PGNAA Spectral Classification of Metal With Density Estimations
Helmand Shayan*, Kai Krycki, Marco Doemeland, and Markus Lange-Hegermann*

Abstract—For environmental, sustainable economic and political reasons, recycling processes are becoming increasingly important, aiming at a much higher use of secondary raw materials. Currently, for the copper and aluminum industries, no method for the non-destructive online analysis of heterogeneous materials is available. The prompt gamma neutron activation analysis (PGNAA) has the potential to overcome this challenge. A difficulty when using PGNAA for online classification arises from the small amount of noisy data, due to short-term measurements. In this case, classical evaluation methods using detailed peak by peak analysis fail. Therefore, we propose to view spectral data as probability distributions. Then, we can classify material using maximum log-likelihood with respect to kernel density estimation and use discrete sampling to optimize hyperparameters. For measurements of pure aluminum alloys we achieve near-perfect classification of aluminum alloys under 0.25 s.

Index Terms—Classification of metal, kernel density estimation, maximum log-likelihood, online classification, prompt gamma neutron activation analysis (PGNAA) spectral classification, random sampling.

I. INTRODUCTION

The recycling of scrap available in Europe as secondary raw material is the safest, most sustainable, and economical form of raw material supply, which is available despite political conflicts with mining countries. In addition, the conflict between the indigenous population and the mining industry for example regarding human rights can be avoided or reduced in these countries [1], [2]. Due to the high and heterogeneous mass flows in copper and aluminum production, there is great interest in the classification of recycling materials in real time in order to classify the secondary metallic raw materials according to existing standards and regulations.

In a digitized recycling process, precise testing of inhomogeneous materials online would allow optional control of the composition of the recycled product (alloy-to-alloy recycling). In particular, more scrap metal could be recycled to produce high-quality alloys in a targeted manner, making the production of metal economically and environmentally more sustainable. According to the state of the art, there is currently no non-destructive metrological solution for copper or aluminum production.

Scrap is currently assessed using samples that are viewed as representative. Processes such as X-ray fluorescence analysis (XRF), optical emission spectroscopy (OES) or laser-induced breakdown spectroscopy (LIBS) only allows surface-based analysis. This can only be used for homogeneous materials or requires complex sample collection and chemical preparation. These are often neither economically feasible nor can they be carried out online.

The measuring systems based on prompt gamma neutron activation analysis (PGNAA) allow nondestructive elemental analysis of complex material flows or material batches and differ from existing methods in that the material to be measured is analyzed integrally. During a measurement, a neutron-induced gamma spectrum is recorded, the evaluation of which allows the complete elemental composition of the material batch to be determined. With PGNAA, neutrons penetrate the sample material, interact with the nuclei therein and generate atoms in an excited state. For this work, a demonstrator measurement facility was used, wherein free neutrons are produced using a neutron generator. Monoenergetic neutrons of 2.45 MeV are moderated to thermal energies to maximize the probability of neutron capture within the sample material. The successive relaxation of the atomic nuclei of the sample material induces characteristic gamma radiation for the elements (even nuclides) contained in the sample material, which is measured with a detector. Subsequently, the elemental composition of large-volume samples and any material flows is analyzed nondestructively, regardless of their chemical condition, coatings or impurities. This means that inhomogeneous materials can be analyzed without costly sampling and chemical preparation, which are destructive and often can neither be carried out economical nor online. The measuring method is robust and is used, among other things, in oil exploration, in the detection of explosives and as online capable method for quality assurance in the cement industry and coal mining [3], [4], [5].

Through modern, high-resolution detector systems such as high-purity germanium (HPGe) detectors and newly developed evaluation algorithm software the problem of element identification in the PGNAA spectra can be solved. The software analyzes the peaks in the PGNAA spectrum (see Fig. 2) in comparison with nuclear databases [6].
The contribution to the improvement of the gamma detectors is done for example by research on the readout electronics of the detectors [7], [8].

Classification by spectroscopy is used in various fields such as the differentiation of tablets, juices, wines [9], the search of iron ore deposits [10], the deciphering of the chemical composition of the atmospheres of extrasolar planets [11], the detection of radioactive materials [12] or for nuclear safety [13]. Different Spectrometer is used, such as FTIR, NIR, MIR and Raman [9], [14], [15], angle-resolved photoemission spectroscopy (ARPES) [16], LIBS [17] or PGNAA [18].

The established analyses in the spectral analysis are based on machine learning (ML) methods. Neural networks (NNs) were already applied in the 1990s for the identification of isotopes in the PGNAA spectra [19], [20], [21]. In certain applications such as radioactive material identification, it has been shown that some newly developed ML and deep learning (DL) methods [deep belief network, random forest regression (RFR), logistic regression (LR)] have better performance than the conventional method based on the region of interest (ROI) [12], [22]. Backpropagation NN (BPNN) is significantly better at recognizing fabrics than Monte Carlo library least-squares (MCLLSs) [18]. It has also been shown that convolutional models should be preferred over fully connected architectures [23]. A comparison of convolutional NN (CNN) to partial least squares-discriminant analysis (PLS-DA), NN, LR, and support vector machine (SVM) was made for NIR, MIR, Raman spectra. CNN generally performed better on raw data than the classification and regression models [9].

For the classification of nuclear material, the decision tree, random forest, NN, and Bayesian network methods were used. The accuracy of each method was between 98% and 100%. However, under certain conditions (a p-value of 1e−09), the decision tree classifier achieved the highest accuracy of 99.6% [13].

The simulation of the data is done by Monte Carlo methods (MCNPX, MCNP, MCNP4C) [24], [25], [26] a coupled MCNP and GADNASDFR approach [23], matrix-based method [27] and sampling methods for the addition of noise [16].

We aim to fill the literature gap by presenting the approach of online classification of metal alloys by PGNAA as a novelty. This approach has not been used by anyone before. Furthermore, we propose new access to online classification by interpreting a spectrum as a probability distribution. Specifically, we interpret each measured gamma energy value as the probability of its occurrence. Here we do not restrict to individual peaks or energy ranges, instead, we use the complete energy range and thus all information of the spectrum. For this, we only need one fully measured spectrum (see Figs. 2 or 3) per material as training data and no data preprocessing. This allows us to use probabilistic methods (kernel density estimator, maximum log-likelihood method) for classification in order to significantly and sustainably improve scrap recycling and its economic and environmental aspects.

For the classification task, a fully measured spectrum is obtained for each material. Using a kernel density estimator, the corresponding probability distribution can be generated for each of the materials’ spectra. The kernel density estimator uses the known (stochastic) densities from the data analysis. To assign an unknown short-time measurement to a material, we use the maximum (log-)likelihood method. The maximum (log-)likelihood method assigns the short-time measurement to the most fitting distribution of a fully measured spectrum and thus to the corresponding material.

This method does not reduce the spectra to their individual peaks but uses the entirety of the measured data. This has the advantage that all details of the data are used for the classification. In this way, even similar copper and aluminum alloys can be classified in under 0.5 s with a certainty of over 90% (see Figs. 10 and 11).

We simulate new spectra by sampling. For that, we need only one complete measured spectrum of material to gain training, validation, and test data. Therefore, any number of spectra can be generated easily and quickly from a single spectrum. Depending on the size of the random samples, any short measurement times can be simulated. This method generates 50 short-time spectra/s. This saves the costly acquisition of new data. Furthermore, training, validation, and test data are very essential for parameter estimation of the kernel density estimator and training of any models such as NNs.

In contrast to regression, each material class must be clearly defined by means of a completely measured spectrum of a material. With the method mentioned, we can carry out online classification of heterogeneous substances. This means that similar substances such as aluminum and copper alloys can in principle be classified online. We test our method to classify 20 substances. These included five aluminum and six copper alloys. The presented method scores better than a convolution NN (CNN). CNN does not classify short time spectra (measurement time less than 1 s) of copper and aluminum alloys as well as compare [28].

The aim of Section II is to introduce the PGNAA and the structure of the data. The methods for classification are presented in Section III and the method for data acquisition introduced in Section IV. The optimization of the hyperparameter and the results of the classification are dealt with in Section V. Finally, Section VI concludes our findings.

II. PGNAA AND DATA

Neutron activation analysis (NAA), in which the sample material is bombarded with neutrons, is used to determine the metal compound. There are different types of NAA, such as PGNAA, delayed gamma NAA (DGNA), instrumental NAA (INAA), and radiochemical NAA (RNAA) [4].

PGNAA analyzes material continuously by irradiating it with a neutron beam. In this process, the atomic nuclei are excited. Various nuclear reactions can be induced by neutron irradiation. The excited nucleus can relax by emitting one or more gamma quanta (see Fig. 1), [6]. The excitation of the 1All measurement times are stated with respect to the PGNAA demonstrator facility used in the research project MetalClass.
atomic nuclei of the sample material induces a characteristic gamma radiation for the sample material, which is measured with a gamma ray spectrometer. The gamma energies are thereby stored in a table (see Table I). The row “Counts” gives the amount with which the corresponding energy values were measured. From Table I we see the number of channels, the difference between two neighboring energies (about 0.7 keV), typical numbers of counts and the energy range we measured.

We did neither analyze changing external circumstances nor different calibrations, so throughout all datasets the measurement background and energy calibration are kept as fixed as possible.

All PGNAA spectra used in this article were acquired with an HPGe detector. The relationship between the energies and the absolute frequencies from the dataset (see Table I) can be visualized in a histogram, see, for example, Figs. 2 or 3. From the figures, the similarity between the alloys and in particular between Cu_1 and Cu_2 can be seen.

The zoomed areas in Figs. 2 and 3 represent the same areas of the corresponding spectra. The zoomed area in Fig. 2 shows an additional peak of Cu_5 compared to Cu_1, Cu_2. The alloys from Fig. 2 and analogy the alloys of Fig. 3 are later used in the classification dependent of time in the same relationship. Thus, the bigger differences between the spectra of the copper alloys in Fig. 2 lead to the quicker classification seen between these copper alloys in Fig. 7 and the smaller differences between the spectra of the copper alloys in Fig. 3 lead to the much slower classification between these copper alloys seen in Fig. 8.

III. KERNEL DENSITY ESTIMATION AND MAXIMUM LOG-LIKELIHOOD METHOD

For the classification of the short-time spectra, we use the probability distribution of a single completely measured spectrum. To obtain this distribution, we use the kernel density estimator (see [29, Ch. 2]). The kernel density estimator satisfies the definition of a probability distribution and can be understood as the averaging of density functions concentrated around the individual data points. Based on this distribution, a short-term measurement can be classified using the maximum likelihood method (see [30, Ch. 2.2]).

Given a completely measured spectrum with energies \((γ_1, \ldots, γ_n)\) with \(γ_i < γ_{i+1}\) and corresponding counts \((c_1, \ldots, c_n)\) with \(c_i \in \mathbb{N}_0\). In our case, the materials are always measured fixed at the same energy values. We obtain the corresponding discrete probability distribution \(\hat{f}(γ_1), \ldots, \hat{f}(γ_n)\) of the energy of a measured photon by using the following kernel density estimator:

\[
\hat{f}(γ_j) = \frac{1}{nha} \sum_{i=1}^{n} c_i k\left(\frac{γ_j - γ_i}{h}\right)
\]

where the kernel \(k\) is a nonnegative integrable function with integral value 1, \(h > 0\) is the smoothing factor called bandwidth and \(a = \sum_{j=1}^{n} 1/(nh) \sum_{i=1}^{n} c_i k((γ_j - γ_i)/h))\) is a normalization factor for the discrete case. For example, \(k(x) = 1/((2\pi)^{1/2}) \exp(-(1/2)x^2)\) is a Gaussian kernel and \(k(x) = 1/(π(1 - x^2))\) a Cauchy kernel (see [29, Ch. 3]).
The choice of bandwidth and kernel affects the shape of the density obtained. For small bandwidths, the density converges to the discrete estimated distribution.

The maximum log-likelihood method can be used to classify a short-term spectrum. It assigns a short-term spectrum to the best-fitting distribution. Let \( S \) be the set of all completely measured spectra and let a probability distribution obtained by kernel density estimation from a spectra \( S \in S \) be given as \( (\hat{f}_S(\gamma_1), \ldots, \hat{f}_S(\gamma_n)) \). Furthermore, let a short-time measurement \( s \) be given with the gamma energies \( (\gamma_1, \ldots, \gamma_n) \) and the measurement frequencies \( (c_1, \ldots, c_n) \). Evaluation of the short-time measurement according to the maximum log-likelihood method for the spectrum \( S \) with corresponding probability distribution yields

\[
\log(p(s|S)) = \log \left( \prod_{i=1}^{n} \hat{f}_S(\gamma_i)^{c_i} \right) = \sum_{i=1}^{n} c_i' \log \hat{f}_S(\gamma_i). \tag{1}
\]

Maximum log-likelihood assigns a short-term measurement to the distribution whose likelihood evaluates to the largest value

\[
\max_{S \in S} \log(p(s|S)). \tag{2}
\]

Expression (2) can be determined with the help of matrix-vector multiplication, where the matrix and vector entries are \( \log \hat{f}_S(\gamma_i) \) and \( c_i' \) respectively.

IV. DATA CREATION

Acquiring new data is always associated with high costs and is a necessary component of ML. Consequently, we present a methodology for generating training, validation, and test data. We use the obtained data for parameter estimation and NN training.

Since the completely measured spectrum provides us with a representative set of data, we can interpret it as a probability distribution by normalization, which allows the use of probabilistic techniques. With this distribution, we can generate an unlimited amount of new data by sampling as follows: Let \( (\gamma_1, \ldots, \gamma_n) \) be the gamma energies with corresponding counts of measured photons \( (c_1, \ldots, c_n) \). The gamma energies and their count rate should be representative of a completely measured spectrum. By dividing the count rate \( c_i \) by the total sum \( u = (c_1 + \cdots + c_n) \) we obtain the relative frequencies \( (c_1/u, \ldots, c_n/u) = (p_1, \ldots, p_n) \). Through this procedure, we obtain a discrete distribution of the fully measured spectrum (see Fig. 4). With this distribution, we can now sample the energies by sampling with replacement, by the size and number of times of drawing, we can simulate any measurement time as many times as necessary. It should be noted that the sum of the absolute frequencies is proportional to the measurement time. In our considerations, we set 1 s as 50,000 counts for all materials. We observed this number of counts for our measurement setup in real 1 s measurements. Fig. 5 shows a comparison between a simulated and real spectrum.

V. RESULTS

A. Choice of the Bandwidth

In kernel density estimation, the choice of bandwidth and kernel affects the classification quality. To select the optimal parameters we use cross-validation (see more details in [31, Ch. 11]). A parameter is trained on a certain part of the data and tested on the remaining part. This procedure is repeated several times for each parameter and the test results of each parameter are averaged. The averaged results are then compared to select a suitable parameter. For the required training data, we use drawing without replacement. We see that the optimal choice of bandwidth is close to 0, since higher values lead to better classification and the Cauchy kernel achieves slightly larger values than the Gaussian kernel near 0 (see Fig. 6). Due to the results of Fig. 6, we perform all
Fig. 7. Classification reliability of copper alloys (Cu_2, Cu_5) as a function of the measurement time (between 0.03 and 3 s) of the spectrum. The longer the measurement time, the more reliable the classification.

Fig. 8. Classification reliability of copper alloys (Cu_1, Cu_2) as a function of the measurement time (between 0.03 and 3 s) of the spectrum. The most similar alloys represent the worst case in the classification.

Fig. 9. Simulated spectrum of copper alloy Cu_1 with a measurement time of 0.5 s.

Fig. 10. Simulated spectrum of copper alloy Cu_1 with a measurement time of 0.5 s.

Fig. 11. Simulated spectrum of copper alloy Cu_1 with a measurement time of 0.5 s.

Fig. 12. Simulated spectrum of copper alloy Cu_1 with a measurement time of 0.5 s.

B. Classification Reliability Independent of Time

As each measured gamma ray yields an additional summand in (1), we can visualize the classification between two classes depending on the measurement time of a sample. For this, we consider the sample size from the short-time measurement \( s(t) \) for two classes \( S_k \) and \( S_l \) the difference \( \log(p(s(t)|S_k)) - \log(p(s(t)|S_l)) \) can be considered as classification base. In this context we can consider a visualization of the function \( D(t) = \log(p(s(t)|S_k)) - \log(p(s(t)|S_l)) \) and if the curve is below the classification threshold, it is a misclassification. (see Figs. 7 and 8). The classification reliability, which increases linearly with the sample size, can be seen in the increasing differences. This shows that the shorter the measurement time of the alloy, the more difficult it is to classify the metal alloys. This is because the shorter the measurement time, the stronger the noise and the smaller the amount of measurement of individual energies (compare the height of the counts and the noise between Figs. 2 and 9). The classification of the worst case is shown in Fig. 8.

Spectra are required continuously during the irradiation of the sample. Therefore, prompt gamma radiation accounts for the vast majority of the signal. The proportion of delayed gammas in the spectra has not been quantified but is expected to be more than one order of magnitude lower than prompt gammas. The acquisition times shown here are not comparable to typical measurement times for DGNAA at research reactors, since the neutron flux in the sample is approximately three to four orders of magnitude lower for the MetalClass demonstrator facility.

C. Classification Evaluation

A confusion matrix or error matrix (see [32, Ch. 3]) is a tool for visualizing and evaluating the predictive performance of a classifier. The accuracy, given as a probability between 0 and 1, can be understood intuitively.

The following confusion matrix (see Fig. 10) shows classification results of five copper alloys (Cu_1, Cu_2, Cu_3, Cu_4, Cu_5). One-thousand test data per alloy with a measuring time of 0.5 s were prepared for the classification. The bandwidth 0.00065 and Cauchy density were chosen for the Kernel density estimation. The results clearly show that alloys Cu_1 and Cu_2 can be distinguished from each other slightly worse than the rest of the copper alloys.

The next confusion matrix (see Fig. 11) presents the classification results of aluminum alloys (Al_1, Al_2, Al_3, Al_4, Al_5). For aluminum, the measurement time was set at 0.25 s. In this case, all five alloys have approximately the same degree of difficulty in distinction.

It should be noted that all the alloys studied, with the exception of the copper alloys Cu_1 and Cu_2, can be classified almost 100% in a time of less than 0.25 s.

To illustrate that different materials can be classified very easily, we reduce the measurement time of the test data to 0.0625 s and Fig. 12 is the comparison of different materials (such as aluminum, cement, copper, E-scrap and stucco). We also classified soil, batteries, and ore among themselves and melamine, PVC, ASILIKOS among themselves and
Due to the binning of the existing detector channels, a slight drop in the classification rate can be observed with different measuring times of spectra. For example, after quartering the number of channels by adding the energies of the corresponding channels for the five copper alloys with a measurement time of 0.25 s and a bandwidth of 0.00065, the accuracy decreases by about 1.8%.

VI. CONCLUSION

The goal of optimizing recycling processes for aluminum and copper alloys through online classification can be achieved using the kernel density estimator and the maximum likelihood method. For example, most alloys can be classified close to 100% at 0.25 s. We can classify faster than a CNN and only need a single fully measured spectrum of the material to be classified by using the full information of the spectrum. We can classify online without data preprocessing and without additional training data. Nevertheless, we have introduced a simple and fast method for simulating an unlimited number of different short- and long-term spectra. In doing so, we can generate 50 spectra under 1 s. This can be of great advantage for various methods and areas of AI such as comparing, training, validating and optimizing models.

It remains to be investigated whether the classification can be further optimized by feature engineering, since the measurement method and spectrum have many physical features.

Alternative detector types with lower resolution but faster signal acquisition may also become interesting due to the fast detection.

ACKNOWLEDGMENT

The copper alloys were provided by Wieland-Werke AG, Ulm, Germany. The authors would like to thank Dr. Stefan Theobald and Sebastian Bender for support and discussions.

REFERENCES

[1] G. Bridge, “Contested terrain: Mining and the environment,” Annu. Rev. Environ. Resour., vol. 29, pp. 205–259, Nov. 2004.

[2] D. Kemp, C. J. Bond, D. M. Franks, and C. Cote. “Mining, water and human rights: Making the connection,” J. Cleaner Prod., vol. 18, no. 15, pp. 1553–1562, Nov. 2010.
[3] R. Paul and R. Lindstrom, “Prompt gamma-ray activation analysis: fundamentals and applications,” J. Radioanalytical Nucl. Chem., vol. 243, no. 1, pp. 181–189, 2000.

[4] M. D. Glascock, An Overview of Neutron Activation Analysis. Columbia, MO, USA: University of Missouri Research Reactor (MURR), 2006.

[5] R. R. Greenberg, P. Bode, and E. A. D. N. Fernandes, “Neutron activation analysis: A primary method of measurement,” Spectrochimica Acta B, vol. 66, nos. 3–4, pp. 193–241, Mar. 2011.

[6] A. Havenith et al., “QUANTOM non-destructive scanning of waste packages for material characterization,” EPJ Web Conf., vol. 225, Jan. 2020, Art. no. 06013.

[7] X. Wang, P. Cao, Y. Wang, and Q. An, “Readout electronics of deep-sea in-situ active neutron detector,” in Proc. 23rd Virtual IEEE Real Time Conf., 2022, p. 73.

[8] X. Li et al., “Readout electronics for the gamma detector of the HIRFL-CSR external target facility,” in Proc. 23rd Virtual IEEE Real Time Conf., 2022, p. 97.

[9] I. L. Jernelv, D. R. Hjelme, Y. Matsuura, and A. Aksnes, “Convolutional neural networks for classification and regression analysis of one-dimensional spectral data,” arXiv:2005.07530.

[10] M. Kitzig, A. Kepic, and A. Grant, “Near real-time classification of iron ore lithology by applying fuzzy inference systems to petrophysical downhole data,” Minerals, vol. 8, no. 7, p. 276, Jun. 2018.

[11] K. T. Matchev, K. Matcheva, and A. Roman, “Unsupervised machine learning for exploratory data analysis of exoplanet transmission spectra,” Planet. Sci. J., vol. 3, no. 9, p. 205, 2022.

[12] V. Vigneron, J. Morel, M.-C. Lepy, and J.-M. Martinez, “Statistical modelling of neural networks in γ-spectrometry,” Nucl. Instrum. Methods Phys. Res. A, Accel. Spectrom. Detect. Assoc. Equip., vol. 808, pp. 123–127, Feb. 2016.

[13] H. Sahiner, Gamma Spectrosc. by Artif. Neural Netw. Coupled With MCNP. Missouri University of Science and Technology, 2017.

[14] B. Ayhan, C. Kwan, K. A. Islam, A. Stavola, S. Hendry, and J. Li, “High-performance remote radioactive material identification of mixtures,” IEEE Trans. Nucl. Sci., vol. 69, no. 1, pp. 86–97, Jan. 2022.

[15] J. R. Curtis, “Special nuclear material classification and mass content estimation using temporal gamma-ray spectroscopy and machine learning methods,” Ph.D. dissertation, Nucl. Sci. Eng., Oregon State Univ., Corvallis, OR, USA, 2019.

[16] Y. Balatskyi, J. Bendesky, T. Paul, G. Hagen, and K. McNear, “Raman spectroscopy in open world learning settings using the Objectosphere approach,” Anal. Chem., vol. 94, no. 44, pp. 15297–15306, 2021.

[17] J. Liu, M. Osadchy, L. Ashton, M. Foster, C. J. Solomon, and S. J. Gibson, “Deep convolutional neural networks for Raman spectrum recognition: A unified solution,” Analyst, vol. 142, no. 21, pp. 4067–4074, 2017.

[18] Y. Kim et al., “Deep learning-based statistical noise reduction for multidimensional spectral data,” Rev. Sci. Instrum., vol. 92, no. 7, Jul. 2021, Art. no. 073901, doi: 10.1063/5.005920.

[19] K. Bhardwaj and M. Gokhale, “Semi-supervised on-device neural network adaptation for remote and portable laser-induced breakdown spectroscopy,” 2021, arXiv:2104.03439.