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Classification of wrought aluminum alloys by ANN evaluation of LIBS spectra from aluminum scrap samples☆

B. Campanella [a], E. Grifoni [a], S. Legnaioli [a,b,*], G. Lorenzetti [a], S. Pagnotta [a], F. Sorrentino [c], V. Palleschi [a,b]

[a] Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds, Research Area of National Research Council, Via G. Moruzzi 1, 56124 Pisa, Italy
[b] National Interuniversity Consortium of Materials Science and Technology (INSTM), Italy
[c] Istituto Nazionale di Fisica Nucleare, sezione di Genova, via Dodecaneso 33, 16146 Genova, Italy

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ABSTRACT

Every year throughout the world >50 million vehicles reach the end of their life, producing millions of tons of automotive waste. The current strategies for the separation of the non-ferrous waste fraction, contain mainly aluminum, magnesium, zinc and copper alloys, involve high investment and operational costs, and pose environmental concerns. The European project SHREDDERSORT, in which our research group was actively involved, aimed to overcome this issue by developing a new dry sorting technology for the shredding of non-ferrous automotive wastes. This work represents one step of the complex SHREDDERSORT project, dedicated to the development of a strategy based on Laser Induced Breakdown Spectroscopy (LIBS) for the sorting of light alloys.
LIBS was here applied in laboratory for the analysis of stationary aluminum shredder samples. To process the LIBS spectra a methodological approach based on artificial neural networks was used. Although separation could in principle be based on simple emission line ratios, the neural networks approach enables more reproducible results, which can accommodate the unavoidable signal variations due to the low intrinsic reproducibility of the LIBS systems. The neural network separated samples into different clusters and estimates their elemental concentrations.

1. Introduction

In the EU, the amount of waste generated by the automotive industry raised up to 10 million tons in 2010, and it is foreseen that it will increase by 40% until 2015 [1]. About 8% of the total weight in the automotive shredder corresponds to non-ferrous metals, whose recycling process has a strong relevance from the environmental and economic point of view due to the presence of aluminum and other valuable metals and alloys (e.g., copper, brass, magnesium, lead, stainless steel, and zinc) [2]. Currently, an effective separation of these metals is partially achieved by heavy-media separation techniques, which have several practical drawbacks such as high cost, substantial metal losses after separation due to corrosion in the wet media, a significant contamination of each density fraction, and the inability to separate alloys with similar composition [3]. Other conventional bulk separation techniques, such as magnetic, eddy current and color sensing, are not helpful because the difference in the physical properties of aluminum alloys are to small [4]. These techniques can also require a thermal and chemical pre-treatment etching step, which raises obvious environmental and cost concerns [5]. Several novel scrap sorting techniques have been proposed to overcome these problems, such as X-ray transmission (XRT) and hand-held X-ray fluorescence (XRF). The high cost of XRF units prevents its pervasive use in scrap processing yards. Moreover, the spectral ratios of scrap materials are determined according to their major alloying element because aluminum has a very low characteristic radiation which cannot be read unless under vacuum or fluxing with helium. Studies on the commercial applicability of XRF in sorting have shown it to be capable of separating by major alloy family but cannot determine specific alloys [6].

A joint European project, named SHREDDERSORT (Selective Recovery of non-Ferrous Metal Automotive Shredder by Combined Electromagnetic Tensor Spectroscopy and Laser-Induced Plasma Spectroscopy), has been funded by the CE 7th Framework for Research with the purpose of developing a new dry sorting technology for non-ferrous automotive shredder according to their alloy composition. According to the objectives of the Project, the light fraction of the shredders (Al and Mg alloys) will be alloy-sorted using Laser Induced Breakdown Spectroscopy (LIBS), whose potential for the recovery of Mg and Al alloys has already been established at the laboratory and

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* Corresponding author at: Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds, Research Area of National Research Council, Via G. Moruzzi 1, 56124 Pisa, Italy.
E-mail address: stefano.legnaioli@cnr.it (S. Legnaioli).

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plant scale [7–14]. In particular, LIBS performs best for low-Z elements than other hand held units such as XRF.

On the other hand, the LIBS technique when used in-situ without any sample pretreatment notoriously suffers from analytical problems related to its rather poor sensitivity, reproducibility and accuracy [15], which place the LIBS technique below the standards as an analytical laboratory technique. However, in many applications (e.g. in the industry) sensitivity and accuracy issues might play a minor role with respect to the possibility of operating fast classification or comparing the composition of unknown objects with reference standards. In several research papers the use of artificial neural networks (ANNs) in LIBS quantitative analysis has been proposed because of the quickness and robustness of the algorithms [16–17].

The aim of this study was to develop a fast and reliable analytical procedure to distinguish the composition variation between different wrought aluminum alloys, allowing their classification and sorting. The work constitutes a "feasibility study" which investigates the application of ANN analysis to real aluminum scrap samples for the industrial environment. This experimental strategy has been developed for operating in the same conditions that characterize the at-line analysis of wrought aluminum alloys in the production line. At the basis of the method is the determination of the concentration of some key elements of the specific alloy by double-pulse LIBS. In order to speed up the procedure of analysis and to take into account potential nonlinearities contained into the LIBS spectra, an ANN approach was applied.

2. Experimental

Laboratory tests were realized using Modì, a mobile LIBS instrument equipped with a dual pulse laser (Nd - YAG, $\lambda = 1064$ nm, single pulse energy up to 80 mJ in 10 ns) and a non-intensified double grating spectrometer (AvaSpec Dual-Channel Fiber Optic Spectrometer from Avantes). The spectrometer covers simultaneously the spectral interval between 200 and 430 nm (with resolution of 0.1 nm) and between 415 and 900 nm (with resolution of 0.3 nm) [18–19].

The samples used for the test were 39 real Al scrap samples already characterized, in terms of their composition, using Spark-Optical Emission Spectroscopy analysis by the Instituto Superior Técnico de Lisboa (Portugal), in order to evaluate the predictive ability of LIBS. Samples were not cleaned before the analysis to simulate 'real environment' scenarios.

For all samples, three double-pulse LIBS spectra were collected in different points (selected casually) of the surface of any sample, for a total of 117 spectra for ANN building. This experimental strategy corresponds to what occur in the real industrial conditions, on samples moving at a speed of several meters per second on a conveyor belt. Also the power of the laser beams and the interpulse delay were set for obtaining conditions similar to the ones of the SHREDDERSORT instrument that will be used for the on-line sorting at the plant ($E = 60$ mJ per pulse in 10 ns, interpulse delay $= 1$ μs). All the spectra were acquired 200 ns after the second laser pulse, with an integration time of about 2 ms.

In order to process the LIBS spectra, the Neural Network Toolbox of MATLAB R2014b (The Mathworks Inc. USA) was used. A MATLAB script was written which loaded the data file, trained and validated the network, and saved the model architecture.

The input of ANN were 564 intensity values from 105 LIBS spectra (3 spectra per 35 samples) in four spectral windows, 279.1:289.1, 322.1:340.3, 355.1:392.1, 401.2:408.2 nm; selected according to the most intense emission lines of the elements considered. We used as output a 4×1-column vector directly encoding the class of the metal alloys: 3xxx = [1 0 0 0], 5xxx = [0 1 0 0], 6xxx = [0 0 1 0], and 7xxx = [0 0 0 1].

The hidden layer had 4 neurons, the chosen transfer function was hyperbolic tangent and the back-propagation optimization was realized using the Levenberg-Marquardt method [20]. Data was randomly distributed into the learning (70%) and verification (30%). The performance of the neural network model was evaluated by the root mean square error (RMSE) and the linear correlation coefficient (R^2) between the modeled output and measures of the training and validation data set. The ANN was considered valid when the RMSE was at the minimum and R^2 was higher than 0.95. The performances were also directly evaluated on the basis of the reliability of the classification proposed for the sample analyzed in this work.

3. Results and discussion

Few years ago, applications of ANN in LIBS spectroscopy have been demonstrated for classification and prediction [21–29] thanks to the quickness and robustness of the algorithms, and the availability of specialized commercial and open-source software. Since now, however, no study has faced the division into classes of aluminum alloys, which is the main problem to be addressed by sorting industry.

Another specific reason of the success of ANN in LIBS analysis is the extreme facility by which is possible, in a LIBS experiment, to accumulate hundreds of spectra, thus providing a quite large base of data for the most critical steps of the ANN procedure, i.e. the training and validation of the ANN model. In the ANN approach the inputs (LIBS spectrum intensities) are combined (non-linearly) in order to produce some output. The coefficients of the non-linear combination of the inputs are optimized in order to find the best correspondence between inputs and outputs, on a set of test samples. The reliability of the results is then validated on a different set of (known) samples.

LIBS spectra of different alloy samples were recorded and analyzed using an ANN model. In their work Philip et al. [30] have pointed out that using as input in ANN a complete spectrum would increase the complexity of the model under training. The presence of noise in the data makes also the model inefficient. For this reason we concentrated on four spectral windows which can provide the concentration information of the interesting elements to increment the robustness of the models. The lines were chosen with the preference given to: (a) strong lines in the working spectral range; (b) minimum overlapping with other lines and (c) minimum self-absorption or detector saturation.

In this work, a total of 39 samples were analyzed in triplicate (117 spectra). Thirty-five samples were used to build and train the ANN and a separate set of 4 samples were selected to test the network, chose among those with intermediate concentrations in the range of the certified values. In fact, it is important to stress that the ANN approach is a method based on calibration. Therefore, as in classical calibration curves approaches the ANN should not be used for extrapolating results outside the range of the calibration. The test of

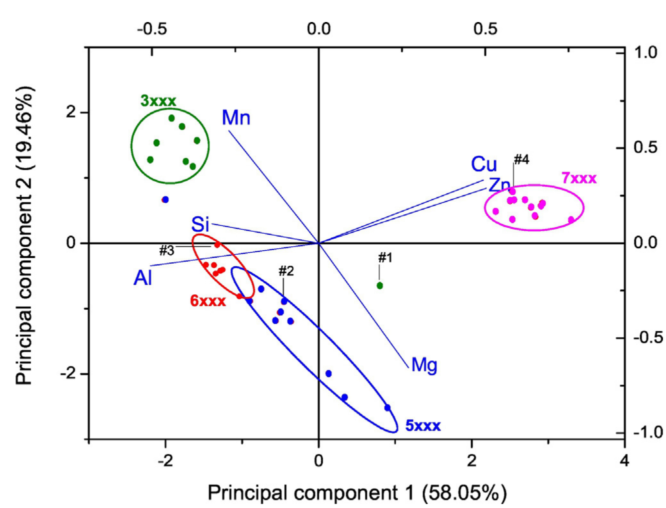

Fig. 1. PCA classification of the 35 samples according to their nominal composition. The numbers #1, #2, #3, #4 identify the four samples predicted by ANN-1.

Table 1
Identification of class by ANN (three spectra per sample acquired). Numbers in bold indicate the final class chosen for each sample.

Class	Sample-1 (alloy 3xxx)			Sample-2 (alloy 5xxx)			Sample-3 (alloy 6xxx)			Sample-4 (alloy 7xxx)		
3xxx	0.1	−0.5	−0.2	0.2	0.1	0.2	−0.1	0.0	0.0	0.2	0.2	0.3
5xxx	**1.1**	0.5	**0.8**	**1.0**	**1.1**	**1.0**	0.1	0.0	0.0	−0.3	−0.3	−0.3
6xxx	−0.1	0.5	0.2	0.0	−0.1	−0.1	**0.8**	**1.0**	**1.0**	0.3	0.3	0.4
7xxx	−0.1	0.5	0.2	−0.2	−0.1	−0.1	0.1	0.0	0.0	**0.7**	**0.7**	**0.6**

the goodness of the ANN must be performed using samples with concentration values within the interval covered by the samples used for the network training.

Wrought aluminum alloys can be divided into eight classes (1xxx, 2xxx, 3xxx, …) depending on the principal alloying element. The samples analyzed in this work belonged to class 3xxx (manganese 0.4–1.2%), 5xxx (magnesium 1–5%), 6xxx (magnesium 0.5–1% and silicon 0.5–1.4%), and 7xxx (zinc 1–7.6%).

Automated LIBS sorting systems have been already developed for aluminum cast and wrought alloy recycling [31,32].

Our analytical approach has the goal of reproducing at the best the results of conventional laboratory analysis, in the same conditions of application of the online SHREDDERSORT instrument, simulating 'real environment' scenarios. If we report the nominal concentrations evaluated by Spark-Optical Emission Spectroscopy for the 35 samples used for build the ANN, it is possible to classify them using a simple Principal Component Analysis (PCA). Including the predicted four samples (#1,#2,#3,#4) in the PCA plot (see Fig. 1), we can note that samples #2, #3, #4 are correctly classified in their corresponding class. Sample #1, instead, is not associated to a specific cluster, probably due to Mg overestimation.

The conventional way of applying an ANN to the study of industrial samples is based on the prediction of the nominal concentrations of the alloys; this approach has been already validated in the past for several industrial applications. However, the classification model sometimes would fail even when the elemental concentrations are determined

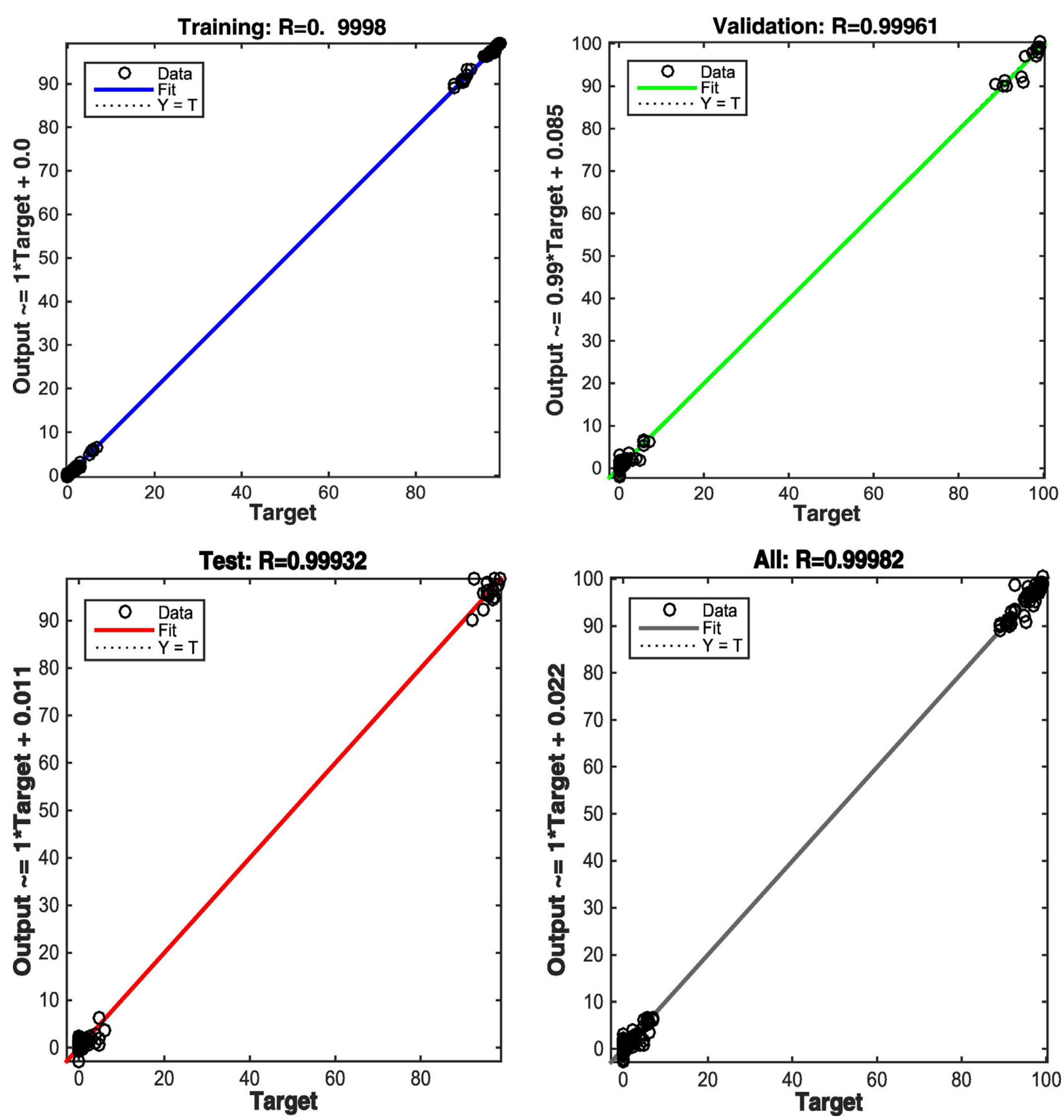

Fig. 2. Regression performance of the ANN predictions with respect to the nominal alloys classes for training, validation and test sets, and the whole data set. Continuous lines correspond to the ideal condition where the output coincides with target.

with consolidated laboratory analytical techniques, depending on the precision in the determination of the key elements and on the reliability of the model. Moreover, since many of the lines used for analysis are unresolved, a highly accurate quantitative analysis is difficult to perform.

Considering that the major need of recycling industry is the effective separation of aluminum alloys into different groups, depending on their future applications, an ANN algorithm was ~~also~~ developed for direct samples separation into classes. At first, we used as output of the network, for the 35 samples, the number of the respective class (3, 5, 6, or 7). The resulting ANN was applied to the classification of four samples, one from each class. For each sample, the results presented correspond to the three spectra per sample that were acquired. For three samples (class 5xxx, 6xxx, and 7xxx) the correct classification was obtained for all the three spectra acquired. On the other hand, the three spectra from the sample belonging to class 3xxx were not correctly classified, with one spectrum even assigned to the non-existent class 9, since the ANN algorithm works with continuous and not discrete variables.

To overcome this problem, we codified each class as a 4×1-column vector, 3xxx = [1 0 0 0], 5xxx = [0 1 0 0], 6xxx = [0 0 1 0], and 7xxx = [0 0 0 1]; in this new approach, the vector replaced the number of the class as output in the ANN algorithm. The output of the network on the test samples returns a 'fuzzy' classification, in which the components of the vector express the degree of belonging of the sample to the class or, in other words, the probability that the 'unknown' sample would belong to each of the four classes. The main class of the sample is the one corresponding to the largest component of the output vector (largest probability).

In our case, the classification resulted satisfactory for all the samples, except for sample-1, belonging to class 3-xxx, but classified as class 5xxx in all the three spectra acquired (see Table 1).

For each spectrum, the ANN closes to 1 the sum of the four vector components. If the predicted value is <0.5 the spectrum is non-associated to the class.

Figs. 2 and 3 show the regression graphs and the error histogram for the training, validation and test sets.

The samples that should be used for the validation of the ANN built with element concentrations are limited in number by the requirement of having the concentration of the main elements within the limits defined by the calibration (training) set. The 'fuzzy' approach implemented by our ANN has the interesting by-product of relaxing the constraints on the elements' concentration in the validation set, since the classification in this case does not pass through the determination of the elements' concentration. The only constraint in this case is for the training set to represent the variability of the samples within the different classes, and the external test set to belong to the same classes. We exploited this characteristic of the 'fuzzy' approach to verify the quality of the ANN network, using an extension of the Leave-one-out procedure, described in ref. [33]. We extracted from the samples four elements at a time, from the four different classes, rebuilding every time a new network with the 35 remaining samples up to ten times.

Fig. 4 shows the results obtained for the classification of the samples with the 'fuzzy' approach.

For class 7xxx we obtained the highest percentage of correct classifications (90%). This is not surprising, as class 7xxx was well separated by the others in the PCA analysis based on the nominal concentrations (see Fig. 4). For class 5xxx and 6xxx satisfactory results were obtained (70 and 83%, respectively), while class 3xxx obtained the lowest degree of correct classification. Considering the totality of the samples, the percentage of samples correctly identified is 74%, while wrong identifications are 15%. Eleven percent of the samples were not classified. In the literature there are few examples of similar applications with better results using more performing LIBS systems [34–36]. However, we have to take into account that in this case, real unclean samples using just one laser shot has been analyzed instead of clean reference materials. Thus, in the case of alloys identification realized with single-shot measurements for a large material set, it seems to us that 74% could be a satisfying result.

Most samples from class 5xxx were marked as belonging to class 6xxx. In terms of automotive recycling, the interchange between 5xxx or 6xxx alloys is not particularly problematic, as they can be sorted as a unique class.

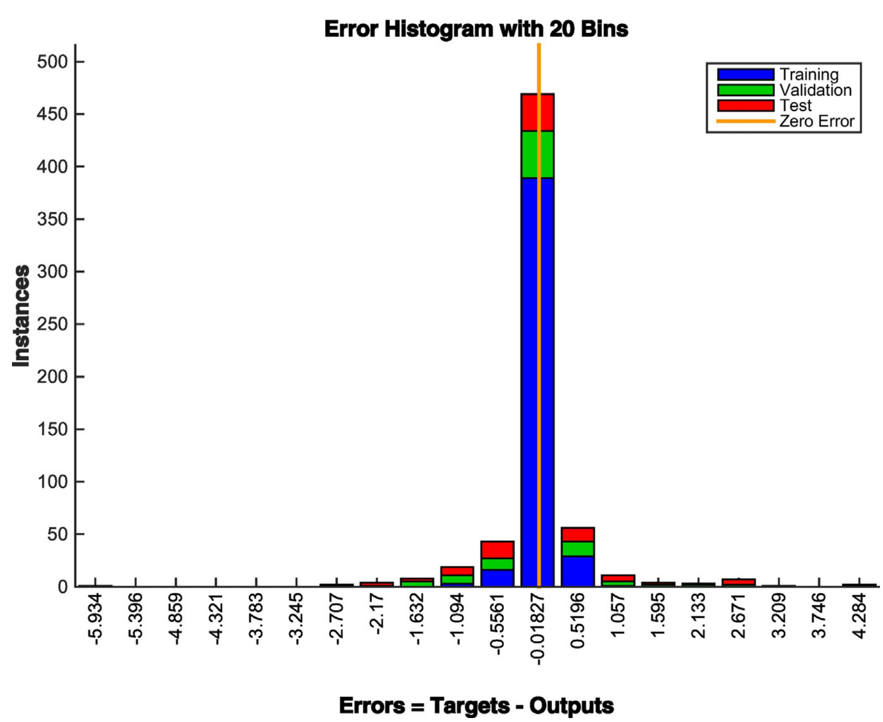

Fig. 3. Error histogram of the ANN predictions with respect to the nominal alloys classes for training, validation and test sets.

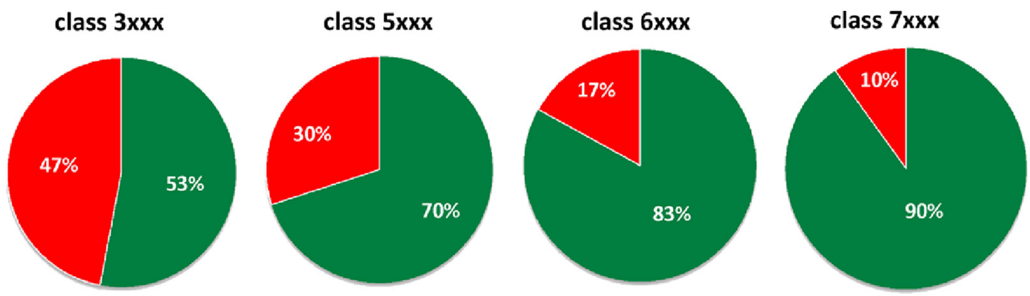

Fig. 4. Percentages for each alloy-class of samples correctly (green) and wrongly (red) classified by ANN-2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Thus, in principle, it would be possible to divide the alloys into three broad groups: class 5xxx and 6xxx (from automotive shredding), class 7xxx (from aircraft), and the remaining classes. The combination of the class 5xxx and 6xxx improves the percentage of correct classifications for the samples belonging to this group, bringing it to 90%.

Although the fuzzy approach used in ANN does not directly determine the elemental composition of the samples, it's still true that the percentage of correct classifications strongly depends on the elements that characterize each class. Class 7xxx is well separated by the others, as its key element, zinc, is present at much higher concentrations than in the other three classes. On the other hands, the concentration intervals of magnesium and manganese, key element for the sorting of class 3xxx, 5xxx and 6xxx, are not so different among the samples. Moreover, these two elements may be present in abundance as contaminants on the surface of unclean samples, and a single laser shot could be not sufficient to reach the surface below the dirt coating. Several strategies have been proposed to overcome the issue of oxide layer on samples surface (e.g., laser pre-ablation, the use of high frequency or high power lasers). However, nowadays high-repetition-rate lasers still work at distances too short to be compatible with the 3-D shape of industrial scrap samples. Pre-ablation is required mainly in quantitative applications, and it is scarcely suited to samples movement on the industrial tape.

By using the 'fuzzy' approach implemented by the ANN, 84.4% of samples effectively belonging to class 7xxx were correctly identified, while 15.6% of samples from other class were wrongly misclassified as class 7xxx. For class 5xxx + 6xxx, we obtained 91.5% of right classification and 8.5% of false positives.

In the application at the recycling plant, the aluminum scraps on the conveyor belt are analyzed on-line by a set of lasers; the output of the ANN would activate, and at the end of the belt, a sorting device that will divide the scraps into different sub-funds. We verified that the ANN algorithm enables the separation of wrought aluminum into three groups (class 5xxx + 6xxx, class 7xxx, other classes), thus it can be apply for a proper recovery strategy, which is valid for the large majority of aluminum scraps (see confusion matrix shown in Table 2).

The speed of LIBS analysis is of the order of fractions of second, while classification by ANN is almost instantaneous (ever faster than the measure itself). Classification speed could be improved by optimizing the transfer of the emission lines of interest respect to the entire spectrum.

Table 2
Confusion matrix according to the LIBS/ANN determined composition of the scraps.

		Predicted class			
		3xxx	5xxx	6xxx	7xxx
Actual class	3xxx	2	1	1	1
	5xxx	0	3	0	0
	6xxx	0	0	3	0
	7xxx	0	0	0	3

We can conclude that the use of LIBS, combined with ANN analysis, could be a valuable tool for a fast and at-line separation of wrought aluminum alloys for automotive recycling industry.

4. Conclusion

The development and application of automated sorting technologies capable to detect, select and separate different alloy types could be of crucial importance in the progression of the recycling loop.

The results obtained in the framework of the SHREDDERSORT project on the use of a LIBS/ANN method for classification demonstrate the possibility of an efficient (>75%) classification of non-ferrous metallic automotive scraps working in conditions simulating the industrial environment (dirty samples, single shot for each sample).

An innovative 'fuzzy' ANN approach, which directly differentiates the alloys according to their class, has been found to be more reliable and performing with respect to a conventional ANN approach where the classification of the sample is obtained after the quantitative determination of the elemental composition of the scraps.

In view of the on-line application of LIBS at a recycling plant, the performances of the LIBS/Fuzzy ANN for classification and sorting of the Al alloys is satisfactory, considering the recovery percentages guaranteed by the ANN and the constrains associated to the requested measurement conditions.

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