Towards High-Speed Raman Spectroscopy for Industrial Sorting Applications

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Abstract— **A real-time Raman mapping system for detecting and discriminating a range of industrially relevant materials such as glasses and various minerals is presented. The system is built from components that are suitable for industrial conditions. Together with a signal processing and a chemo-metric model, the system was shown to be capable of discriminating between the test materials. We argue that the approach is a novel alternative to established sorting sensors.**

Keywords- Raman, spectroscopy, industry, high-speed

I. INTRODUCTION

Sensor based sorting has been a subject of research for many decades. Current methods use various regions of the electromagnetic spectrum: near-infrared, X-ray and visible light [1, 2, 3, 4]. Sensor based sorters are important at two stages of processing. They can be used as a preliminary sorting method to reduce the throughput and they can also be applied to purify an already high concentrate which can be sold to sub-contractors. In both cases sensor based sorters can also reduce the consumption of energy in the process [2].

This paper describes a macroscopic Raman mapping prototype for industrial sorting of glasses minerals.

A. Glass sorting

As with polymer [5, 6] and paper recycling [7], recycled glass must be sorted within the recycling process. However different glass formulations have different melting points. An uncontrolled mixture of glass types will result in recovered glass that is prone to cracking during cooling, and non-molten components in the melt can damage production machines [8]. The standard methods are: sorting with visual camera systems—these have limited selectivity; and x-ray fluorescence systems, which are expensive. As an alternative, the viability of Raman spectroscopy for glass sorting has been investigated.

B. Mineral sorting

The majority of all ore minerals belong to the sulfides group. Yet sulfides are difficult to detect with current sensors [3]. X-ray fluorescence (XRF) sensors are limited to minerals which can be excited to fluorescence---this is rare for sulfides.

Visible light (VIS) systems are also very limited for sulfides because the proportion of ore minerals in sulfides is often small and have the same color as the rock in which they are embedded. Near-infrared (NIR) techniques are limited to minerals which are sufficiently reflective or sufficiently transparent [9]. Raman spectroscopy can give information about the mass composition of the analyzed object. This property is critical for minerals sorting because the concentration of the mineral in the rock affects the desired result of the sorting process [9].

In this paper we describe experiments in which a specially built Raman system was used to classify mineral samples. Samples of important mineral groups: dolomite, marble, calcite and pyrite were measured with the Raman system. The measured spectra were then processed to isolate the Raman peaks from the ambient components of the spectrum. The estimated Raman spectra were used with a correlation classifier to determine which measurements belong to which class of material. We found that although several of the material classes can be easily discriminated, the spectra of calcite and marble, and pyrite and some samples of dolomite, were sufficiently similar to cause confusion between the classes. Nonetheless the ability of the approach to discriminate calcite from dolomite and pyrite makes Raman spectroscopy a promising approach for mineral sorting.

II. RAMAN SPECTROSCOPY

Raman spectroscopy is classical laboratory method for material analysis and, until recently, was considered unsuitable for most industrial imaging applications as it requires long measuring times and is sensitive to stray light. Advances in camera and spectrometer technology now allow Raman signals to be acquired with high spatial and spectral resolution. It can be applied to determine the chemical composition quantitatively and qualitatively and can measure the chemical structure of almost any kind of object. It can be used to identify single materials as well as composites of several materials. Like NIR and XRF sensors, Raman analysis is limited to the surface of objects.

The Raman effect occurs when light is scattered by the chemical structures in a material. While most of the incident light is elastically (Rayleigh) scattered at the wavelength of the excitation light source, a small proportion is in-elastically scattered. This causes an energy difference between the incident light that can be measured as a wavelength shift in the spectrum. The shift is characteristic of the material's molecular composition and is referred to the material's fingerprint.

III. MEASUREMENT SYSTEM

A. Raman measurement system

A custom measurement system consisting of an OEM Raman spectrometer (Horiba Scientific) and a Raman measurement head (or super head) measures point spectra of the samples. The super head consists of a narrow-band pass filter that blocks the sidebands of the excitation laser and a Rayleigh filter that blocks Rayleigh scattered light in the Raman spectrum. Raman shifts between -233 cm^{-1} and 3300 cm^{-1} can be measured with a spectral resolution of about 4 cm^{-1}. To achieve the maximum possible signal intensities a back thinned CCD sensor is used in the spectrometer. A 532nm fiber coupled laser with an output power of 2W (post fiber approximately 1.5W) is used to excite the measurement samples. The described measurement system was installed into a Titech scanner housing, see Figure 1. A specifically designed front lens (diameter of 3 inches) focused the laser spot to a spot size of around 600µm^2 on the measurement samples at a distance of 250 mm. The front lens also collected the scattered Raman light from the measurement samples. A scanning mirror was used to measure the Raman signals at different positions on the conveyor belt.
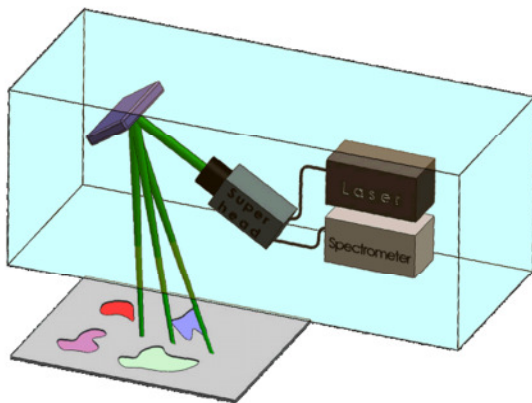

Figure 1 Industrial Raman prototype

IV. MEASUREMENTS & ANALYSIS

A. Mineral Sorting

We measured dolomite, marble, calcite and pyrite samples approximately 1 to 10 cm in diameter. The samples differed slightly in color and shape. An example for each class is shown in Figure 2.

For the data analysis we resolved the Raman peaks from the ambient spectrum by fitting a 4th order polynomial curve to the raw spectrum and then measuring the difference between the raw and fitted curves. This residue spectrum contains both random noise and distinctive sharp peaks; we will assume that

these peaks are due to Raman scattering, Figure 3. We can improve the estimate of the Raman spectra by further processing the residue. First we apply a median filter and subtract the result from the residue. Then we apply a smoothing filter to the new residue.

Figure 2 Mineral samples. Marble (a), dolomite (b), calcite (c) and calcite/dolomite + pyrite (d)

Next we model the residual as a sparse Gaussian mixture using a greedy estimation algorithm. The residue spectrum is modeled as a Gaussian centered at the maxima of the spectrum using a simplex fitting algorithm. The fitted Gaussian is then subtracted from the spectrum and the process is repeated. After nine repetitions the list of Gaussians is pruned to exclude Gaussians whose standard deviation exceeds 5 nm. The standard deviations of remaining Gaussians are then doubled and the distributions used to construct a mask. The earlier result of filtering the residue is then multiplied by this mask to suppress non-Raman components of the spectrum.
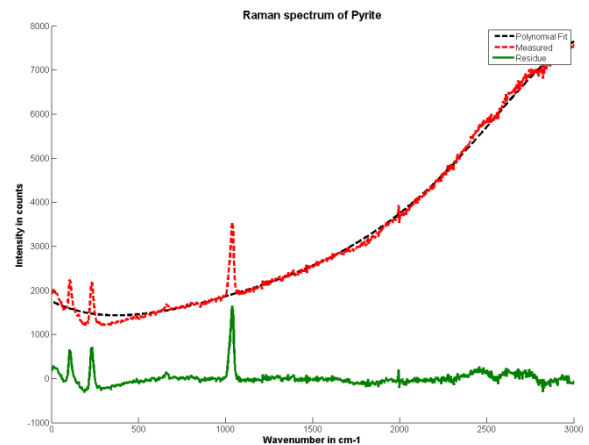

Figure 3 Measured, fitted and residue spectra for a pyrite sample

Figure 4 shows typical Raman spectra of the investigated minerals. The spectra were processed as described earlier. Although the test materials have a similar molecular structure, differences of the Raman peaks are apparent. The main differences between the materials lie in the relative heights of their Raman peaks. Using the processed Raman spectra we created Raman maps of the measurement results. An example Raman map of a marble sample is shown in Figure 5. The left

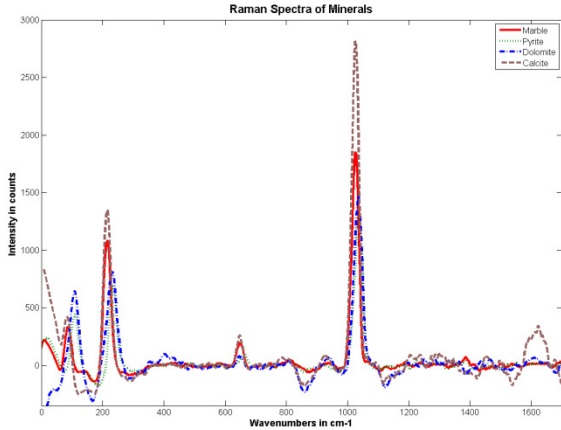image in the figure shows an intensity map of the marble sample.

Figure 4 Raman spectra of the minerals marble, pyrite, dolomite and calcite.

The spatial structure of the sample can only be approximately inferred. This is because we measured with a relatively low resolution--measurements were made at intervals of 1 mm. The right hand image in Figure 5 shows the corresponding classification result of the Raman intensity map. Pixels in the classification result with label zero belong to the background, label one pixels mark calcite, label three pixels dolomite and label five pixels mark marble. The measurement result shows that the classification works well for marble. Some pixels classified as dolomite, but the majority of the sample is correctly classified as marble.
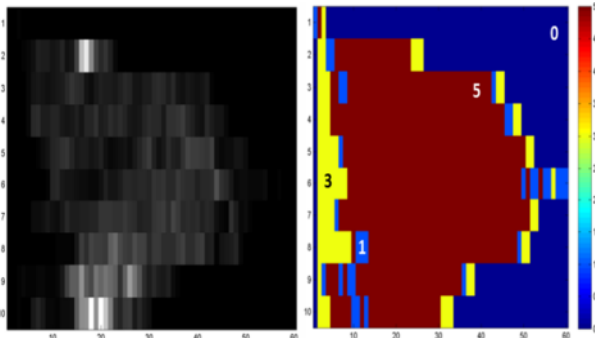

Figure 5 Raman classification result of a marble sample. 0 represents the background, 1 calcite, 3 dolomite and 5 marble.

Figure 6 shows a correlation matrix of all the minerals under investigation. The main tasks are to discriminate between calcite and dolomite and to detect pyrite inclusions in marble. The confusion matrix shows that there is some correlation between calcite and dolomite, but the correlation is not high. Therefore these two materials can be distinguished using Raman spectroscopy. As there is a high correlation between pyrite and dolomite, detecting the inclusion in marble is a challenging task and would need further data analysis. Moreover, the discrimination of calcite, dolomite, pyrite and marble needs a lot of data analysis as there are correlations between all the materials. This is clearly shown by the correlation matrix.
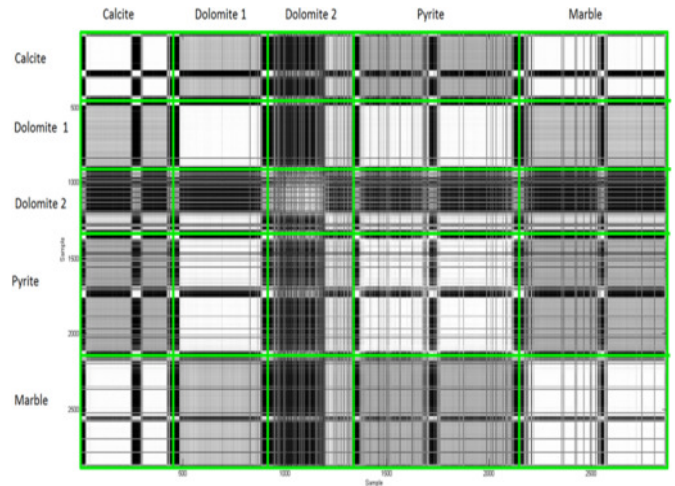

Figure 6 Correlation matrix of the analyzed data sets

B. Glass Sorting

Test sets of samples of mineral glasses and fireproof glasses approximately 1 -2 cm in diameter were extracted from an industrial recycling process and Raman spectra of the samples measured using our industrial Raman prototype. The mineral glasses were divided into green glass, flint glass and amber glass. Fireproof glasses were divided into 8 classes: peach glass, caramel glass, faint yellow glass, yellow glass and honey glass. An example of each class is shown in Figure 7.

Figure 7 Glass samples extracted from an industrial sorting process

Figure 8 shows mean spectra of the different glass types. The data was acquired with an integration time of 100 ms. As a post-processing step we used a first order Savitzky Golay with a filter width of 30 cm^{-1} and calculated the L1-norm of the Raman spectra in the range from 200 cm^{-1} to 1200 cm^{-1}. In the Raman shift range there is one significant feature for fire protection glasses at 477 cm^{-1} and there are two features for mineral glasses at 552 cm^{-1} and 1080 cm^{-1}.

$$F_n = \frac{I(A)+I(B)}{2} - I(C) \dots (\text{Eq. 1})$$

For the following scatter plot we used the equation Eq. 1 to calculate the local peak intensity of the spectral features. The Raman shifts used for A, B and C are listed in Table 1.

Table 1 Raman shift features

	A	B	C
Feature 1	427 cm^{-1}	499 cm^{-1}	477 cm^{-1}
Feature 2	537 cm^{-1}	594 cm^{-1}	552 cm^{-1}

Plotting the two features in a 2D scatter plot shows that the point clouds of mineral glasses and fire protection glasses are separable.
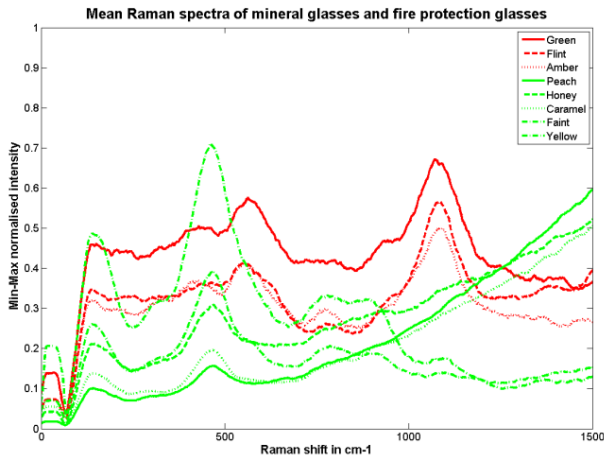

Figure 8 Typical Raman spectra of different glass types

V. CONCLUSION

In this paper we have shown that Raman spectroscopy is a promising technique for mineral sorting. Inhomogeneous mineral samples were scanned: i.e. Raman spectra were measured at a series of points on the sample's surface to give a low resolution image. The Raman peaks were resolved from background fluorescence using signal processing techniques. The similarity of measurements was calculated using the correlation of the estimated Raman spectra. A feature based on this correlation was used to classify the spectra, and so segment the image. Our classification results are mixed: the Raman spectra for several material classes were indistinguishable; other classes have distinctive spectra. Raman spectroscopy, is not, of itself, a universal solution for mineral sorting. However, it does give information that is useful for discriminating between several mineral classes.

Our results showed also that mineral glasses and fireproof glasses are linearly separable using two peaks in the Raman spectrum at 470 cm^{-1} and 540 cm^{-1}.

The main obstacle to applying Raman spectroscopy to both mineral sorting and glass sorting is not the accuracy of classification, but rather the speed of the measurement. The Raman effect is faint; to detect it we require intense illumination and long exposure times. State of the art sorting systems, working in the NIR, scan between 25 kHz and 80 kHz-our system operates currently at only 10 Hz. The exposure times used in this paper preclude the application of this technique from industrial systems that require high speed sorting. We are currently working to increase the intensity of illumination and the optical efficiency of the sensor. We argue that once the speed of the system has been sufficiently improved, the system can be applied to sorting applications in an industrial recycling facility.
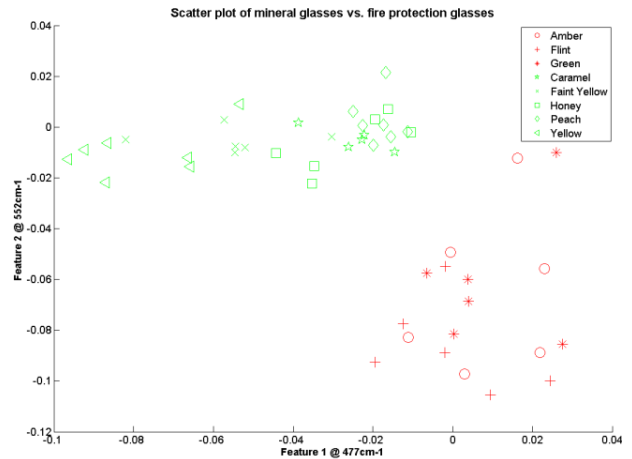

Figure 9 Scatter plot of mineral glass vs. fire protection glass with an integration time of 100ms

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