, and bromine are used in many industrial processes and are contained in many

technical materials and products. The safe handling of halogens in materials production and recycling is an important issue as these elements are chemically very reactive and potentially hazardous. Polyvinylchloride (PVC, monomer formula C_2H_3Cl) is a chlorine containing polymer with widespread use in different segments like building and construction, packaging, automotive, electrical and electronic, textile, and others. PVC is among the top 3 materials by market share accounting for 11% of the total European demand for plastics (47 Mio tons in 2011) [19]. End-of-life PVC-based materials can be recycled delivering high-value secondary raw material for the construction and building sector, for example. More than 59% of the post-consumer plastic waste in Europe was recovered in 2011 either by recycling (6.3 Mio tons) or by energy recovery (8.6 Mio tons). For the energy recovery of mixed polymer waste, the PVC fraction is usually to be sorted out to avoid formation of HCl and other detrimental or toxic substances. Fractions of low PVC content can be used, for example, as surrogate fuel in cement industry [20]. Optical emission spectroscopy of halogens is complicated by the high excited state energies and rather high LOD values ($\gg 30$ ppm) are reported for halogens like Cl in solid matrix using LIBS and related techniques [1–3]. LIBS of PVC materials has been reported recently [21,22]. Standard methods for analysis of chlorine in technical materials are X-ray fluorescence spectrometry (XRF), atomic

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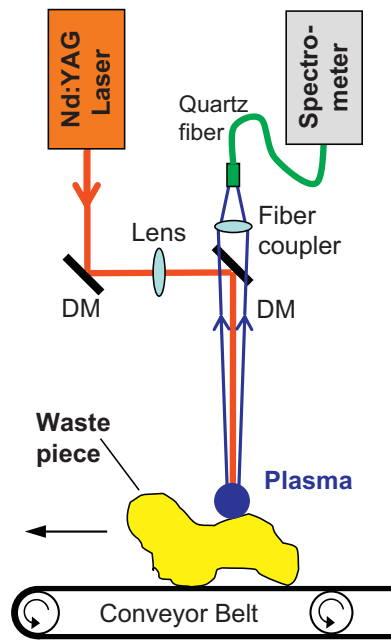


Fig. 1. Schematic setup for in-line LIBS measurements of waste materials in an industrial sorting plant. Nd:YAG laser pulses induce plasma at waste pieces on the conveyor belt (DM dichroic mirrors). Plasma radiation is detected in backward direction using fiber optics and grating spectrometer with CCD detector and fast read-out electronics.

absorption spectrometry, and near infrared reflection measurements.

Here, we report on in-line LIBS measurements of waste polymers and on fast identification of PVC waste in an industrial materials sorting plant. A high-repetition rate laser and fast spectrometer enabled the recording of LIBS spectra with rate of 100 Hz. A linear correlation algorithm was implemented to evaluate the measured LIBS signals in the vicinity of the near infrared Cl I emission line at 837.6 nm for each spectrum quasi in real-time.

2. Experimental

2.1. Measurement system

A rugged LIBS measurement system with protecting metal cabinet has been developed for the in-line measurements at the industrial waste material sorting plant. The schematic of the measurement setup is illustrated in Fig. 1. The radiation of a flash-lamp pumped Nd:YAG laser (Litron, wavelength $\lambda = 1064$ nm, pulse duration $\tau \approx 7$ ns, pulse energy $E_L \approx 80$ mJ, repetition rate $f_r \leq 100$ Hz) was focused on the surface of waste samples on the conveyor belt. The laser beam was directed perpendicular onto the belt surface and the laser spot diameter was approx. 1 mm. The optical emission of laser-induced plasma (LIP) was detected in backward direction using dichroic mirror, fiber optics, and a CCD spectrometer with fast read-out electronics (up to 2000 spectra/s). The CCD detector (Avantes Avabench) covered the spectral range $\lambda = 710$ –895 nm and had 2048 pixel (0.09 nm/pixel on average). For the gating of the detector an electronic trigger signal was used (delay time with respect to the laser pulse $t_d = 1.3$ μ s, gate width $t_g = 1.0$ μ s).

The LIBS sensor head contained the laser, spectrometer, optics, etc. and was installed above the conveyor belt in the plant (Fig. 2). The head had two measurement ports, one for the detection of incoming waste samples transported underneath the LIBS sensor and another for the LIBS measurement. The distance between ports was approx. 1 m. The sensor head was

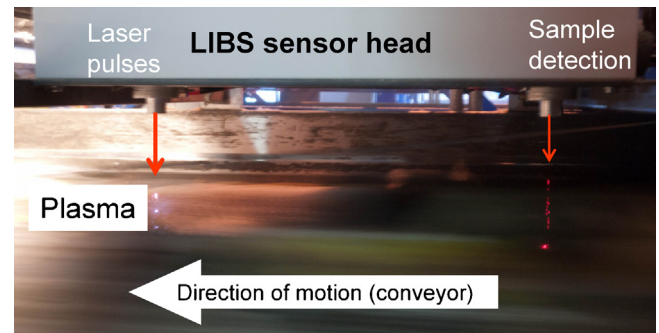


Fig. 2. Photograph of the LIBS sensor head installed above the conveyor belt in the industrial sorting plant. The Nd:YAG laser is triggered by the detection of incoming samples on the measured track (belt speed 2 m/sec).

mechanically stable (no moving parts), sealed against dust, and equipped with air-flushed windows at the measurements ports. The laser-triangulation based sample detector triggered the Nd:YAG laser to avoid laser ablation of the empty conveyor belt. Waste samples on the moving belt appear blurred in the photograph (Fig. 2). Small bright spots in the photo are LIP on the samples surface and scattered red light is from the triangulation laser. The conveyor had a width of 2 m and LIBS signals were collected only for a single measurement track along the belt. Samples lying beside this track were not detected and not analyzed by our LIBS system. Three-dimensional scanning of laser spots for LIBS measurements on conveyor belts has been demonstrated recently [11]. The LIBS sensor head was mounted besides a commercial near infrared (NIR) reflection sensor that can sort various types of technical polymers [23]. The NIR sensor installed at the conveyor was configured to detect PVC and extruded polystyrene (EPS).

The Nd:YAG laser was operated at its maximum pulse repetition rate (100 Hz) and single-pulse LIBS spectra were recorded to avoid summation over spectra acquired from different samples. All LIBS measurements were performed in air on un-treated waste samples as processed in the plant and delivered with the belt. More than 800,000 spectra were recorded during this in-line measurement series (two weeks). The LIBS and NIR signals from the same measurement track were recorded in parallel for direct comparison. Several of the LIBS measured waste samples were analyzed also by XRF in the laboratory. For calibration of the XRF spectrometer appropriate standards were used and waste samples were analyzed without pre-treatment.

2.2. Sample materials

The sample materials stemmed from municipal waste polymer collection and contained various types of polymer-based materials like bags, foils, packaging material, foamed plastic, bands, scarves, cups, bottles, and pipes. Such samples had very different form, colour, shape, and size (typical size was around 10–30 cm). Impurities in the waste material stream were mainly newspapers, aluminium cans, paper, and cardboard.

2.3. Evaluation of LIBS signals

For fast evaluation of LIBS signals the spectrum measured for a polymer waste sample was compared to a reference spectrum. For each LIBS spectrum $I(\lambda_i)$ measured on the sample at wavelengths λ_i the linear correlation coefficient $r(I, I_{ref})$ was calculated

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