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Analysis of Lithium Ores Using Handheld Direct Diffuse Reflectance FTIR Spectroscopy

Fast, direct, and non-destructive identification of rocks with an Agilent handheld 4300 FTIR in direct-DRIFTS mode

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Abstract

This study explores a novel Fourier transform infrared (FTIR) spectroscopic technique—direct diffuse reflectance infrared Fourier transform spectroscopy (direct DRIFTS)—for analyzing lithium (Li) ores, eliminating the need for both sample preparation and liquid nitrogen required in traditional DRIFTS. The direct DRIFTS technique, which provides detailed spectral features of rocks and minerals, is especially convenient when implemented using a handheld FTIR system, such as the Agilent 4300 FTIR fitted with a custom direct-DRIFTS interface.

The 4300 FTIR coupled with its diffuse reflectance sampling interface was used for the direct analysis of spodumene and other Li-containing ores. The direct-DRIFTS method acquired full mid-IR range data from 128 scans at 4 cm^{-1} resolution in less than a minute, enabling the quick identification of ores and minerals associated with Li-bearing rocks with high selectivity and sensitivity.

Introduction

The demand for Li is rising due to the widespread adoption of rechargeable lithium-ion batteries (LIBs), which power various electronic devices and electric vehicles (EVs). LIBs are increasingly used in stationery energy storage systems (SES) to manage electricity generated from intermittent renewable sources, such as wind and solar power. Li or Li compounds are also used in various sectors, including electronics, aerospace, glass and ceramics, pharmaceutical, and chemicals, adding to overall demand. Although Li is not considered to be scarce, it has been classified as a critical mineral in the United States due to its pivotal role in LIBs and risks within the supply chain.[1] Li compounds are often used in the electrolyte and cathode materials of LIBs.[2,3]

The main sources of Li include mining of hard rock (pegmatite) deposits and extraction from desert basin lake brine deposits.[4] While the LIB recycling industry is expected to play an increasingly significant role in supplementing the global supply chain of Li in the future,[5] there has been an increase in the exploration of Li ores. Despite there being over 150 Li-bearing minerals in the Earth's crust, spodumene is the most significant ore industrially, followed by petalite, amblygonite, and lepidolite.[6]

Spectroscopy has a long history in mineral analysis, and spectroscopic techniques are widely used in geological and mining applications. X-ray, nuclear magnetic resonance (NMR), UV-Vis, Raman, laser imaging detection and ranging (LIDAR), and FTIR have all been used to record spectra for characterization purposes by measuring the interaction between source radiation and mineral samples.[7]

In FTIR, a sampling technique known as diffuse reflectance is effective for the characterization of minerals. The IR beam from the instrument interacts with the sample, and the diffusively scattered beam is then collected. The mid-IR region in FTIR is highly informative for a wide range of mineral classes, including oxides, fluorides, carbonates, silicates, phosphates, sulfides, and more. Spectra can be collected and analyzed visually or electronically to discern differences or similarities either by searching for specific names or features within the data.[8]

The lightweight 4300 handheld FTIR spectrometer can be fitted with the widest selection of interfaces of any portable FTIR, including two internal reflection interfaces (diamond ATR and germanium ATR) based on attenuated total reflectance (ATR) geometry, and three external reflectance sampling interfaces: specular reflectance, grazing angle, and diffuse reflectance. In this study, the 4300 was fitted with a diffuse reflectance interface, which is well suited to the direct, non-destructive, in situ analysis of mineral powders, rocks, and drill cores.[9]

Owing to the unique optical design of the 4300 FTIR, implementing the DRIFTS technique with the instrument enables direct measurements compared to traditional DRIFTS. As outlined in Figure 1, the main advantages of direct-DRIFTS include the speed and ease of data collection, and the elimination of sample preparation requirements and nitrogen. Many sample types have been successfully analyzed using the 4300 direct DRIFTS technique, including both natural and manufactured minerals and materials like mineral ores, rocks, drill cores, and a wide range of treated minerals. Some example sample types are shown in Figure 2.

This application note includes examples of selected diffuse spectra collected using the 4300 FTIR compared to diffuse reflectance FTIR library spectra, which were collected from verified USGS mineral ore samples.[10] Compared to ATR and transmission, diffuse reflectance FTIR spectra are influenced by grain size, crystallinity, texture, crystal habit, and inclusions, making them useful for the identification of rocks and minerals.[11] The study also includes some quantitative models of the direct-DRIFTS data that can assist in the identification of prospective Li ore deposits.

Traditional DRIFTS compared to direct DRIFTS using an Agilent 4300 FTIR
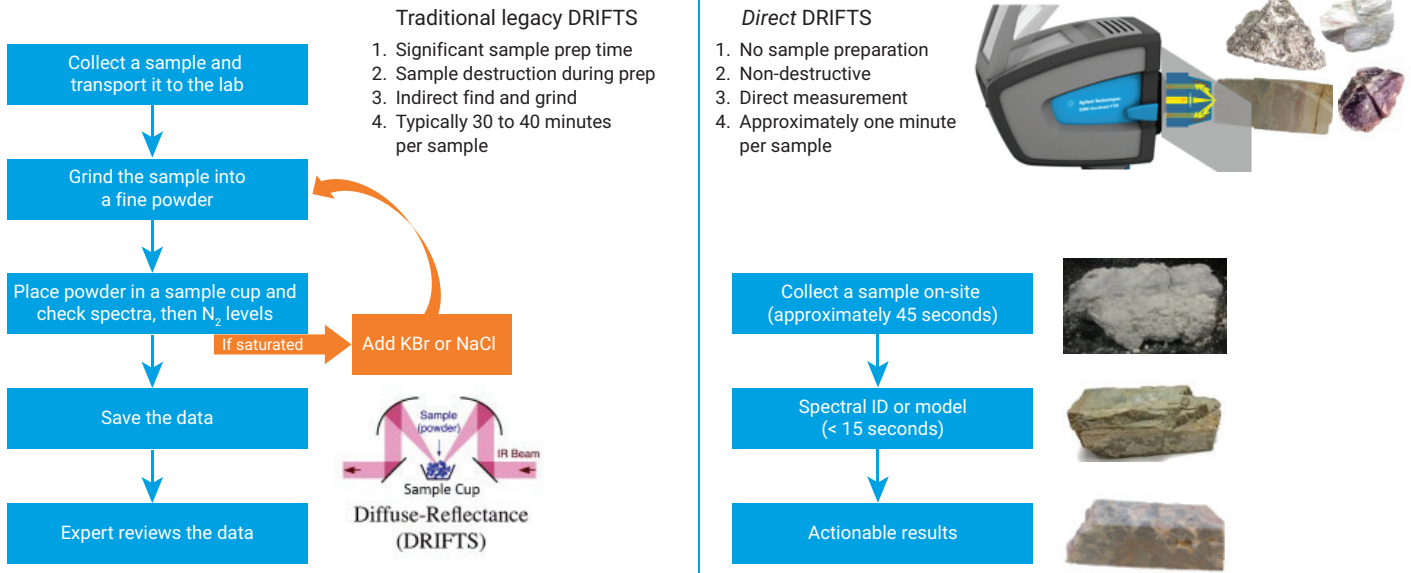
Traditional legacy DRIFTS
1. Significant sample prep time
2. Sample destruction during prep
3. Indirect find and grind
4. Typically 30 to 40 minutes per sample

Direct DRIFTS
1. No sample preparation
2. Non-destructive
3. Direct measurement
4. Approximately one minute per sample

Collect a sample and transport it to the lab

Grind the sample into a fine powder

Place powder in a sample cup and check spectra, then N_2 levels

If saturated → Add KBr or NaCl

Save the data

Expert reviews the data

Sample (powder)
IR Beam
Sample Cup
Diffuse-Reflectance (DRIFTS)

Collect a sample on-site (approximately 45 seconds)

Spectral ID or model (< 15 seconds)

Actionable results

Figure 1. Workflows for traditional benchtop DRIFTS (left) and Agilent 4300 FTIR direct DRIFTS (right).

Figure 2. Examples of samples examined directly and nondestructively using the Agilent 4300 FTIR with diffuse interface in direct-DRIFTS mode. All the pictured samples have all been measured without any sample pretreatment.

Experimental

Instrumentation

Direct-DRIFTS measurements were made using a standard Agilent 4300 FTIR equipped with a diffuse reflectance sampling interface. The sample spectra were compared to diffuse reflectance reference spectra contained in the industrial ore (165 spectra) and standard geology (971 spectra) libraries available for the Agilent MicroLab Mobile software. The library spectra had been collected from 650 to 5,000 cm^{-1} at 4 cm^{-1} resolution with Happ-Genzel apodization based on 128 background and 128 sample scans.

Software

MicroLab Mobile software was used to set up the direct-DRIFTS method, collect data, and process the data against the library spectra. Data can be easily transferred to a computer installed with Agilent MicroLab PC suite to further examine the data. PC-based Agilent MicroLab Expert software can also be used to create quantitative models of the data set if required.

FTIR measurements displayed using spectroscopy scale and geologist scale

FTIR spectroscopists typically use wavenumber (cm^{-1}) as the frequency scale (X-axis) and absorbance (Abs) as the measurement scale (Y-axis). Geologists tend to use wavelength (μm) and reflectance (R) scales, respectively. These scales are interchangeable in the MicroLab Expert software package, as shown in the spectra for kaolinite rock in Figure 3.

Spectroscopically, the wavenumber is directly related to frequency (v) and wavelength (λ), or to energy (eV). Because these scales are interconnected mathematically, the X-axis can be converted to any of these values (although the eV scale is rarely used). Analysts can select the scale for numerical convenience or for the type of irradiation applied to the sample.

In FTIR, the wavenumber is simply the number of waves per centimeter and the most common scale is usually displayed from high to low. This scale is a convenient measure of frequency, where a higher wavenumber indicates a higher frequency and therefore higher energy, while allowing whole numbers to be attributed to groups and bonds.

In the absorbance spectrum for kaolinite rock (Figure 3A) normal peaks are positive (indicated by the upward arrows) while negative Reststrahlen peaks (indicated by the downward arrows) occur at lower wavenumbers due to the Christiansen effect.[12] The inflexion point for kaolinite rock is around 1,500 cm^{-1}. The presence or absence of these features is consistent for each mineral.

Both the spectroscopy and geologist scales are equally valid and there are many more options for the X and Y axis in use today. Some scales are historical, while others are based on operational protocols and data integration. However, the scales are all mathematically interconvertible, much like temperature that can be read in Celsius, Kelvin, or Fahrenheit. Less well-known scales used throughout scientific history include Rankine, Rømer, Newton, Delisle, Réaumur, Gas mark, Leiden, and Wedgwood.

Regardless of the scale used to display the FTIR data, minerals typically have highly detailed and specific spectral signatures that relate to their chemical and physical forms. Diffuse spectral details can be interpreted mathematically, either qualitatively using a library search or using principal components analysis (PCA), or quantitatively using multivariate analysis. Since DRIFTS measures scattered light, it deviates from the principles outlined in the Beer-Lambert law. For quantitative work, multivariate modeling such as partial least squares (PLS1) is often applied to compensate for this divergence.
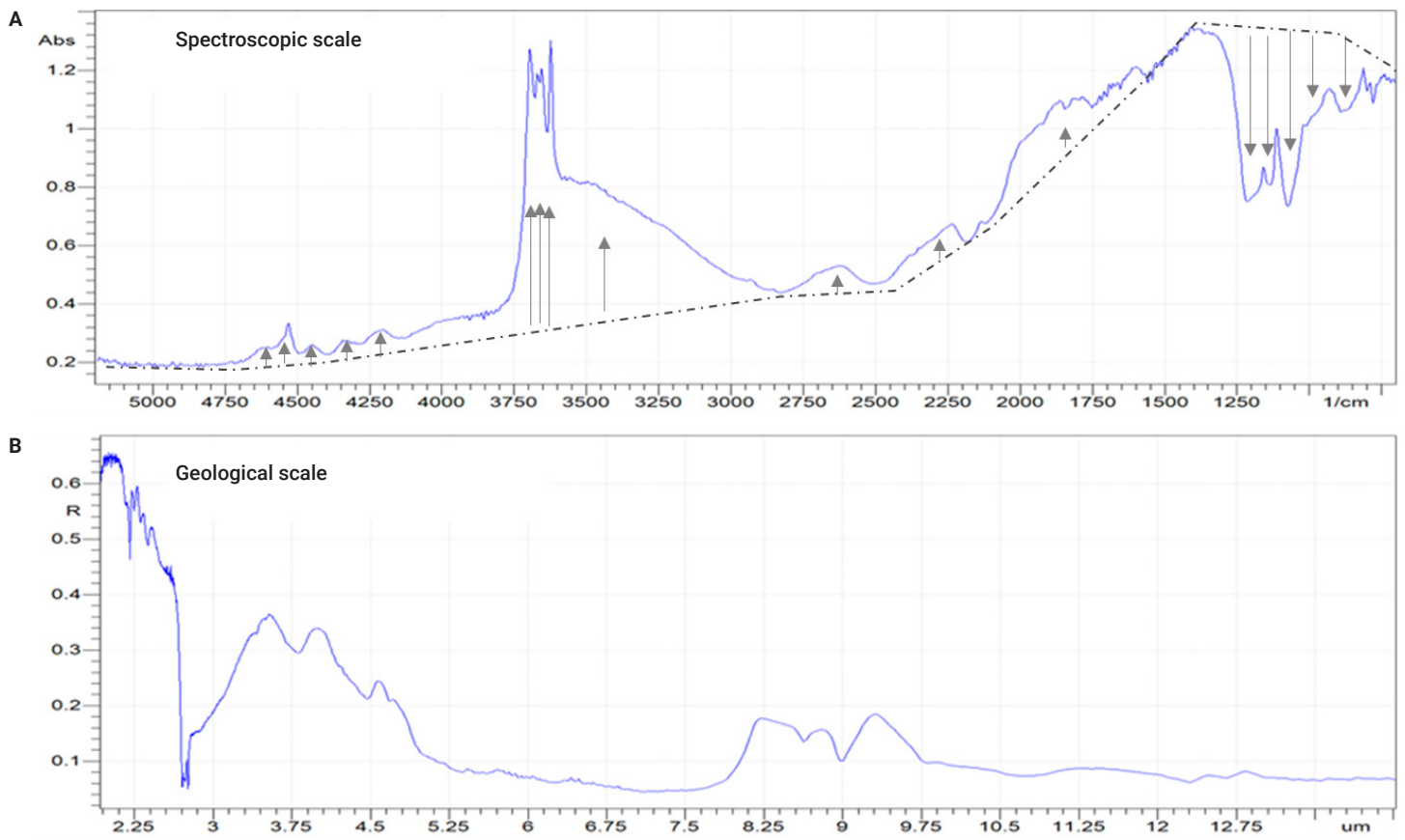
Figure 3. Direct-DRIFTS spectra of kaolinite rock acquired using the Agilent 4300 handheld FTIR spectrometer fitted with a diffuse reflectance interface. (A) A typical FTIR spectroscopic scaling of absorbance (Abs) versus wavenumber (cm⁻¹). (B) Geological scaling of reflectance (R) versus wavelength (μm).

Results and discussion

Direct diffuse compared to ATR

Typically, diffuse-FTIR spectra of minerals contain much more information than comparable ATR (or transmission) spectra. Figure 4 shows two spectra of kaolinite rock, $Al_2Si_2O_5(OH)_4$. Initially, the rock was analyzed directly using the 4300 fitted with a diffuse reflectance interface. The sample was crushed in a mortar and pestle, then analyzed using the 4300 fitted with a diamond ATR interface. (Far fewer details would be seen in the ATR spectrum if the sample had not been crushed).

The blue spectrum in Figure 4 was collected directly from the kaolinite rock using the 4300 handheld FTIR with diffuse interface, without any sample preparation and with no pressure applied to the rock surface. The series of positive peaks around 3,600 cm⁻¹ are due to various -OH stretches that relate to the composition of the sample. The peaks around 1,000 cm⁻¹ are Reststrahlen, with a point of inflexion at 1,250 cm⁻¹. These effects represent inherent properties of mineral samples, so are highly repeatable.

The comparison of sampling interfaces for the 4300 FTIR shows the advantage of using diffuse reflectance over ATR. The direct-DRIFTS method produces detailed spectra that have higher intensity features (size of peaks) and features that extend into the near infrared (NIR) region. There are more measurable absorbances (more peaks) around 3,600 cm⁻¹, which are representative of various hydroxyl counter ions.
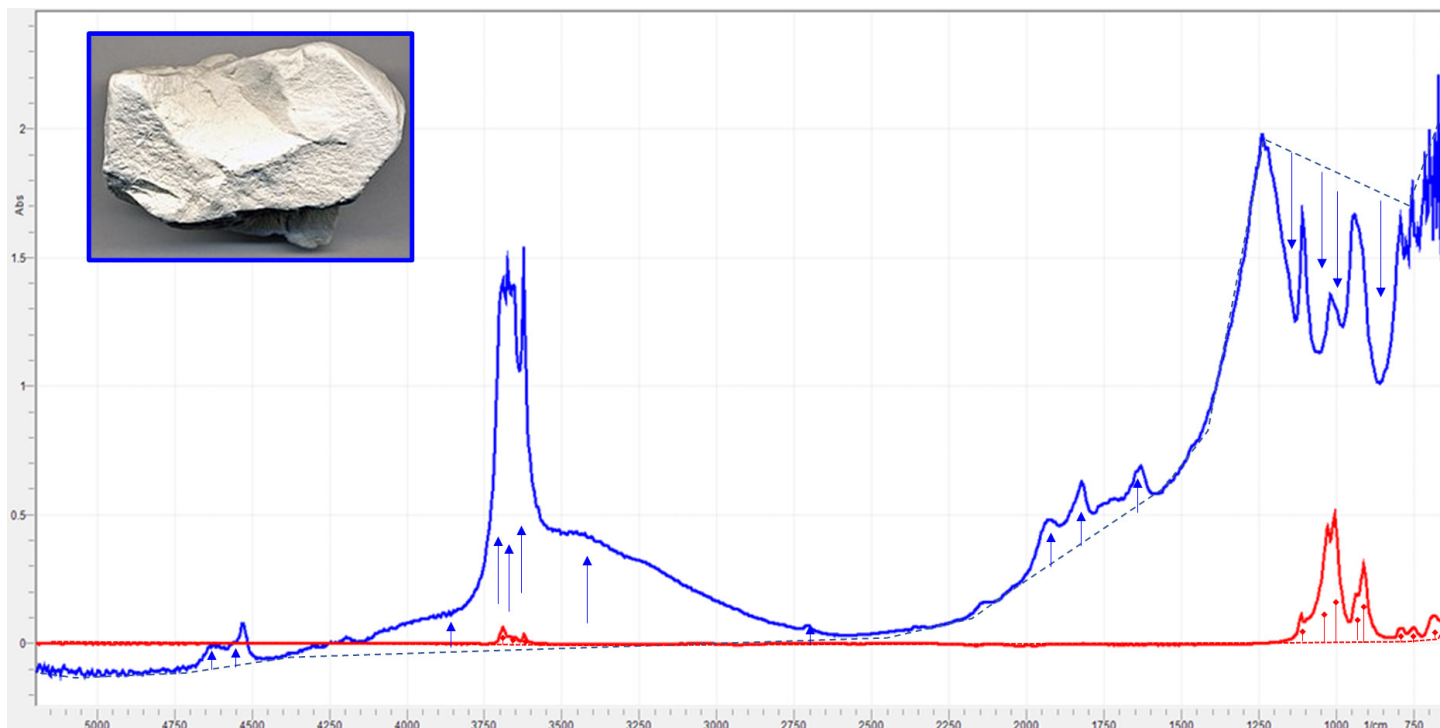

Figure 4. Kaolinite rock spectrum (blue) collected by the Agilent 4300 handheld FTIR spectrometer with the direct diffuse interface and ground kaolinite rock powder (red spectrum) collected by the 4300 with a diamond ATR interface. The same instrument was used to acquire both spectra.

Direct-DRIFTS spectra of common lithium mineral ores

Commercially valuable hard rock Li ores typically originate at depths of 1 to 2 km and at relatively high temperatures (250 to 500 °C). These deposits are commonly found close to postmagmatic processes. Figure 5 shows spectra of the five most significantly mined hard rock ores collected using a 4300 handheld FTIR with a diffuse interface.

Spodumene is the most economically important Li ore due to its mineral form that requires fewer and simpler processing steps, saving time, energy, and costs. Li is frequently transported as the carbonate or hydroxide rather than as the base metal for safety reasons. However, Australia exports Li in the form of a concentrated ground spodumene powder called "SC6", differing in its export approach compared to most other countries.[4]
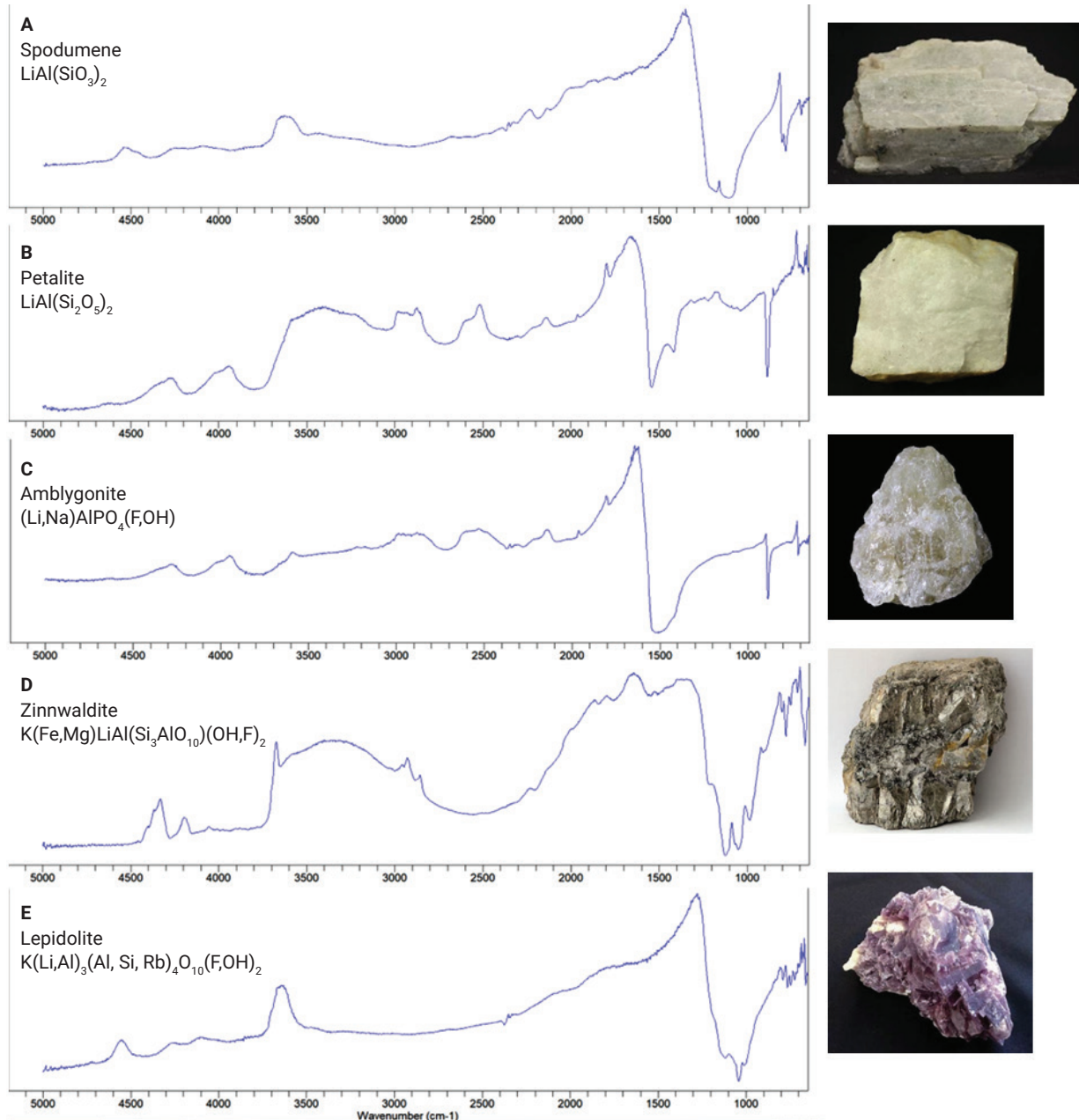

A
Spodumene
$LiAl(SiO_3)_2$

B
Petalite
$LiAl(Si_2O_5)_2$

C
Amblygonite
$(Li,Na)AlPO_4(F,OH)$

D
Zinnwaldite
$K(Fe,Mg)LiAl(Si_3AlO_{10})(OH,F)_2$

E
Lepidolite
$K(Li,Al)_3(Al, Si, Rb)_4O_{10}(F,OH)_2$

Wavenumber (cm-1)

Figure 5. The five industrially most significant Li ores. The canonical formula of the repeating unit is also given. The lithium oxide percentage (% Li_2O) of each ore are as follows: (A) 6 to 7%, (B) 3.5 to 4.9%, (C) 8 to 10%, (D) 3.0 to 3.5%, and (E) 4 to 6%. All spectra were collected by the Agilent 4300 handheld FTIR spectrometer in direct-DRIFTS mode.

Not all granitic pegmatite rocks contain lithium, but their association with Li-bearing minerals such as spodumene makes them valuable indicators in lithium exploration. Granitic pegmatite rock typically consists of quartz, alkali feldspar, and a broad class of minerals called plagioclase that do not contain lithium. However, some of the accessory (minor) minerals in pegmatite rocks, such as biotite, garnet, tourmaline, and apatite, act as indicators to Li ores. Figure 6 shows spectra of the common minerals and minor minerals in granitic pegmatite rocks.

The 4300 handheld FTIR coupled with the direct-DRIFTS interface collects detailed spectra that can be easily used to distinguish between different minerals in a completely force-free and non-destructive manner.

An example of library matching is shown in Figure 7. The spectrum obtained for a sandstone drill core was identified as andesine using a near perfect match with a reference spectrum in the standard geology library within the MicroLab Mobile software. Andesine is a plagioclase feldspar silicate, which makes it a useful indicator in lithium exploration studies.
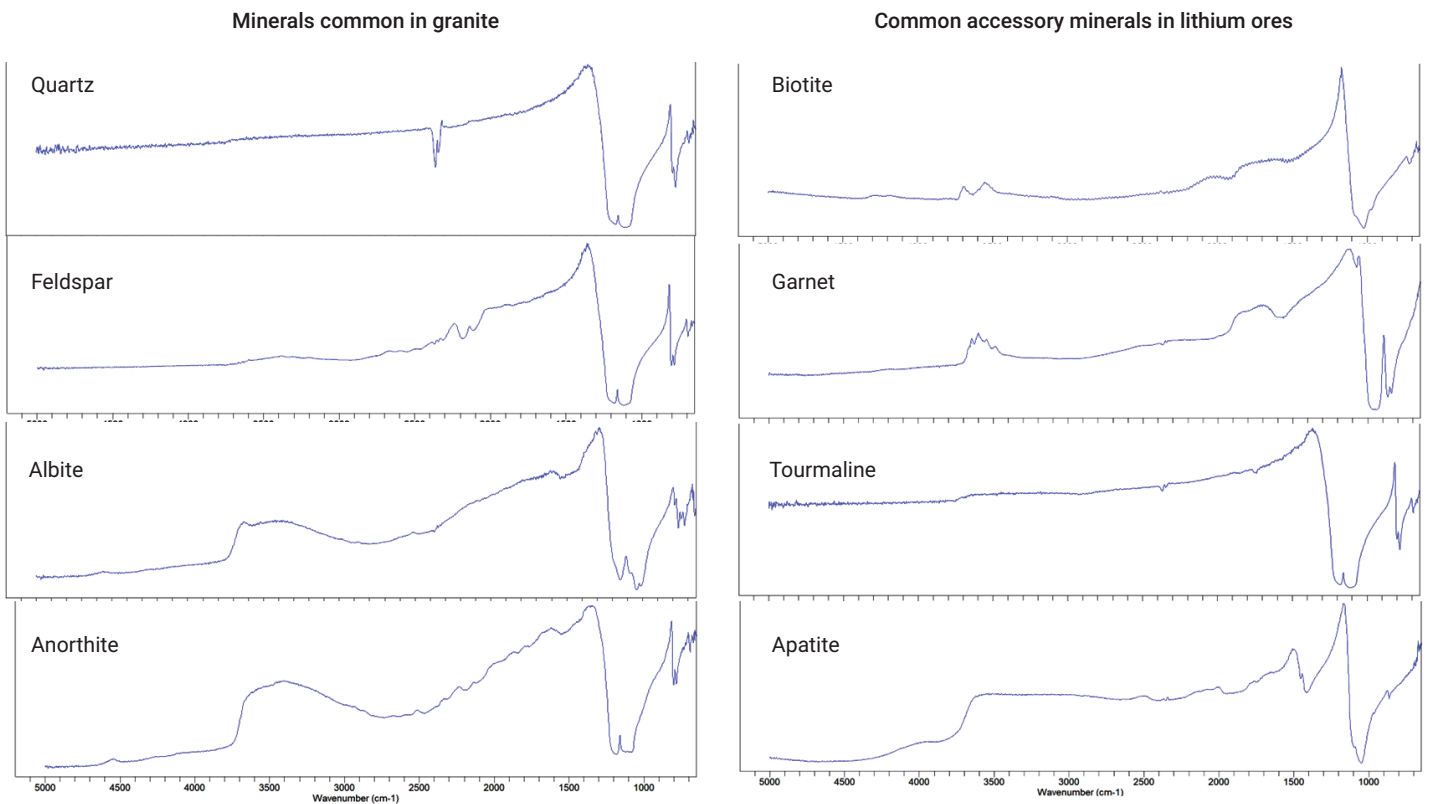
Minerals common in granite

Common accessory minerals in lithium ores

Figure 6. Common minerals in granite (A) and common accessory minerals associated with lithium ores (B). All spectra were collected by the Agilent 4300 handheld FTIR spectrometer in direct-DRIFTS mode.
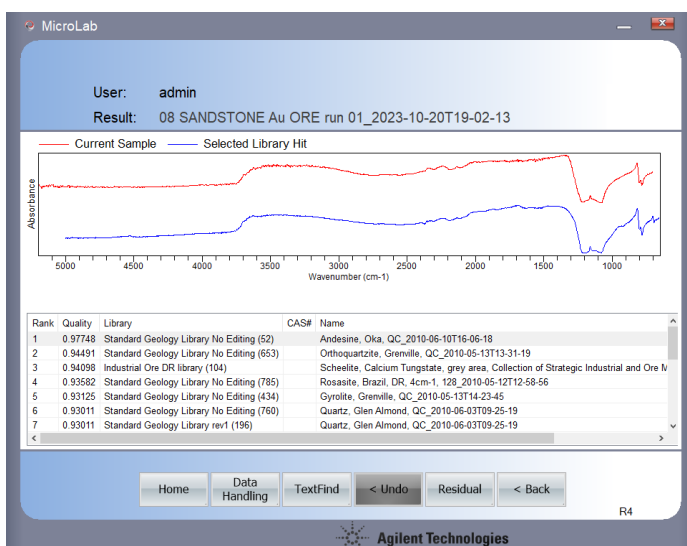
Figure 7. Library match of the sandstone gold ore drill core with andesine, which is a plagioclase silicate.

The Agilent direct-DRIFTS spectral libraries can be easily extended with new geological-specific spectra, or users can build their own on-board libraries. The spectral data can also be used to develop quantitative methods, as discussed in the following section.

Multivariate quantitative modeling for minerals

The use of multivariate (MVA) modeling for diffuse FTIR spectra enables the spectral complexity inherent in the spectra to be modeled, which is difficult to accomplish using conventional peak analysis methods. The modeled quantity can be a value, percentage, or condition.

For this study, spectra collected directly from various positional depths of drill cores were examined both by X-ray powder diffraction (XRPD) (to assess the percentage of calcite) and direct DRIFTS using the handheld 4300 FTIR. The quantitative models were created using the PC-based MicroLab Expert software, based on the analysis of suitable standards. Once a model has been developed, it can be loaded onto the handheld FTIR.

Multiple models can be added to the same instrument, enabling multiple attributes to be calculated from a single spectrum. Figure 8 shows the capability to calculate both the depth and percent calcite from the DRIFTS spectra of a drill core sample. Calcite is a known vector mineral for Li ores.
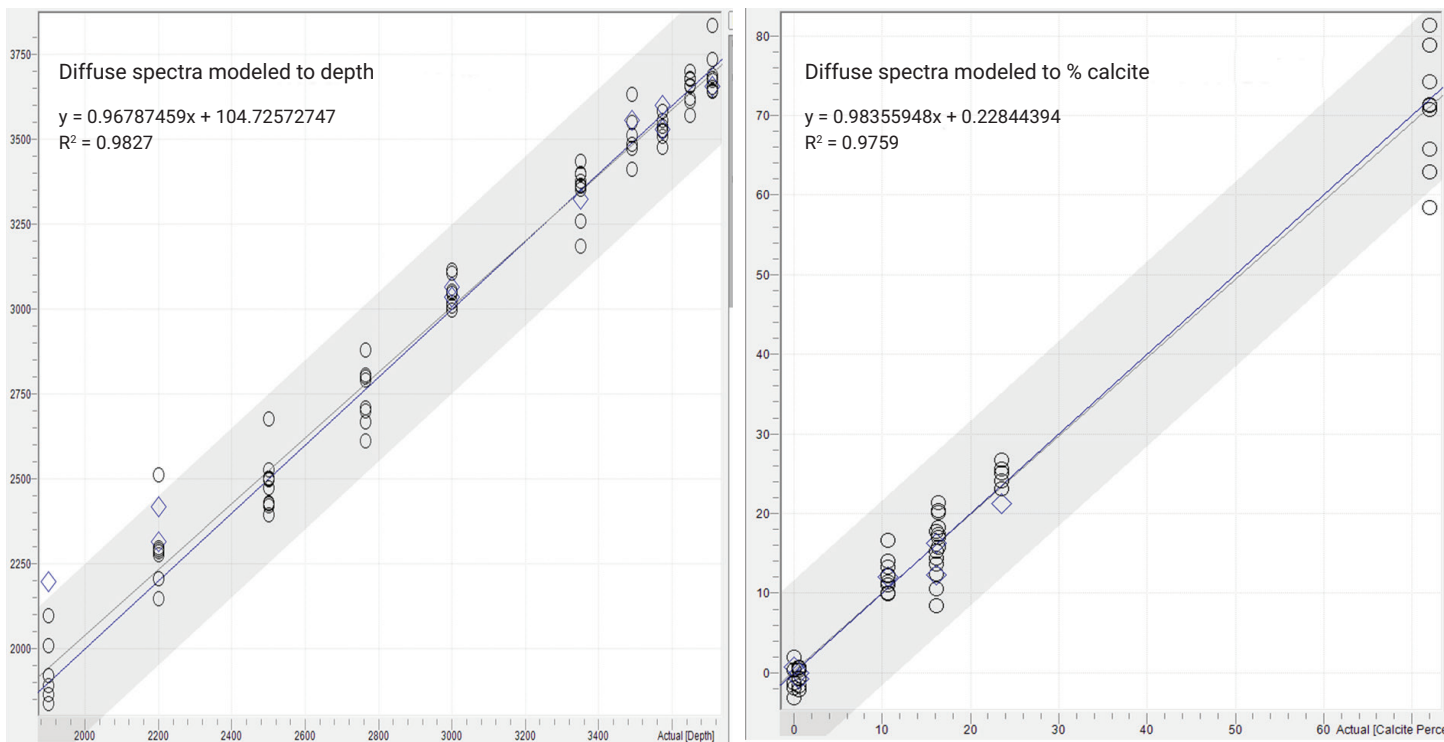

Diffuse spectra modeled to depth

$y = 0.96787459x + 104.72572747$
$R^2 = 0.9827$

Diffuse spectra modeled to % calcite

$y = 0.98355948x + 0.22844394$
$R^2 = 0.9759$

Figure 8. (A) Agilent 4300 FTIR direct-DRIFTS method spectra modeled to depth. (B) 4300 FTIR direct-DRIFTS spectra modeled to % calcite, as verified by XRPD.

Once the quantitative model has been created, a sample of unknown characteristics can then be analyzed by direct DRIFTS with the 4300 FTIR. The software then automatically compares the acquired spectral data against the model to calculate the drill core depth and percent calcite of the sample. The method provides the user with valuable information to determine whether the drill core samples are approaching or diverging from a potential Li ore target, based on depth and percent calcite.

In Figure 9, the percent of spodumene or petalite was calculated to a high degree of confidence based on diffuse FTIR spectral data acquired using the 4300.[13] SC_6 is an important spodumene concentrate that contains around 6% Li_2O—which represents close to pure (100%) spodumene. The high-grade ore is valued as a raw material for producing lithium compounds used in LIBs and other applications, so it is important that the percent spodumene can be established.
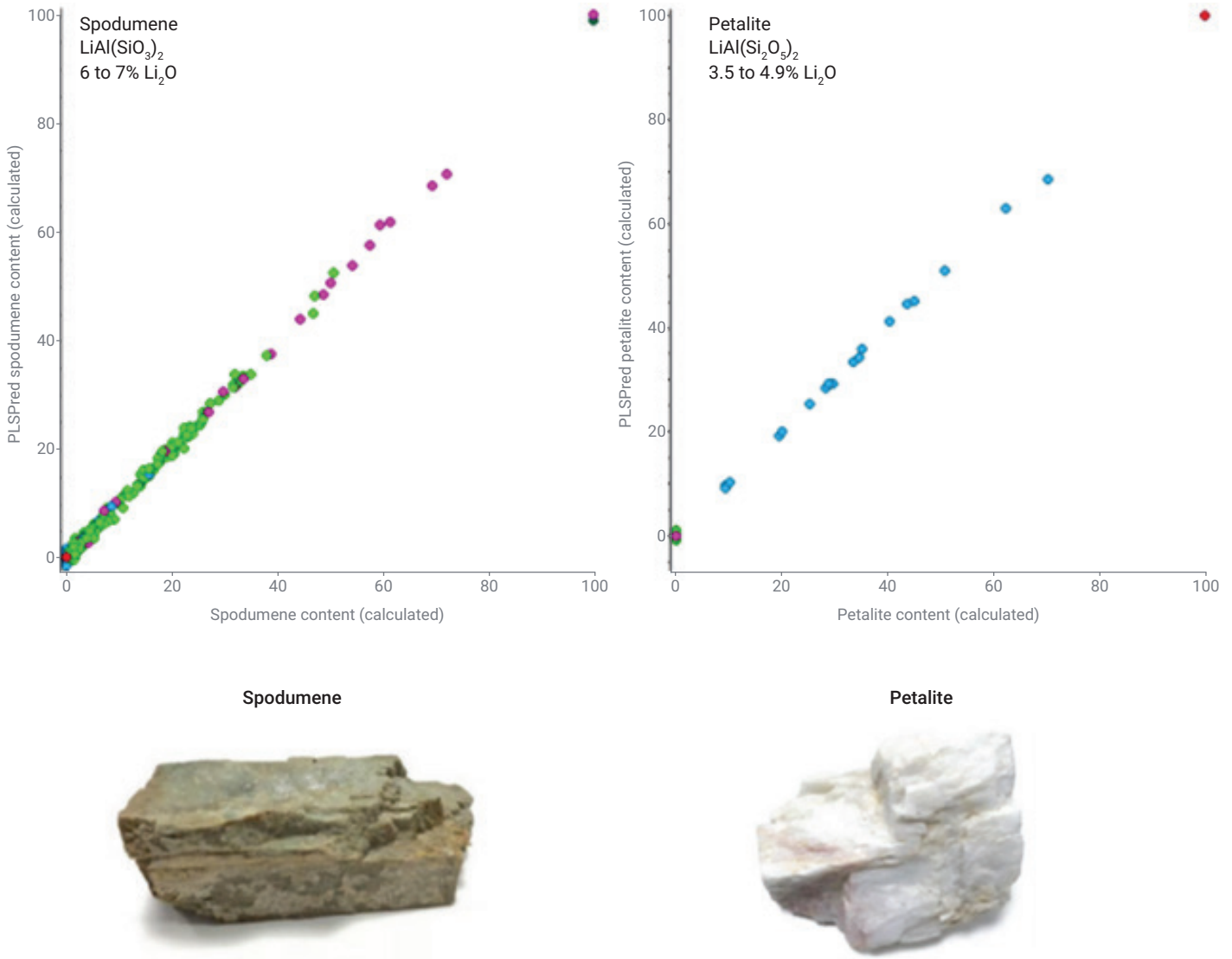

Spodumene
$LiAl(SiO_3)_2$
6 to 7% Li_2O

Petalite
$LiAl(Si_2O_5)_2$
3.5 to 4.9% Li_2O

Figure 9. Agilent 4300 direct-DRIFTS spectra modeled and correlated to % spodumene (A), where 100% = SC_6, spodumene concentrate 6% Li_2O equivalent, and % petalite (B), where 100% = 4.9% Li_2O equivalent. Reproduced with permission of CSIRO Mineral Resources, Australia.[13]

Conclusion

The demand for lithium is increasing, but identifying valuable Li-bearing ores, such as spodumene, and establishing the quality of the ores can be difficult. This study has shown that DRIFTS spectra collected using an Agilent 4300 handheld FTIR spectrometer fitted with a diffuse reflectance sampling interface exhibited detailed features of rocks and minerals. When compared to spectra contained in DRIFTS geological libraries, samples can be identified with a high degree of accuracy.

The spectral data can also be used to develop quantitative methods based on MVA modeling. The models included in the study were used to calculate both the depth and percentage of calcite—a known vector mineral for Li ores—in drill core samples, and to identify the quality of Li ores such as spodumene and petalite.

The handheld FTIR system does not require any sample preparation, so can be used in the field. The instrument's "point and shoot" mode of operation simplifies the process of collecting high-quality data.

The 4300 direct DRIFTS method can be used to examine rocks, powders, drill cores, as well as treated and refined mineral powders. This convenient method can assist in the exploration, mining, and extraction of lithium, while also ensuring the quality of lithium materials supplied to industries such as lithium-ion batteries and others.

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