Raman mapping of fluorescent minerals – comparison of time-gated and continuous wave setups

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Rare earth elements (REE) are globally considered as critical raw materials. At the Norra Kärr Alkaline Complex in southern Sweden, REE-bearing minerals, namely eudialyte group minerals, e.g. $Na_4(Ca,Ce)_2(Fe^{2+},Mn,Y)ZrSi_8O_{22}(OH,Cl)_2$ and catapleiite ($Ca/Na_2ZrSi_3O_9 \cdot 2H_2O$), can especially be found with high proportion of valuable heavy rare earth elements (HREEs).

However, the measurement of Norra Kärr rock samples is challenging with Raman analysis due to their high fluorescence. The fluorescence may be reduced, if the sampled location can be first irradiated at high laser power. The thermal degradation of the samples during this photobleaching is not typically of concern in the mineral samples, but when constructing maps of thousand points, the total measurement time is notably increased. On the other hand, the fluorescence occurrence depends on the excitation wavelength and it may be avoided, if a longer laser wavelength is used. However, the longer excitation wavelength reduces the Raman signal.

As a promising alternative, the maps of the fluorescent minerals can be constructed using time-gated Raman, where the material is excited with a short laser pulse at a range of $100*10^{-12}$ s. The Raman signal can be detected in a very short time window matched to the width of a laser pulse prior to the formation of a strong fluorescent signal with a lifetime of nanoseconds and can be separated in a time domain allowing signal readout by single-photon avalanche diode (SPAD) array with significantly reduced or negligible fluorescence background[1]. In this current study, the results obtained by mapping the fluorescent Norra Kärr rock samples with using the green 532 nm laser excitation, the traditional continuous wave (CW) and time-gated Raman, are represented. The identification of the main minerals in the maps is based on the multivariate data analysis called singular value decomposition (SVD). The classification, as demonstrated earlier for laser-induced breakdown spectroscopy (LIBS)[2], utilizes the whole measured spectral range, and divides the measured locations according to their greatest variance in the spectra.

[1] Nissinen, I., Nissinen, J., Keränen, P., Länsman, A-K., Holma, J. & Kostamovaara, J., *IEEE Sensors Journal*, **2015**, 15, 1358-1365.
[2] Romppanen, S., Häkkänen, H. & Kaski, S., Spectrochim. Acta B, **2017**, 134, 69–74.