In Situ Time-Gated Raman Monitoring of Lithium Mineral Calcination in a Rotary Furnace

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Time-gated Raman spectroscopy (TG-Raman) was investigated for online monitoring of lithium mineral calcination in a laboratory-scale rotary kiln. Industrial calcination environments present significant challenges for optical measurements due to elevated temperatures, moving heterogeneous material streams and process-related optical background. TG-Raman enabled continuous mineral-specific monitoring of a blended spodumene-lepidolite feed under representative process conditions. A custom stand-off optical configuration provided stable measurements of discharged material downstream of the kiln while calcination temperature was increased from 900 to 975 °C. Calcination-induced mineralogical changes were observed directly from the process stream through systematic changes in the Raman spectra, including a progressive decrease of the characteristic α-spodumene band near 704 cm^{-1}. A simple Raman process indicator based on the 704 cm^{-1} and 606 cm^{-1} bands showed a clear monotonic response to temperature and provided separation between different calcination states. Continuous measurements additionally enabled estimation of process response delays and transition periods following furnace temperature adjustments. The results demonstrate the potential of stand-off TG-Raman spectroscopy for real-time monitoring of lithium mineral calcination and future process control applications.

1. Introduction

The global transition toward electrified transportation, renewable energy generation and large-scale energy storage has significantly increased demand for lithium, driven largely by the rapid deployment of lithium-ion batteries in electric vehicles and energy storage systems (IEA 2025). Among lithium-bearing minerals, spodumene and lepidolite are important commercial lithium sources recovered from hard-rock pegmatite deposits. In industrial lithium chemical production, thermal treatment is commonly applied to concentrate feedstocks prior to downstream extraction. For spodumene-bearing materials, calcination is particularly important because naturally occurring α-spodumene exhibits a dense monoclinic crystal structure that is relatively resistant to chemical attack. During calcination, α-spodumene undergoes a sequence of phase transformations involving the formation of a metastable γ-spodumene phase and ultimately β-spodumene (Moore, et al. 2018). The resulting phase transformation is a prerequisite for efficient lithium extraction from spodumene concentrates and therefore has a strong influence on downstream process performance (Dessemond, et al. 2019). As a result, the degree of spodumene conversion is a critical process parameter influencing both lithium recovery and process efficiency.

Monitoring mineralogical transformations in industrial calcination processes remains challenging. Rotary furnaces operate at elevated temperatures and process continuously flowing heterogeneous material streams containing both lithium-bearing and gangue minerals. Process performance is commonly assessed through periodic sampling followed by laboratory-based analyses such as X-ray diffraction, resulting in delayed feedback and limited visibility into ongoing process changes. Consequently, operators often lack real-time information regarding the progression of mineralogical transformations and the quality of the calcined product. The availability of online mineralogical measurements could therefore support improved process understanding, optimization and control.

Raman spectroscopy is a non-destructive analytical technique capable of providing mineral-specific information based on vibrational properties of crystal structures. The technique has been widely applied for mineral identification and characterization because of its high chemical specificity and limited sample preparation requirements (Havisto, et al. 2026). However, conventional Raman measurements can be significantly affected by fluorescence, thermal radiation and other sources of optical background, particularly in industrial environments and high-temperature processes. Time-gated Raman spectroscopy addresses these limitations by combining pulsed laser excitation with temporally selective signal acquisition. Since Raman scattering occurs essentially instantaneously while fluorescence emission persists on a longer timescale, time-gated detection can selectively record Raman signals while suppressing unwanted background contributions. Time-gated Raman spectroscopy has demonstrated the capability to suppress fluorescence and thermal background interference under challenging measurement conditions (Kögler and Heilala 2021). Furthermore, the technique has previously been applied to the monitoring of α-to-β spodumene conversion in heat-treated spodumene concentrates, demonstrating its potential for calcination process monitoring (Timegate Instruments Ltd. 2017).

Although Raman spectroscopy has been successfully applied to laboratory characterization of lithium minerals and calcined spodumene samples, demonstrations of continuous online Raman monitoring under rotary kiln calcination conditions remain limited. This study investigates the applicability of time-gated Raman spectroscopy for online monitoring of lithium mineral calcination in a laboratory-scale rotary kiln. The work focuses on demonstrating continuous stand-off Raman measurements on a moving solids stream, evaluating the ability of the technique to detect calcination-related spectral changes, and assessing the suitability of Raman-derived process indicators for monitoring process state and dynamics under representative operating conditions.

2. Materials and Methods

The study was conducted using an industrially relevant lithium-bearing feed material consisting of a blend of spodumene and lepidolite concentrates. The material was selected to represent a realistic lithium processing feed rather than a purified laboratory mineral specimen, thereby enabling evaluation of the measurement methodology under conditions relevant to industrial mineral processing. Detailed information regarding material origin and quantitative mineralogical composition is not disclosed due to project confidentiality. The blended feed provided a heterogeneous mineral system suitable for investigating the ability of time-gated Raman spectroscopy to detect mineralogical changes occurring during thermal treatment.

Calcination experiments were performed using a laboratory-scale electrically heated rotary kiln operated under continuous processing conditions. The spodumene-lepidolite feed was processed while

the kiln temperature was increased from 900 to 975 °C in 25 °C increments, with each temperature condition maintained for approximately 1.5 hours. Material was discharged continuously throughout the campaign and Raman measurements were performed on the discharged material stream using a stand-off measurement configuration positioned downstream of the kiln outlet. Due to material transport within the experimental setup, a delay existed between changes in kiln operating conditions and their appearance at the Raman measurement location. Consequently, the Raman spectra reflected the mineralogical state of material processed under earlier kiln conditions, corresponding to the residence time of the material between the kiln and the measurement point. Representative product samples were collected at approximately 15 min intervals during the experiments and retained for subsequent laboratory analysis. The resulting dataset covered progressively increasing calcination temperatures and enabled evaluation of spectral changes occurring during thermal treatment together with assessment of the suitability of time-gated Raman spectroscopy for online process monitoring.

Online Raman measurements were performed using a Timegate PicoRaman M3 time-gated Raman spectrometer equipped with a pulsed 532 nm excitation laser. The instrument was operated using an anti-Stokes time-gating configuration, although only conventional Stokes Raman spectra were used in the present analysis. Measurements were acquired using the full available excitation power from the Raman probe (approximately 100 mW at the excitation port) and an integration time of approximately one minute per spectrum. Measurements were primarily performed directly on the discharged material stream using a stand-off measurement arrangement positioned downstream of the kiln outlet. The measurement geometry and process environment at the rotary kiln discharge are shown in Figure 1. A custom stand-off optical assembly was developed to accommodate the geometric and operational constraints of the rotary kiln setup. The optics provided a working distance of approximately 70 mm and enabled non-contact measurements through a protective observation window. In addition to reducing exposure of the instrumentation to the process environment, the increased working distance provided an enlarged depth of focus, improving tolerance to fluctuations in the position and surface profile of the material stream. The resulting configuration enabled stable online monitoring throughout the experimental campaign.

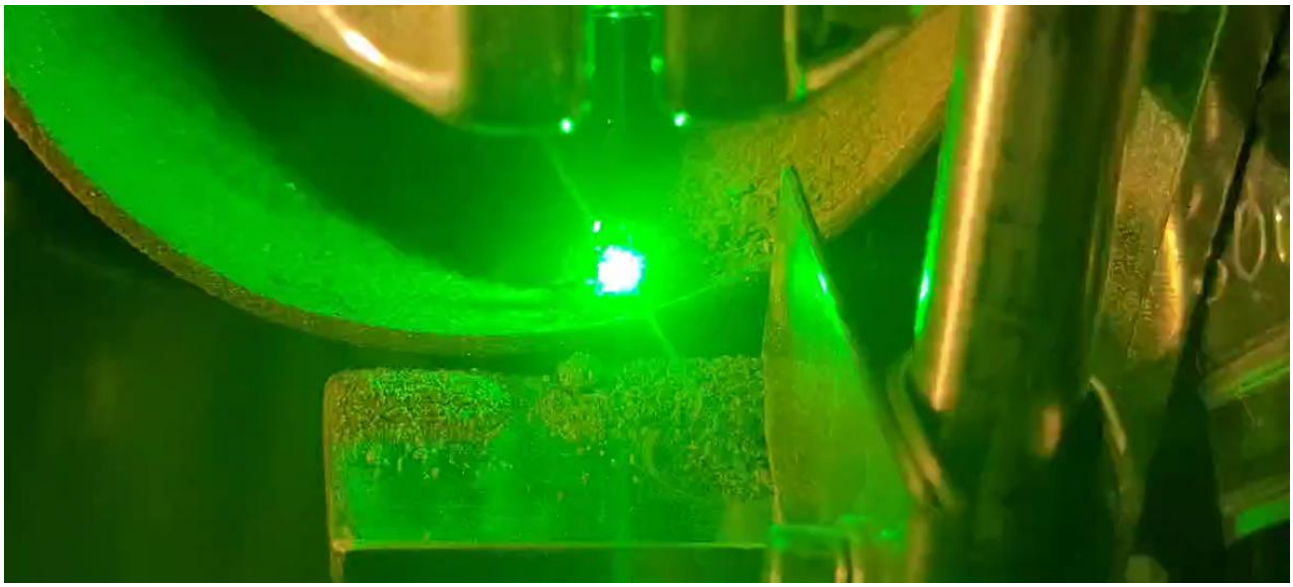

Figure 1. Stand-off time-gated Raman measurement at the rotary kiln discharge. The photograph shows the laser illumination spot and the discharged material stream at the measurement location.

Raman spectra were analysed to evaluate spectral changes associated with calcination. Spectra affected by interruptions in material flow, poor focus or other measurement artefacts were excluded where necessary. To monitor process evolution, characteristic Raman bands were extracted following local linear baseline correction. A band near 704 cm^{-1}, characteristic of α-spodumene and expected to decrease as calcination progresses, was selected as the primary process indicator. To compensate for measurement variability arising from changes in material presentation, a comparatively stable band near 606 cm^{-1} originating from the silica observation window was used as a normalization reference. A Raman process indicator was calculated as the ratio between the baseline-corrected intensities of these bands and evaluated as a function of process time. To reduce short-term variability and improve visualization of process trends, the resulting time series was smoothed using a Savitzky-Golay filter. A piecewise-linear fitting approach was subsequently applied to estimate the onset and duration of the Raman response following furnace temperature adjustments, providing indicative measures of process response dynamics.

3. Results

Online spectral measurements under process conditions

Time-gated Raman measurements were successfully performed throughout the laboratory-scale calcination campaign under continuous operating conditions. The stand-off measurement arrangement enabled non-contact monitoring of the discharged material stream and provided stable signal acquisition across the investigated temperature range. Despite variations in material flow and the heterogeneous nature of the feed material, Raman spectra of sufficient quality for process monitoring were obtained throughout the experiments.

Figure 2 presents representative Raman spectra acquired during stable operating periods at 900, 925, 950 and 975 °C. Several Raman bands exhibited systematic changes with increasing calcination temperature. In particular, the characteristic α-spodumene band near 704 cm^{-1} decreased progressively during calcination, consistent with the expected α-to-β spodumene conversion reported in previous

calcination studies (Timegate Instruments Ltd. 2017). The observed spectral evolution demonstrates that mineralogical changes can be detected directly from the process stream using stand-off time-gated Raman measurements.

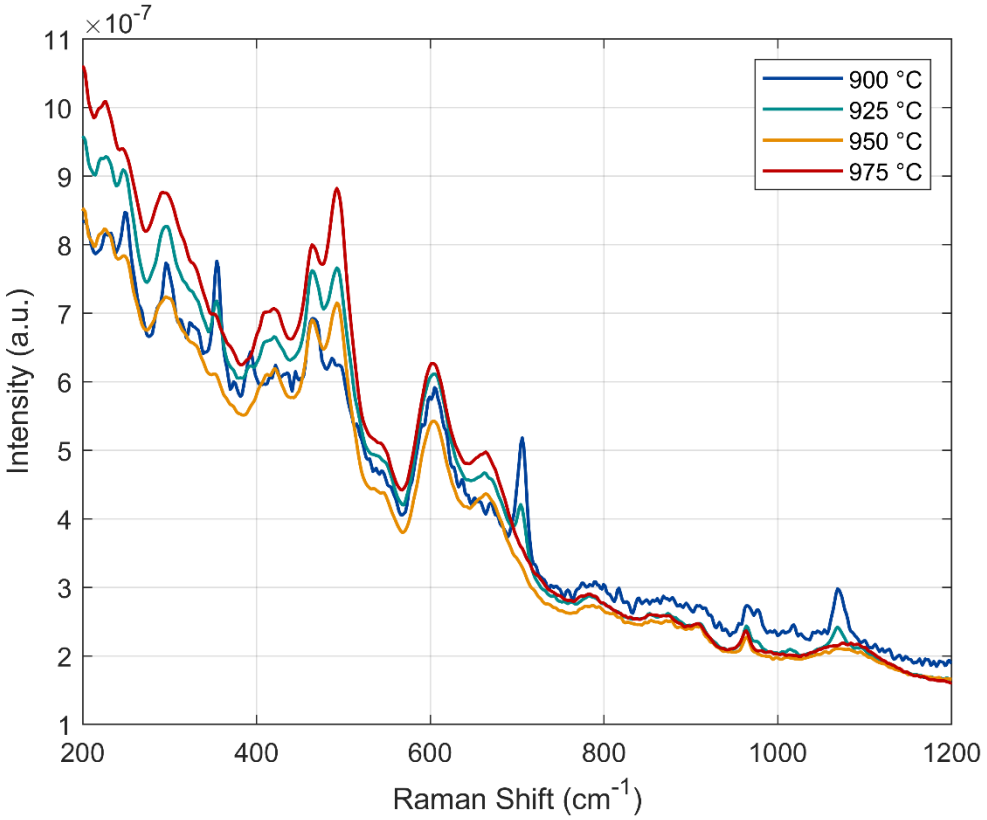

Figure 2. Representative Raman spectra acquired during stable operating periods at different calcination temperatures. Spectra represent averages of measurements collected within the corresponding stable operating regions.

Raman Process Indicator

To quantify the observed spectral changes, a Raman process indicator was calculated as the ratio between the baseline-corrected intensities of the 704 cm^{-1} and 606 cm^{-1} bands. Figure 3 shows the distribution of indicator values obtained during stable operation at each calcination temperature.

The indicator exhibited a clear and monotonic response to increasing calcination temperature. The highest values were observed at 900 °C, followed by a progressive decrease at 925, 950 and 975 °C. The distributions corresponding to the different operating conditions were clearly separated, with only limited overlap between adjacent temperature levels.

The relatively narrow distributions observed within each temperature condition indicate good repeatability of the online measurements during stable process operation. The results demonstrate that a simple Raman intensity ratio is capable of distinguishing between different calcination states and may provide a practical process metric for online monitoring.

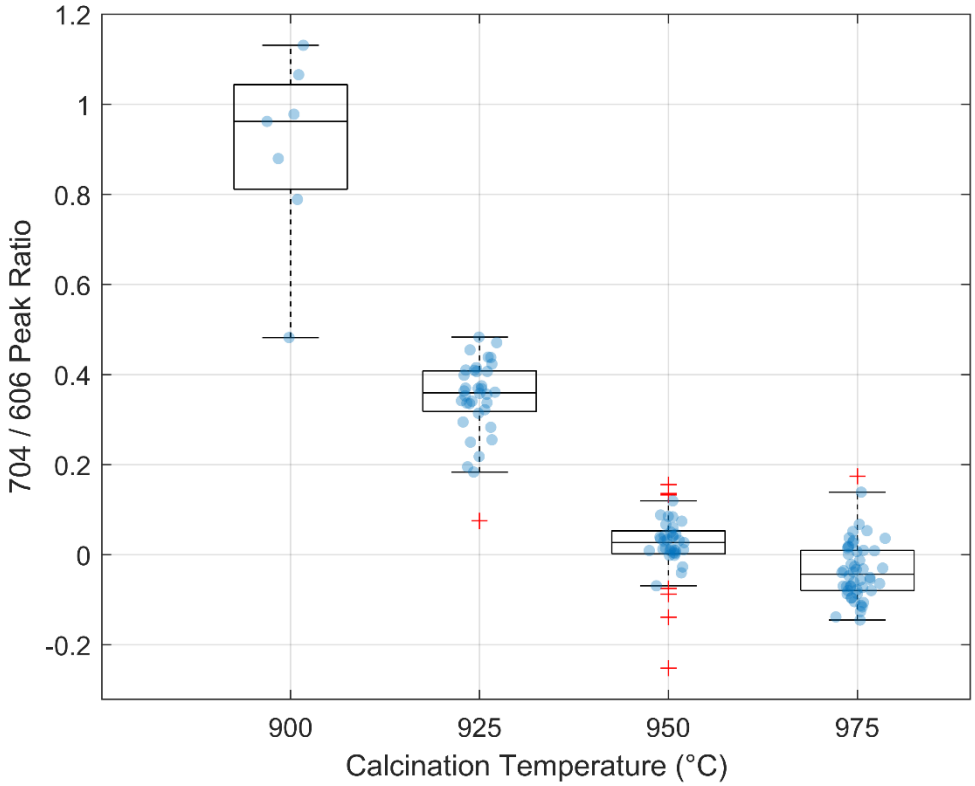

Figure 3. Distribution of the Raman process indicator (704 cm $^{-1}$/606 cm $^{-1}$ peak intensity ratio) for material processed at different calcination temperatures. Data shown correspond to stable operating periods identified from the continuous Raman measurements.

Continuous Monitoring of Process Dynamics

The evolution of the Raman process indicator throughout the experimental campaign is shown in Figure 4. Distinct responses were observed following each increase in furnace temperature, demonstrating the capability of the system to detect process changes in real time.

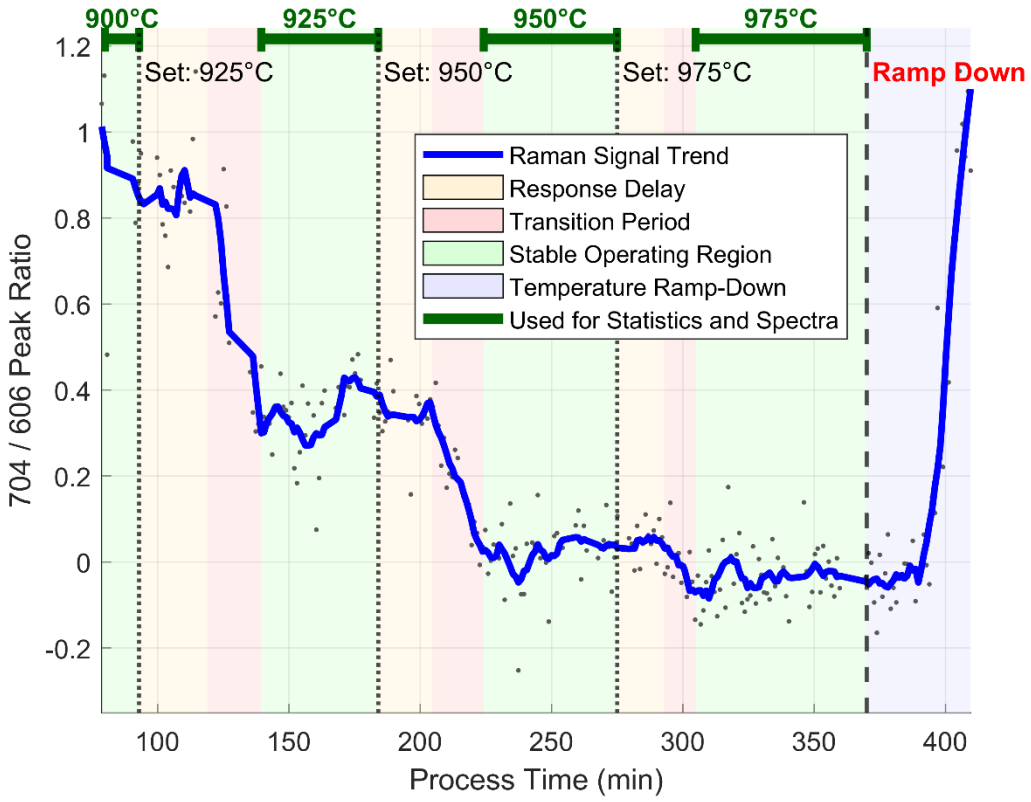

Figure 4. Continuous online Raman monitoring during calcination. Shaded regions indicate response delays, transition periods and stable operating conditions following furnace temperature adjustments.

Following each temperature adjustment, a delayed response was observed before the Raman signal began to change. This was followed by a transition period during which the indicator evolved toward a new stable level. A piecewise trend model was applied to estimate these response characteristics, and the results are summarized in Table 1.

Table 1. Estimated Raman response characteristics following furnace temperature adjustments.

Temperature (°C)	Response delay (min)	Transition duration (min)
925	26.0	20.5
950	20.5	19.7
975	18.0	12.0

Response characteristics were estimated by fitting a piecewise-linear model to the Raman process indicator shown in Figure 4. The estimated response delay decreased from approximately 26 min at the 925 °C condition to approximately 18 min at 975 °C. Similarly, the estimated transition duration decreased from approximately 21 min to approximately 12 min over the investigated temperature range. These observations demonstrate that the Raman measurements were capable of resolving both steady-state operation and transient process behaviour.

4. Discussion

The results demonstrate that time-gated Raman spectroscopy can be successfully applied to monitoring calcination processes under conditions representative of industrial mineral processing. Raman spectra were acquired continuously from a moving solids stream without direct contact between the measurement system and the process material. The stand-off measurement configuration proved capable of operating reliably despite variations in material flow and surface profile at the discharge location. The combination of time-gated detection and custom stand-off optics enabled acquisition of spectra with sufficient quality for process monitoring throughout the campaign. Furthermore, the observed response delays and transition periods demonstrate that the technique is capable of tracking process dynamics rather than only steady-state conditions.

Representative spectra and the Raman process indicator showed clear and systematic changes with increasing calcination temperature. Although detailed phase quantification was outside the scope of the present study, the observed spectral evolution is consistent with mineralogical changes occurring during thermal treatment of the lithium-bearing feed material. The selected Raman indicator provided clear separation between the investigated operating conditions, suggesting that simple spectral metrics may be sufficient for monitoring process state without the need for complex multivariate models. This is an attractive feature for future industrial implementations, where robustness and ease of interpretation are important considerations.

The ability to obtain mineralogical information directly from a calcination process has several potential benefits for lithium processing operations. Online measurements can provide immediate feedback regarding changes occurring within the material stream and may support improved process optimization, product consistency and energy efficiency. An important aspect of the present work is that the measurements were performed on a heterogeneous spodumene-lepidolite feed rather than on a purified laboratory reference material. Future work will focus on linking online Raman signatures to mineralogical reference measurements and evaluating the potential of the technique for advanced process control applications in continuous lithium conversion processes.

5. Conclusions

Online time-gated Raman spectroscopy was successfully demonstrated for monitoring a continuous rotary kiln calcination process treating a lithium-bearing mineral feed. Stand-off measurements were achieved throughout the experimental campaign, enabling continuous acquisition of mineral-specific spectral information directly from the discharged material stream.

Systematic spectral changes were observed as calcination temperature increased from 900 to 975 °C. A simple Raman indicator derived from the 704 cm^{-1} and 606 cm^{-1} bands exhibited a clear and monotonic response to temperature, providing good separation between the investigated operating conditions. Continuous measurements additionally enabled estimation of process response delays and transition periods following furnace temperature adjustments.

The results demonstrate that time-gated Raman spectroscopy can provide real-time mineralogical information under process-relevant conditions and show considerable promise as an online monitoring

technology for lithium mineral calcination. The approach may support future process optimization, product quality monitoring and the development of advanced control strategies for thermal lithium conversion processes.

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