In powder diffraction data analysis, phase identification is the process of determining the crystalline phases in a sample using its characteristic Bragg peaks. For multiphasic spectra, we must also determine the relative weight fraction of each phase in the sample. Machine Learning algorithms (e.g., Artificial Neural Networks) have been applied to perform such difficult tasks in powder diffraction analysis, but typically require a significant number of training samples for acceptable performance. We have developed an approach that performs well even with a small number of training samples. We apply a fixed-point iteration algorithm on the labelled training samples to estimate monophasic spectra. Then, given an unknown sample spectrum, we again use a fixed-point iteration algorithm to determine the weighted combination of monophasic spectra that best approximates the unknown sample spectrum. These weights are the desired phase fractions for the sample. We compare our approach with several traditional Machine Learning algorithms.

**Keywords** machine learning, x-ray diffraction, phase identification, quantitative phase analysis
mineralization events. We therefore developed an approach, described in the next section, for estimating phase fractions given the spectrum of an unknown sample.

**Proposed Algorithm**

We present the proposed model by first describing the training process and then showing how data derived from training is used for estimating phase-fractions for unknown samples. Note that this is a supervised Machine Learning approach, unlike full-pattern summation [5, 4, 12] which requires building a reference library prior to fitting.

We used Leave-One-Out cross-validation by reserving one sample at a time for testing while all others are used for training. Let \( y_i(s) \) represent the intensity value for sample \( s \) at angle \( i \). Let \( \alpha_j(s) \) represent the percentage of phase \( j \) in sample \( s \). Let \( x_i(j) \) denote the reading that would be obtained at angle \( i \) if the sample consisted solely of phase \( j \). We denote the number of samples \( N \), the number of phases \( M \), and the number of angles \( K \).

Consider the model whereby the intensity achieved for sample \( s \) at angle \( i \) consists of a weighted combination of the intensities obtained for the individual components \( j \). As such the reading at angle \( i \) for sample \( s \) is approximated by

\[
\hat{y}_i(s) = \sum_{j=1}^{M} \alpha_j(s) x_i(j)
\]

(1)

Note that in the training set, we know \( \alpha_j(s) \) and \( y_i(s) \) but we do not know \( x_i(j) \) so we use the training set to obtain approximations to \( x_i(j) \) that provides the lowest error. The sum squared error for the approximation for sample \( s \) at angle \( i \) is given by

\[
E^2 = \sum_{i,s} (y_i(s) - \hat{y}_i(s))^2 = \sum_{i,s} \left( y_i(s) - \sum_{j=1}^{M} \alpha_j(s) x_i(j) \right)^2
\]

(2)

We then need to find values for \( x_i(j) \) for all \( i \) and \( j \) that minimizes \( E^2 \). If we take the partial derivative of \( E^2 \) with respect to \( x_i(j) \) we get

\[
\frac{\partial E^2}{\partial x_i(j)} = \sum_{s} -2 \alpha_j(s) \left( y_i(s) - \sum_{j'=1}^{M} \alpha_{j'}(s) x_i(j') \right)
\]

(3)

and setting to zero we get

\[
\sum_{s} \alpha_j(s) \left( y_i(s) - \sum_{j'=1}^{M} \alpha_{j'}(s) x_i(j') \right) = 0
\]

(4)

We use a coordinate gradient descent approach. For each variable, we take the derivative and update to the value that achieves a zero gradient. Note that this is a constrained optimization problem so if the zero gradient is achieved at a negative value then we instead set to zero.

\[
x_i(j) \leftarrow \max \left\{ \frac{1}{\alpha_j(s)^2} \sum_{s} \alpha_j(s) \left( y_i(s) - \sum_{j'=1,j'\neq j}^{M} \alpha_{j'}(s) x_i(j') \right), 0 \right\}
\]

(5)

Next, we describe how testing was performed. Once \( x_i(j) \) is solved for all \( i \) and \( j \), these can be used to compute our estimate of \( \alpha_j \) for a reserved test sample \( s \). These estimated values are denoted as \( \hat{\alpha}_j \). Knowing now \( x_i(j) \) estimated from the training set, we have \( \hat{y}_i(s) \). We now need to find \( \alpha_j(s) \). We let:

\[
\hat{\alpha}_j(s) = \sum_{j=1}^{M} x_i(j)
\]

The sum squared error is again given by

\[
E^2 = \sum_{i,s} \left( y_i(s) - \sum_{j=1}^{M} \alpha_j(s) x_i(j) \right)^2
\]
However, the partial derivative is now taken with respect to $\alpha_j(s)$ giving,

$$\frac{\partial E^2}{\partial \alpha_j(s)} = \sum_i -2x_i(j) \left( y_i(s) - \sum_{j' = 1}^{M} \alpha_{j'}(s)x_i(j') \right)$$

and by setting to zero:

$$\sum_i x_i(j) \left( y_i(s) - \sum_{j' = 1}^{M} \alpha_{j'}(s)x_i(j') \right) = 0$$

We use again a coordinate gradient descent approach. For each variable, we take the derivative and update to the value that achieves a zero gradient. If the zero gradient is achieved at a negative value, then that is instead set to zero.

$$\alpha_j(s) \leftarrow \max \left\{ \frac{1}{x_i(j)^2} \sum_i x_i(j) \left( y_i(s) - \sum_{j' = 1, j' \neq j}^{M} \alpha_{j'}(s)x_i(j') \right), 0 \right\}$$

(6)

The components of $\alpha_j(s)$ must sum to one, hence the following scaling is performed after completing each iteration.

$$\alpha_j(s) \leftarrow \frac{\alpha_j(s)}{\sum_j \alpha_j(s)}$$

(7)

These steps are repeated until convergence is achieved, typically after 15 iterations.

Let us now introduce a suitable performance metric. Consider a test sample, the vector of true phase fractions is denoted by $\alpha$ and the vector of predicted fractions by $\hat{\alpha}$. We write the $\|\alpha - \hat{\alpha}\|_2$ to represent the Euclidean distance between the vectors. The sum of the elements in each of the vectors $\alpha$ and $\hat{\alpha}$ is 1, hence one can show that the maximum value of this distance is $\sqrt{2}$. We define our performance metric $\rho$ as

$$\rho \equiv 1 - \frac{\|\alpha - \hat{\alpha}\|_2}{\sqrt{2}}$$

(8)

If therefore $\alpha = \hat{\alpha}$, then $\rho = 1$ implying a perfect prediction. Supposing there is actually only one phase, and the model predicts one phase as well, but that the predicted is different to the actual, then $\rho = 0$ and the prediction is completely wrong. Consider a bi-phasic sample where the two phases are correctly predicted. However, if the true fractions are 0.5 and 0.5 and the predicted fractions are 0.6 and 0.4, then $\rho = 0.9$ indicating a close but not perfect prediction.

First, all samples were used for training and the predictions computed for each with the above algorithm. This step is equivalent to evaluating the performance of the training set, for which we obtained $\rho = 0.89$. Next, Leave-Out-One cross-validation was carried out such that one sample at a time was reserved for testing while all others were used in training. Here, we obtained $\rho = 0.86$, finding that the model did not over-fit as the testing and training performances are similar. What more is important is the closeness in match of the prediction to the actual for the individual phases. Figure 1 depicts bar charts indicating phase fractions for the 7 possible phases for the 46 samples with LOOCV. Note that the model always correctly predicted the dominant phase even if the actual fractional value did not match perfectly.

Figure 2 visualizes the estimated $x(j)$ intensities versus the angle $i$, illustrating how closely this approach is able to estimate single-phase spectra. We provide an overlay of the spectra of actual monophase samples in orange.

Performance Comparison

We have compared the proposed algorithm with other traditional Machine Learning models. In addition to the $\rho$ metric described in the previous section, we include two additional metrics, Mean Absolute Error (MAE) and Cosine Similarity (CS) defined as:

$$\text{MAE} = \frac{1}{MK} \sum_{s,j} |\alpha_{s,j} - \hat{\alpha}_{s,j}| \quad \text{CS} \equiv \frac{\alpha \cdot \hat{\alpha}}{||\alpha|| \times ||\hat{\alpha}||}$$

(9)

We investigated several regression algorithms including K-Nearest Neighbours (KNN), Support Vector Machine (SVM), Decision Tree (DT), Random Forest (RF), Extremely Randomized Trees (ERT) and Artificial Neural Network (ANN). Note that in order to get the best results for each model, significant additional work was necessary,
Table 1: Leave-One-Out Cross-Validation Performance Results for Phase Fraction Estimation.

|       | KNN  | SVM  | DT   | RF   | ERT  | ANN  | Proposed |
|-------|------|------|------|------|------|------|----------|
| ρ     | 0.8369 | 0.7971 | 0.7438 | 0.7908 | 0.8217 | 0.8582 | **0.8641** |
| MAE   | 0.0520 | 0.0773 | 0.0832 | 0.0778 | 0.0635 | 0.0491 | **0.0454** |
| CS    | 0.9470 | 0.9364 | 0.8211 | 0.9029 | 0.9232 | **0.9662** | 0.9564 |

e.g. hyper-parameter tuning. This is not required for our proposed algorithm. The averaged performance results are summarized in Table 1.

The proposed model performed best in ρ and MAE metrics but not for CS, where the ANN obtained a higher score. However, we noticed the ANN and SVM regressors did not strictly output positive, normalized weight fractions as the KNN and tree-based regressors did. The tabled results follow the performance after we applied these conditions to their outputs. Prior to this, the SVM gave MAE = 0.0913 and CS = 0.9268, and the ANN gave MAE = 0.0594 and CS = 0.9627.

Regarding phase fraction prediction, Lee et al.[10] trained deep convolutional neural networks with millions of synthetic data relating to solid-state electrolytes, but achieved the best results with the SVM followed by RF, KNN and ANN models. For their application in gas-hydrate bearing sediments, Park et al.[14] obtained the best performance with RF amidst testing other neural networks architectures.

In this work, we have presented a new supervised learning approach for estimating phase fractions and illustrated its superiority by comparing with other ML models on our dataset. The assessment of kidney stones is however only one of very many possible contexts to which the approach may be applied. The model computes non-negative fractions, does not require parameter tuning, does not suffer from scaling issues as with other ML algorithms and learns well from small datasets. It also performed well in run-time comparisons. The proposed algorithm thus saves time by automating quantitative phase analysis for future batches of PXRD data acquired in similar context.

References

[1] Ankit Agrawal and Alok Choudhary. Deep materials informatics: Applications of deep learning in materials science. *Mrs Communications*, 9(3):779–792, 2019.

[2] Jonathan Kenneth Bunn, Shizhong Han, Yan Zhang, Yan Tong, Jianjun Hu, and Jason R Hattrick-Simpers. Generalized machine learning technique for automatic phase attribution in time variant high-throughput experimental studies. *Journal of Materials Research*, 30(7):879–889, 2015.

[3] Jonathan Kenneth Bunn, Jianjun Hu, and Jason R Hattrick-Simpers. Semi-supervised approach to phase identification from combinatorial sample diffraction patterns. *Jom*, 68(8):2116–2125, 2016.

[4] Benjamin M Butler and Stephen Hillier. powdr: An R package for quantitative mineralogy using full pattern summation of x-ray powder diffraction data. *Computers & Geosciences*, 147:104662, 2021.

[5] Steve J Chipera and David L Bish. Fitting full x-ray diffraction patterns for quantitative analysis: a method for readily quantifying crystalline and disordered phases. *Scientific Research*, 2013.

[6] Kamal Choudhary, Brian DeCost, Chi Chen, Anubhav Jain, Francesca Tavazza, Ryan Cohn, Cheol Woo Park, Alok Choudhary, Ankit Agrawal, Simon JL Billinge, et al. Recent advances and applications of deep learning methods in materials science. *npj Computational Materials*, 8(1):1–26, 2022.

[7] Robert E Dinnebier and Simon JL Billinge. *Powder Diffraction: Theory and Practice*. Royal Society of Chemistry, 2008.

[8] Jaimie Greasley, Shivan Goolcharan, and Roger Andrews. Quantitative phase analysis and microstructural characterization of urinary tract calculi with x-ray diffraction rietveld analysis on a caribbean island. *Journal of Applied Crystallography*, 55(1), 2022.

[9] Camden R Hubbard, EH Evans, and DK Smith. The reference intensity ratio, i/ic, for computer simulated powder patterns. *Journal of Applied Crystallography*, 9(2):169–174, 1976.

[10] Jin-Woong Lee, Woon Bae Park, Minseuk Kim, Satendra Pal Singh, Myoungho Pyo, and Kee-Sun Sohn. A data-driven xrd analysis protocol for phase identification and phase-fraction prediction of multiphase inorganic compounds. *Inorganic Chemistry Frontiers*, 8(10):2492–2504, 2021.
[11] Jin-Woong Lee, Woon Bae Park, Jin Hee Lee, Satendra Pal Singh, and Kee-Sun Sohn. A deep-learning technique for phase identification in multiphase inorganic compounds using synthetic xrd powder patterns. *Nature communications*, 11(1):1–11, 2020.

[12] Benjamin M Butler and Stephen Hillier. Automated full-pattern summation of x-ray powder diffraction data for high-throughput quantification of clay-bearing mixtures. *Clays and Clay Minerals*, 69(1):38–51, 2021.

[13] Phillip M Maffettone, Lars Banko, Peng Cui, Yury Lysogorskiy, Marc A Little, Daniel Olds, Alfred Ludwig, and Andrew I Cooper. Crystallography companion agent for high-throughput materials discovery. *Nature Computational Science*, 1(4):290–297, 2021.

[14] Sun Young Park, Byeong-Kook Son, Jiyong Choi, Hongkeun Jin, and Kyungbook Lee. Application of machine learning to quantification of mineral composition on gas hydrate-bearing sediments, ulleung basin, korea. *Journal of Petroleum Science and Engineering*, 209:109840, 2022.

[15] Vitalij Pecharsky and Peter Zavalij. *In Fundamentals of Powder Diffraction and Structural Characterization of Materials*. Springer, 01 2003.

[16] H M Rietveld. Line profiles of neutron powder-diffraction peaks for structure refinement. *Acta Crystallographica*, 22(1):151–152, 1967.

[17] Deane K Smith, Gerald G Johnson, Alexandre Scheible, Andrew M Wims, Jack L Johnson, and Gregory Ullmann. Quantitative x-ray powder diffraction method using the full diffraction pattern. *Powder Diffraction*, 2(2):73–77, 1987.

[18] Nathan J Szymanski, Christopher J Bartel, Yan Zeng, Qingsong Tu, and Gerbrand Ceder. Probabilistic deep learning approach to automate the interpretation of multi-phase diffraction spectra. *Chemistry of Materials*, 33(11):4204–4215, 2021.

[19] Hong Wang, Yunchao Xie, Dawei Li, Heng Deng, Yunxin Zhao, Ming Xin, and Jian Lin. Rapid identification of x-ray diffraction patterns based on very limited data by interpretable convolutional neural networks. *Journal of chemical information and modeling*, 60(4):2004–2011, 2020.

[20] Xiang Zhou, Dong Liu, Hongling Bu, Liangliang Deng, Hongmei Liu, Peng Yuan, Peixin Du, and Hongzhe Song. Xrd-based quantitative analysis of clay minerals using reference intensity ratios, mineral intensity factors, rietveld, and full pattern summation methods: A critical review. *Solid Earth Sciences*, 3(1):16–29, 2018.
Figure 1: Phase Fraction Predictions of Proposed Model with LOOCV. Predicted weight fractions are red bars, where the Rietveld-refined values are the blue bars.
Figure 2: Model-Estimated Intensity Spectra for Phase 1-7 (blue) with Overlay of Actual Mono-phase Experimental Examples (orange).