

An Evaluation of Microanalysis Techniques for Materials Characterization in the Terahertz Spectral Region 9 to 1.5 THz (300 to 50 cm⁻¹)

Donna K. Wilson and Edward M. Suzuki, Washington State Patrol Crime Laboratory

Introduction

Infrared spectroscopy in the mid-infrared region (4000-700 cm⁻¹) is widely used in forensic science for the identification, characterization, and comparison of a variety of materials encountered as evidence. Extended range (4000-250 cm⁻¹) FT-IR spectrometers are also used, as the absorptions of many inorganic compounds occur in the lower frequency regions. For even more information about inorganic compounds, especially simple ionic salts, the terahertz region (extending roughly from 333 cm⁻¹ or 10 THz, to 2 cm⁻¹ or 0.06 THz) in the far-infrared region is of great interest and is accessed using an FT-IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and far-IR transparent optics.

There is very little data published on materials in the terahertz region. One of the only references found was published in 1975 and uses mineral oil or nujol mulls in polyethylene (PE) windows.¹ More recent work has focused on absorptions in the terahertz region for the analysis of pigments in paint, in which a common sample preparation includes heating the sample to make PE pellets.^{2,3,4}

Here, the use of a diamond anvil cell (DAC) for transmission spectra of materials in the terahertz region is compared to the use of a diamond element for attenuated total reflectance (ATR) spectra, and data is presented for simple ionic salts and other materials with little to no absorptions in the mid-IR.

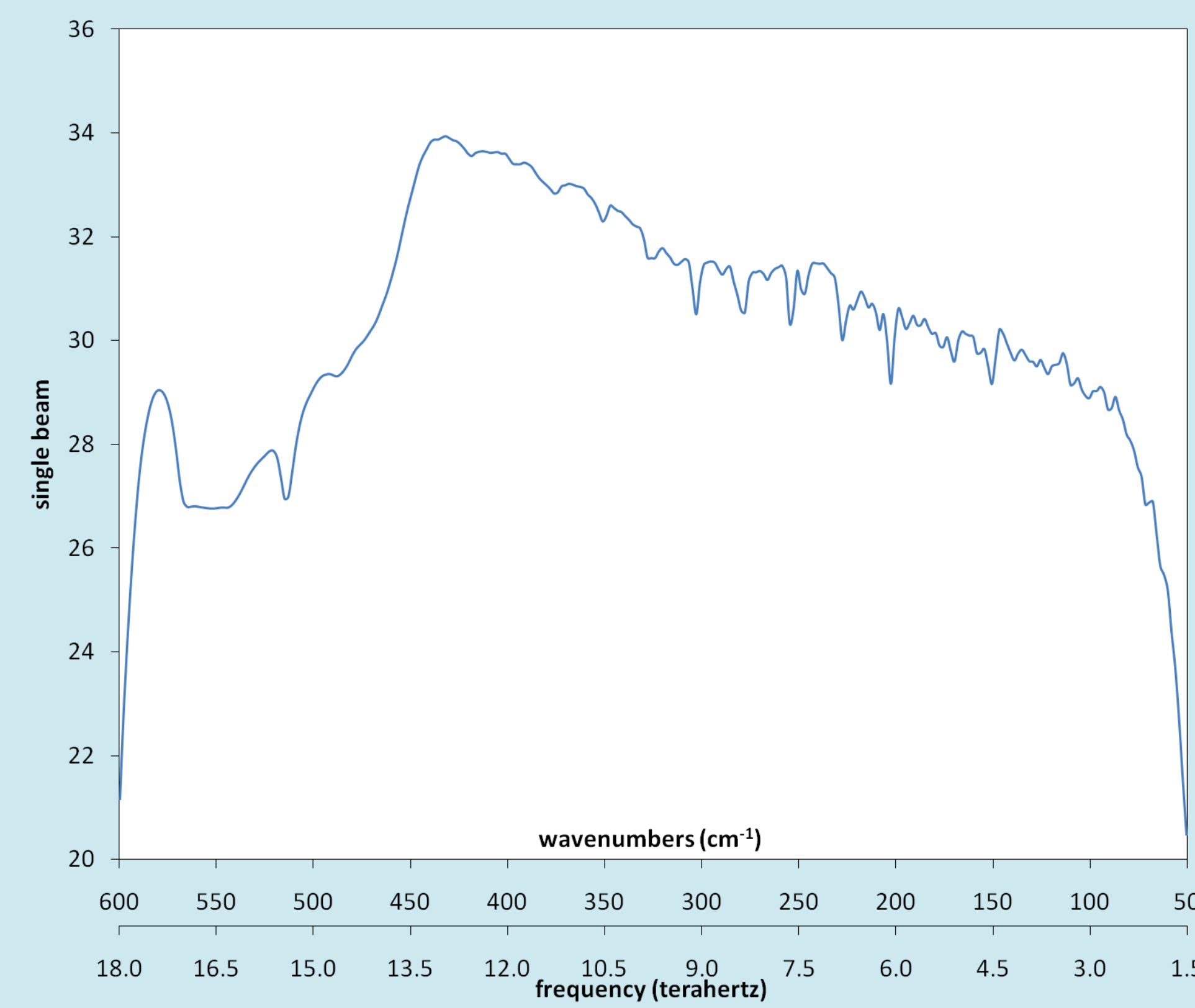


Figure 1: Single beam background from ATR after purging.

Instrumentation

To gather data in the terahertz region, an FT-IR must have transparent optics in this region, such as PE windows and a solid substrate (Si) beamsplitter. The detector and accessories need to be similarly transparent; a DTGS detector with a PE window can scan down to 50 cm⁻¹ and below, and a diamond element or anvil cell will be transparent throughout the far-IR region.

Here, spectra were collected on a Nicolet 6700 FT-IR using either a 4x beam condenser for DAC work, or a SmartOrbit ATR accessory with an all-diamond element (seen below).



Note that DAC spectra are color-coded red or yellow. The percent transmission or reflectance should be taken as a relative amount, since for ease of comparison, some spectra were shifted higher or lower.

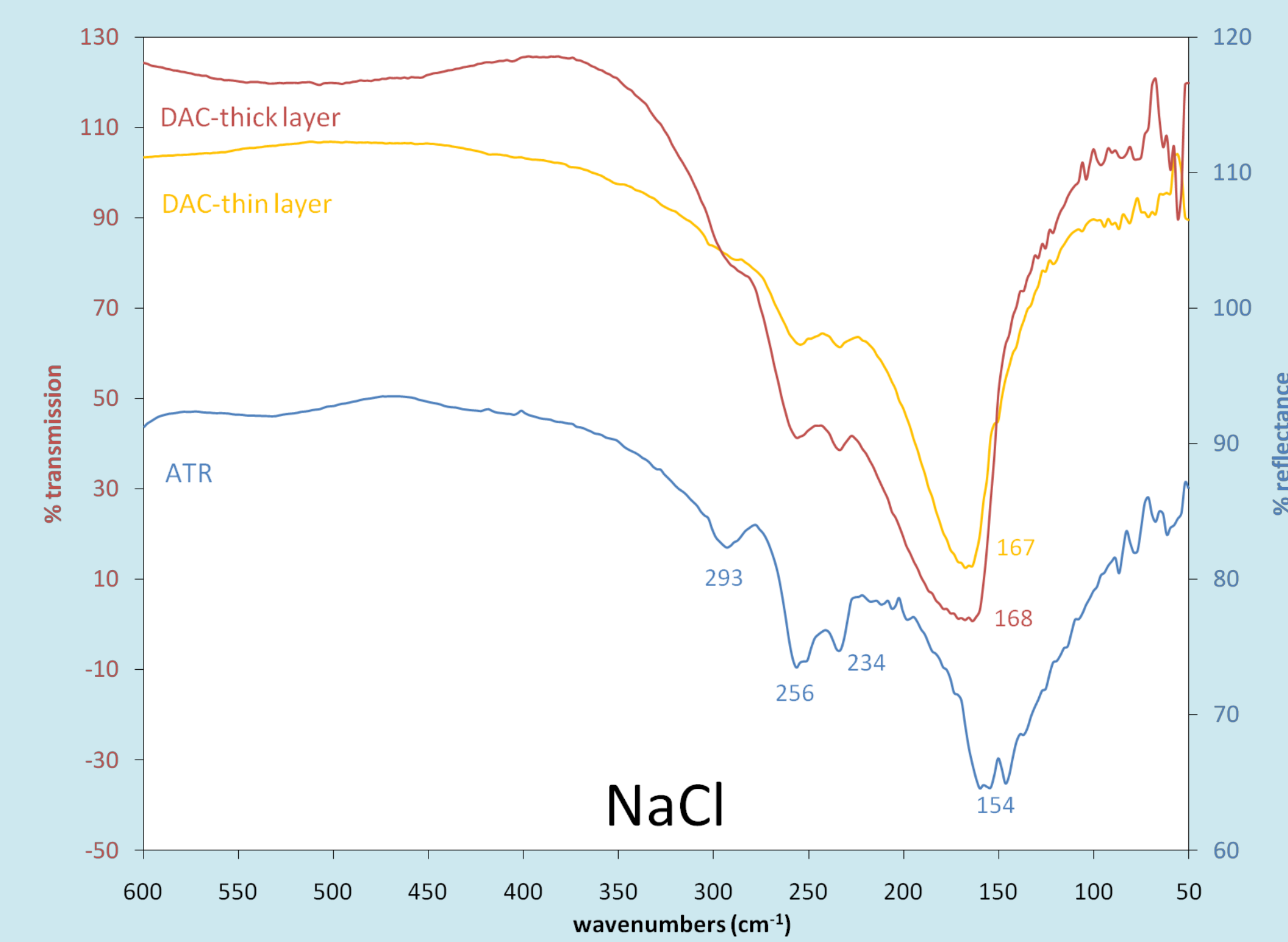


Figure 2: Comparison of sodium chloride on DAC and ATR.

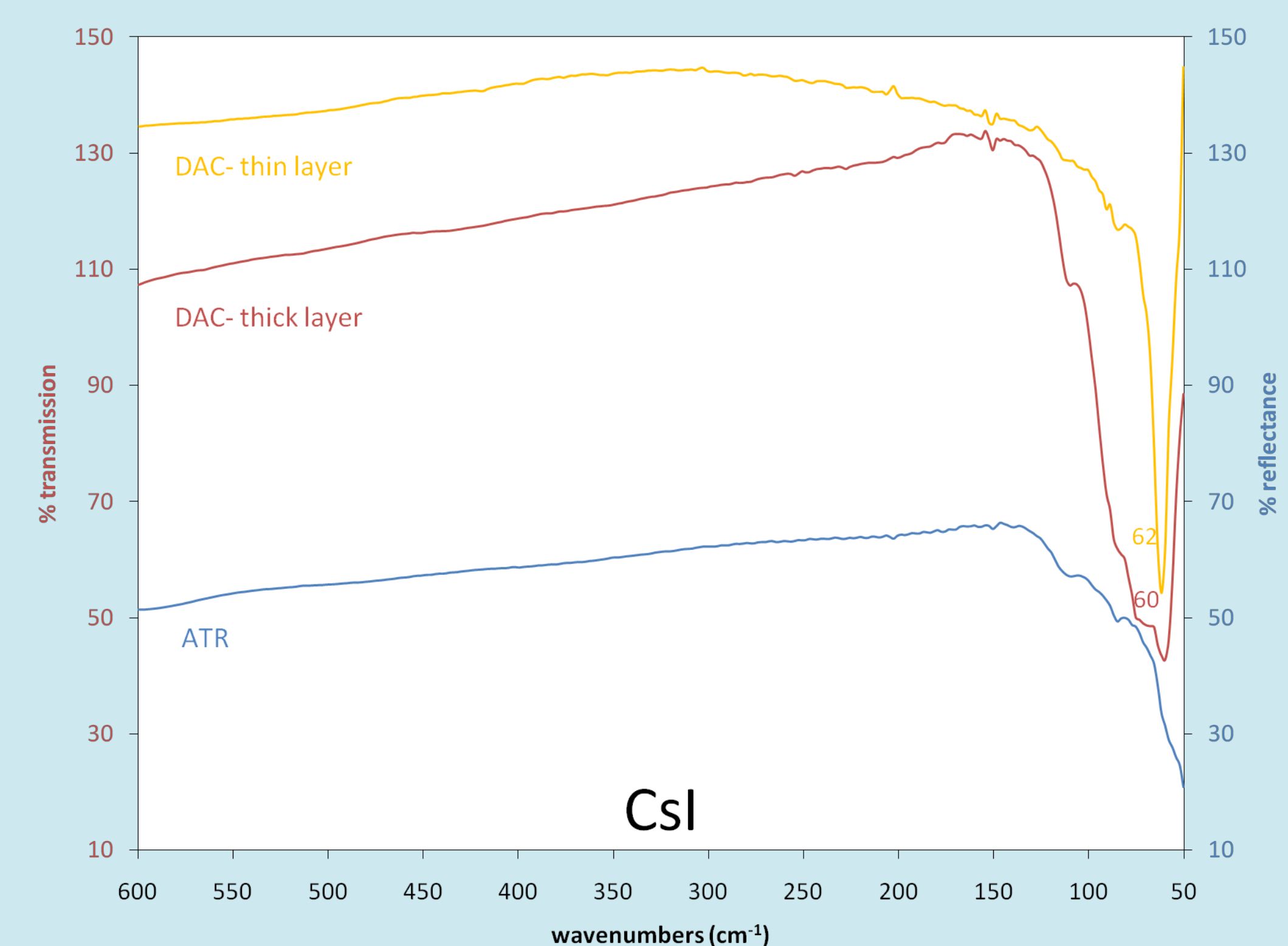


Figure 4: Comparison of cesium iodide on DAC and ATR.

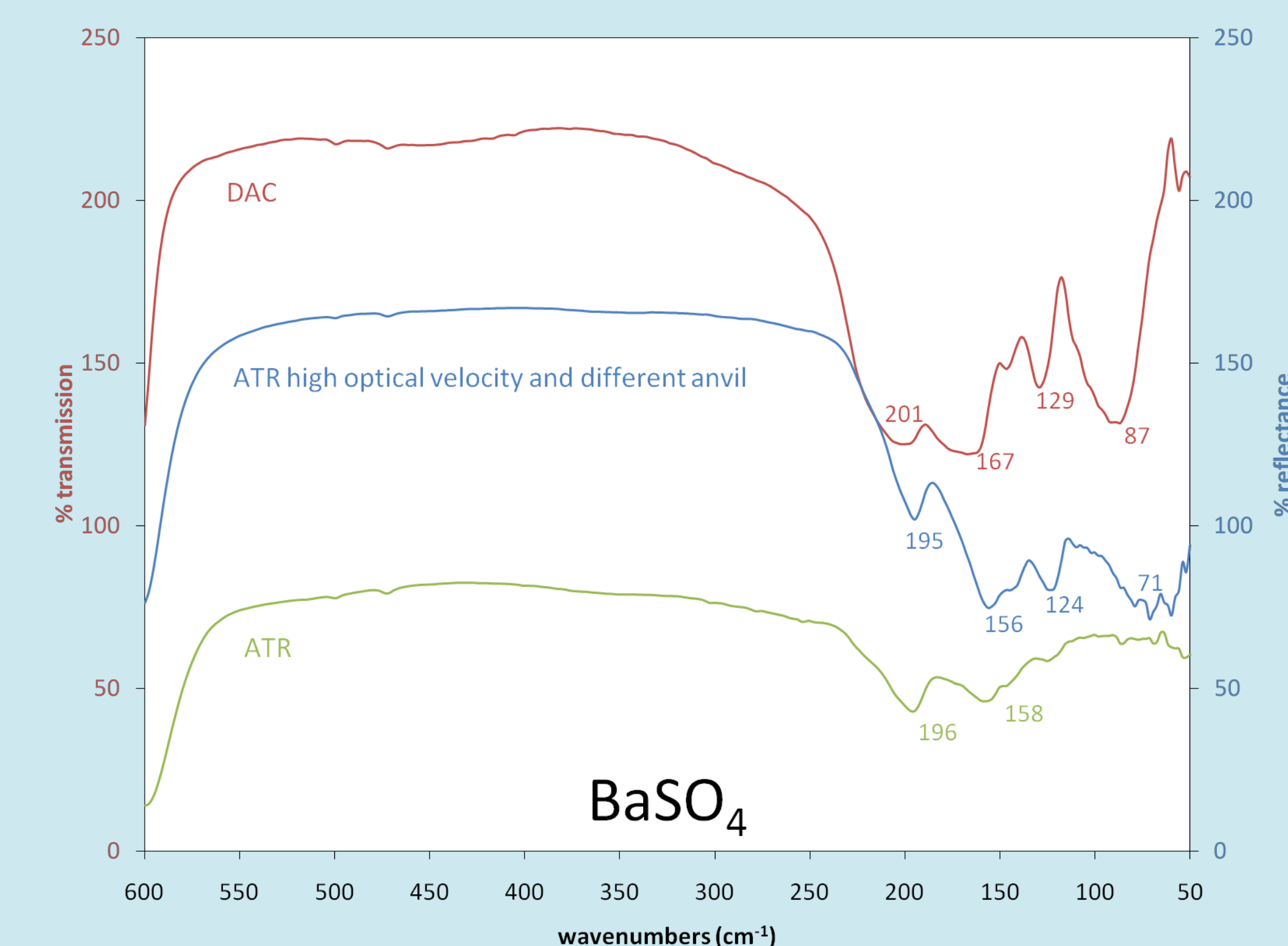


Figure 6: Comparison of barium sulfate on DAC and ATR.

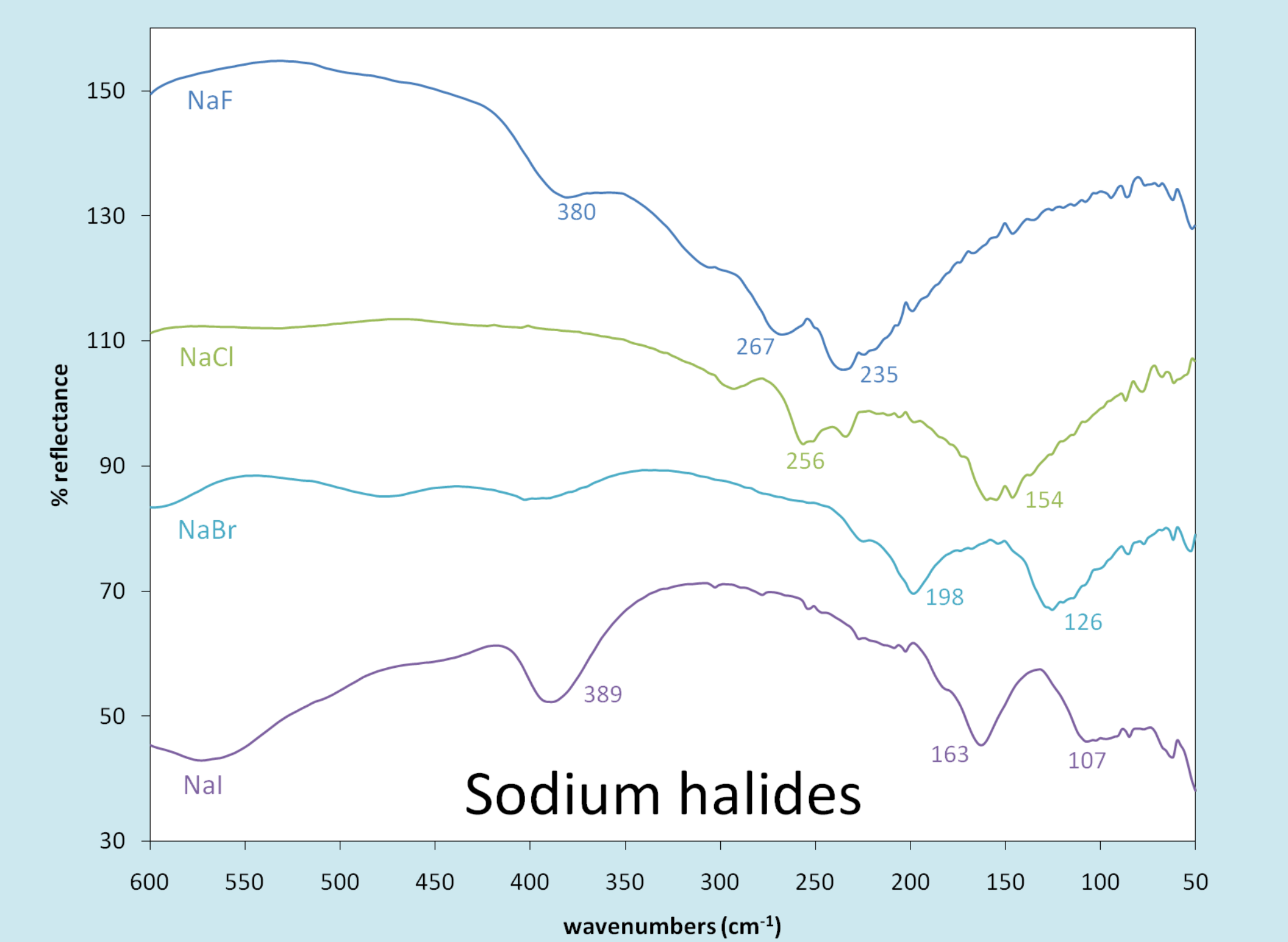


Figure 8: Comparison of sodium fluoride, chloride, bromide and iodide on ATR.

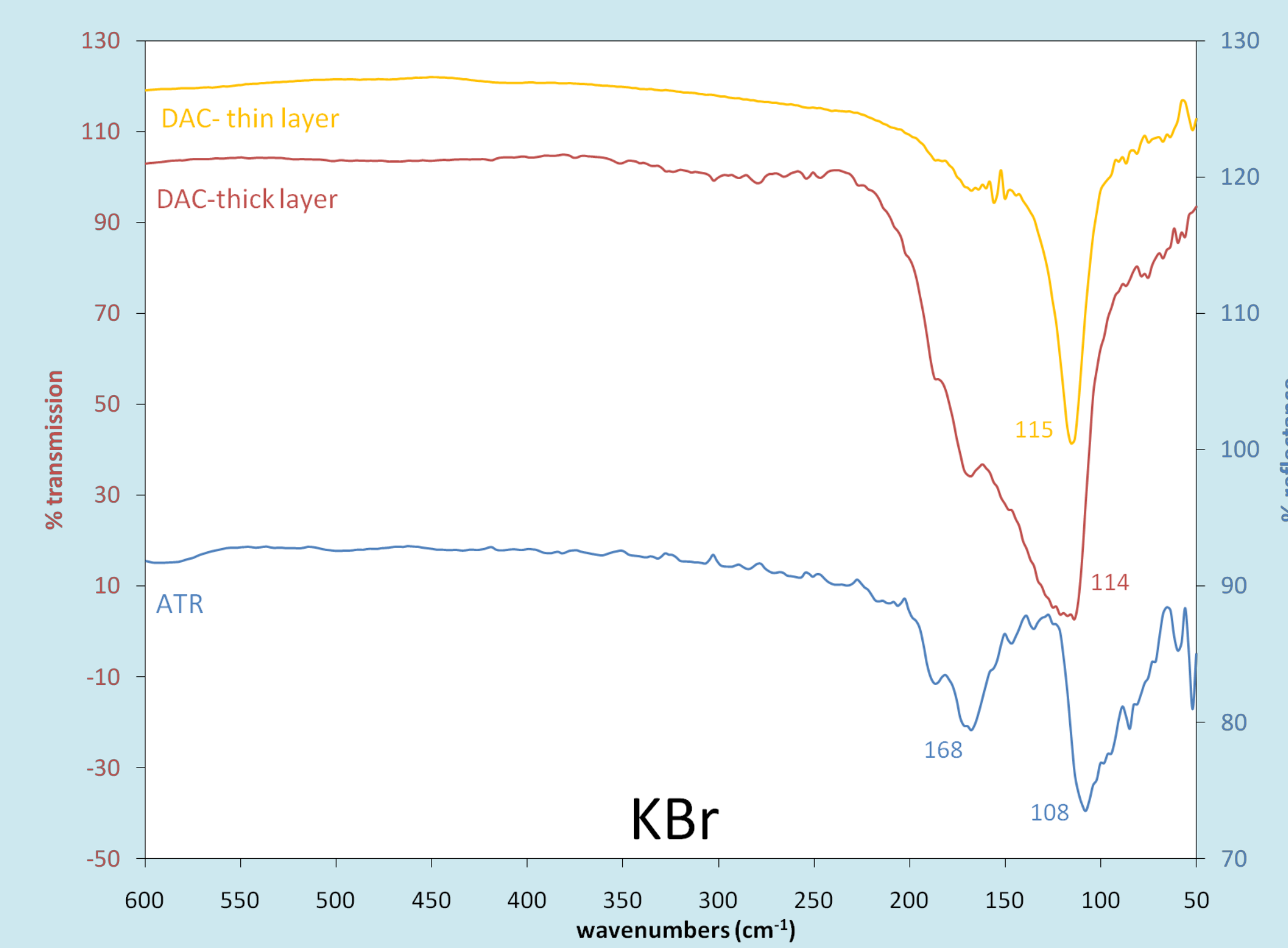


Figure 3: Comparison of potassium bromide on DAC and ATR.

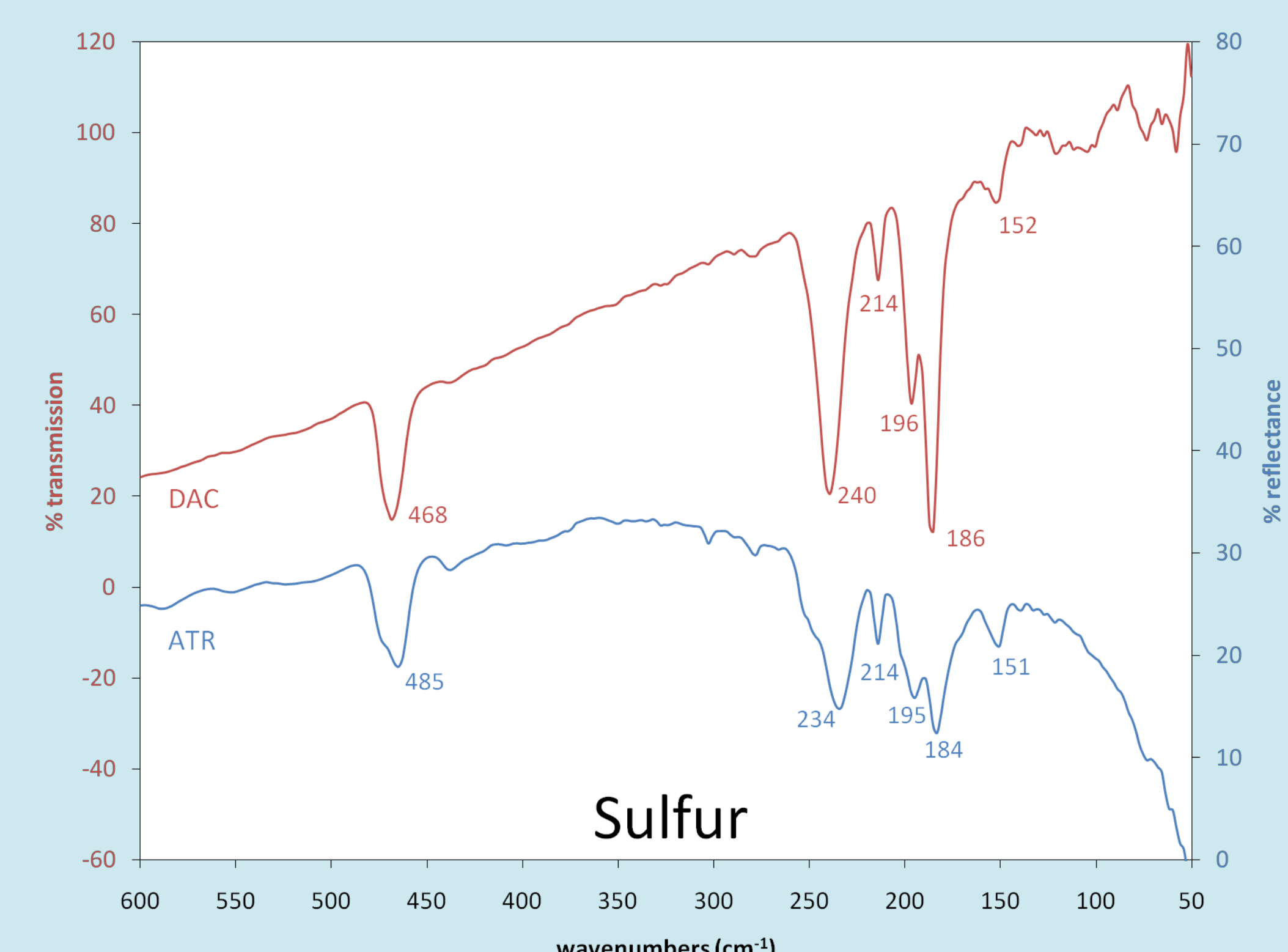


Figure 5: Comparison of sulfur on DAC and ATR.

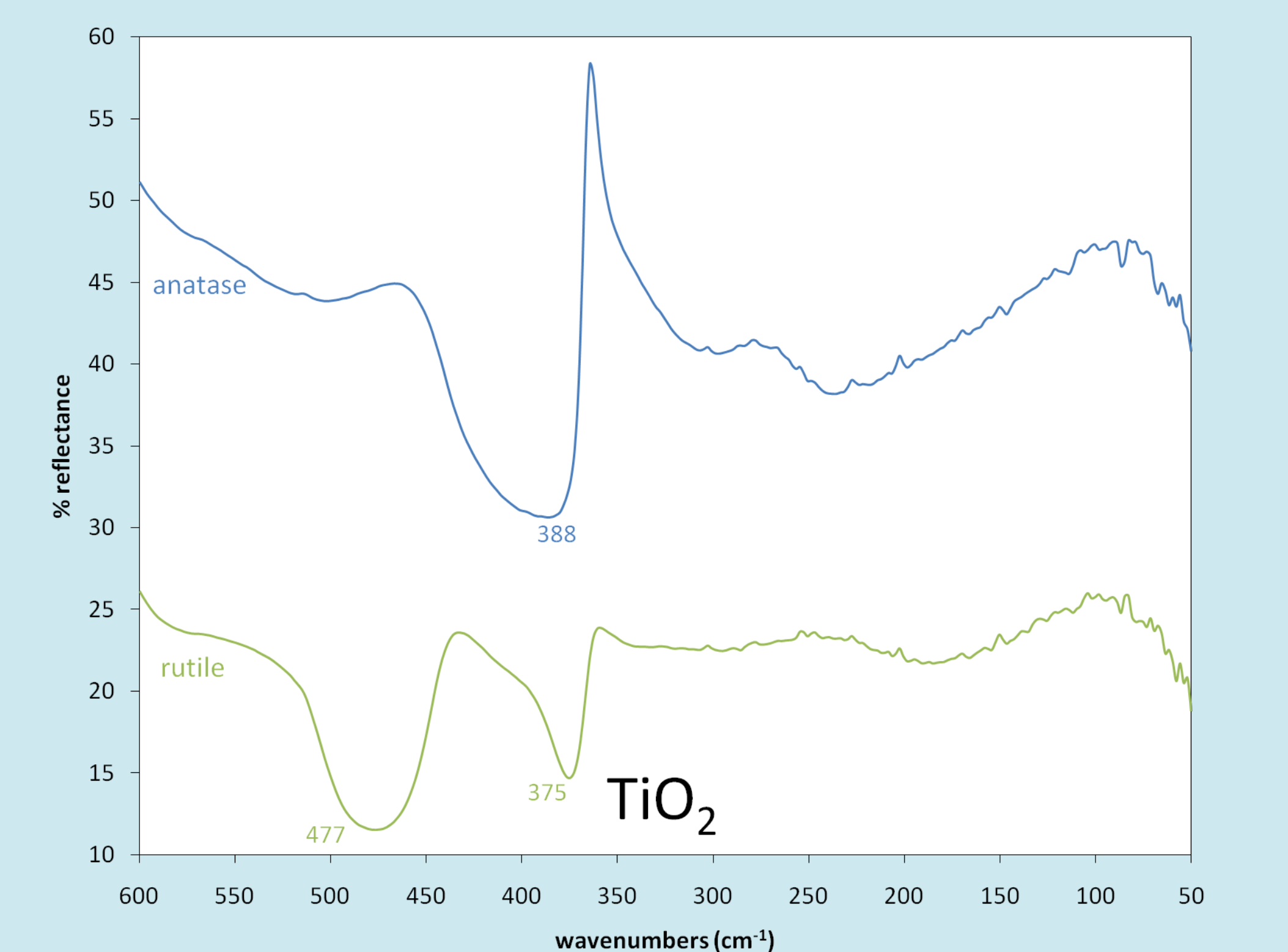


Figure 7: Comparison of anatase and rutile on ATR.

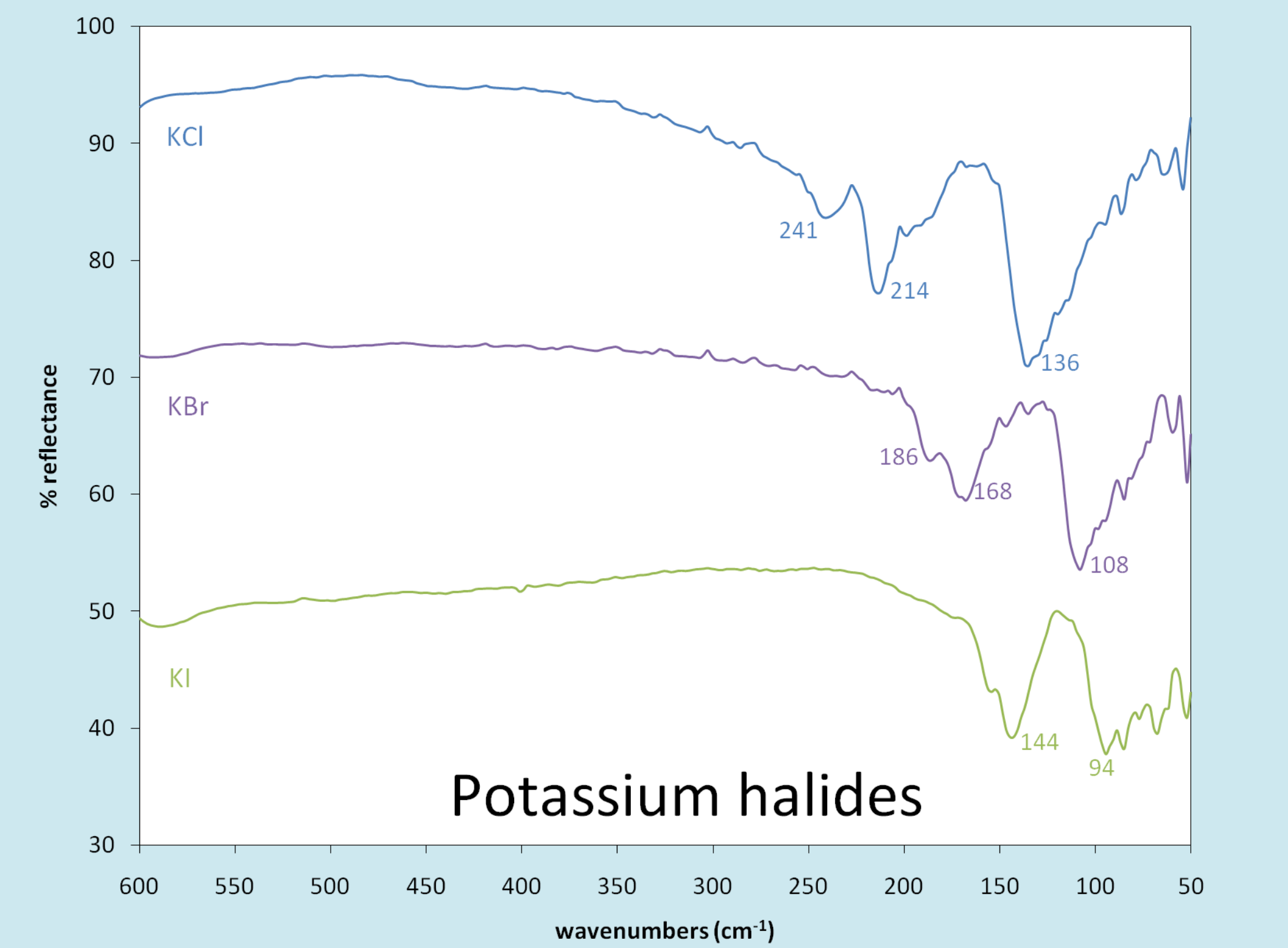


Figure 9: Comparison of potassium chloride, bromide and iodide on ATR.

Methods and Materials

ATR spectra were gathered using 1000 scans for both the background and sample. Resolution was 4 cm⁻¹, sample gain 8.0, aperture 100.0 and optical velocity 0.6329 (except for spectrum in Fig. 6, wherein it was 1.8988). DAC spectra were gathered under the same parameters except aperture was 150.0 for all spectra, and the sample gain was 1.0 for the thick layer of NaCl in Fig. 2. Between 1000 and 8000 scans were collected for the background and sample. Data was collected using a single anvil. Chemicals used were from the laboratory's chemical reference collection from Sigma, Aldrich, J.T. Baker, Farwest Paint and Sachtleben Chemie.

Results and Discussion

Using DAC and ATR requires very little sample preparation, but analysis time can be somewhat lengthy as the instrument must be well-purged first since pure rotational transitions of water vapor occur from 400 to 50 cm⁻¹ region, and also continue below 50 cm⁻¹ (Fig. 1). In addition, the region below 100 cm⁻¹ has greater relative noise, and a longer analysis time is required to obtain well-defined peaks below 80 cm⁻¹. Data collection of 1000 scans took about 20 minutes.

The thickness of the sample on DAC can alter the appearance of the spectra. This can be taken advantage of in order to get sharper peaks (by using a thinner sample) or to get stronger peaks (by using a thicker sample) as seen in Fig. 3. Both sample preparations may be useful when a mixture of materials is present.

Compared to DAC analyses, ATR analyses require less sample preparation but somewhat larger samples. ATR has the advantage that because the depth of penetration of the analysis beam is proportional to wavelength, weaker far-infrared absorptions are more readily observed. See Fig. 3, where peak at 168 cm⁻¹ is much more prominent in the ATR spectrum compared to the two DAC spectra. ATR absorption bands, however, are strongly distorted due to anomalous dispersion, which results in differing penetration depths of the evanescent wave. Therefore, ATR reference spectra should be acquired on the same instrument. As seen in Figs. 2-6, data collected using DAC and ATR techniques are comparable, but ATR bands do show significant lower wavelength shifts versus DAC. See Fig. 4, wherein the peak minimum of CsI is not observed in the ATR spectrum.

An all-diamond ATR element only has a refractive index (RI) of 2.4, making it unsuitable for inorganics (such as TiO₂) that have a higher RI. Despite this, it is still possible to distinguish between the anatase and rutile forms of TiO₂, as seen in Fig. 7, which also shows the strong specular reflectance distortion. It is unclear why a distinct peak (near 70 cm⁻¹) in BaSO₄ (Fig. 6) is not seen when some parameters are changed; however, it illustrates the importance of running sample and reference spectra under the same conditions.

Terahertz absorptions of simple salts can be distinguished since their main peaks differ in frequency (see Figs. 2, 3, 4, 8, and 9). Some compounds, such as BaSO₄ (Fig. 6) have several strong absorptions below 300 cm⁻¹ and a few, such as elemental sulfur (Fig. 5), have their strongest absorptions in this region.

Conclusions and Future Work

The terahertz region can be used for analysis of materials that have minimal absorptions in the mid-IR. Both transmission and ATR methods may be used, although the limitations of each technique should be kept in mind.

Terahertz infrared spectroscopy can complement existing techniques (PLM, XRF, SEM/EDS, CE and mid-IR) to help confirm a salt's presence. PLM bracketing for RI is more time consuming for the analyst. XRF or SEM/EDS may be used, but may require a longer analysis time. XRF cannot see elements below sodium, so oxidized compounds, such as NaClO and NaClO₃, would not be easily differentiated from each other or from NaCl, while EDS cannot go below carbon, so elements such as lithium or boron are inaccessible. Therefore, the terahertz region may be especially useful for the identification of simple ionic salts that may be very difficult to analyze with other elemental methods, such as lithium salts like LiCl, LiF and Li₂O.

References

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