

# Multi-technique surface analysis of mineral oxides species

X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy analytical techniques have become popular due to their flexibility, ease of use, and the wealth of information they provide. Until recently, analysis of a material using these two techniques required the use of two instruments. However, the development of coincident XPS-Raman now allows for fast, straightforward utilization of both techniques, better exposing your sample's properties and opening up exciting, new materials characterization opportunities

## Introduction

XPS is an extremely versatile technique that has found widespread use in a myriad of application areas, from contact lenses to aerospace materials. XPS is unique in that it can quantify the elemental and chemical composition of a material's surface with extreme selectivity, with the typical information depth of XPS being less than 10 nanometers.

Raman spectroscopy is utilized in many similar application areas, as it requires little sample preparation, is non-destructive, provides information on molecular structure, and enables you to identify materials quickly, thanks to extensive spectral libraries.



The implementation of XPS and Raman with other analysis techniques is well established. XPS has a long history of complementary use with related UHV analysis techniques, such as UV photoelectron spectroscopy, Auger electron spectroscopy and ion scattering spectroscopy. In these cases, additional equipment is added to the spectrometer to give coincident, complementary information.

Raman spectroscopy is also frequently used in conjunction with other analytical techniques to provide information on molecular structure and chemical environment. However, coincident XPS and Raman spectroscopy has not been possible. Instead, samples must be transferred between instruments, which not only increases the amount of time required to acquire data but also adds a degree of uncertainty as to whether the analysis has been collected from the same region of the sample.

To overcome these problems, the Thermo Scientific™ Nexsa™ Spectrometer has been integrated with the Thermo Scientific iXR Raman Spectrometer (Figure 1) to provide a multi-modal analysis platform. The system aligns the XPS analysis position exactly with the Raman analysis position, ensuring that the data is collected from the same position.



Figure 1: iXR Raman Spectrometer coupled to a Nexsa XPS System.

## Experiment and results

XPS spectra across a wide range of binding energies, known as survey spectra, were acquired from natural crystals of aragonite and calcite (see Figure 2) to determine the elemental composition. As expected for naturally occurring crystals, surface contamination was observed in the form of silicon and sodium. High-resolution spectra of each photoemission peak were then acquired to allow determination of chemical states present at the surface; the C 1s photoemission peak shows the presence of aliphatic carbon contamination in addition to the carbonate peak. Repeated cycles of sputtering with  $\text{Ar}_{1000}^+$  clusters at 6kV generated by the Thermo Scientific™ MAGCIS™ (Monatomic and Gas Cluster Ion Source) removed aliphatic carbon contamination from the surface (Figure 3), and reacquisition of the survey spectra confirms the removal of silicon and sodium contamination, leaving stoichiometric  $\text{CaCO}_3$ .



Figure 2: Photographic image of aragonite (right) and calcite (left) crystals.

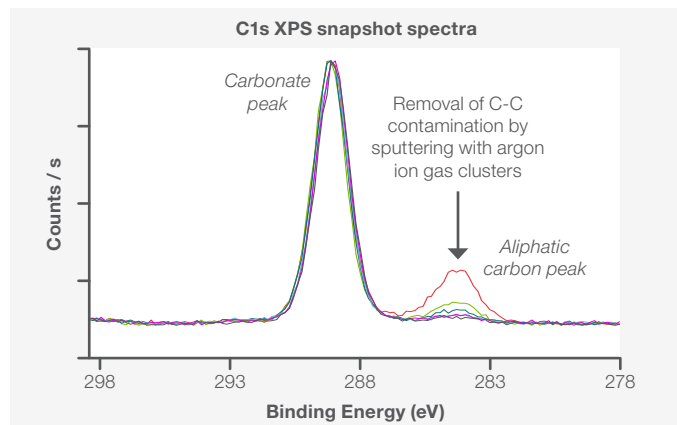


Figure 3: Removal of surface contamination on  $\text{CaCO}_3$  crystals with argon ion gas clusters.

As can be seen from the overlay of the survey and valence band spectra acquired from the cluster-cleaned aragonite and calcite crystals (Figure 4), it is not possible to distinguish between the two different polymorphs of  $\text{CaCO}_3$  using XPS. Nevertheless, the combination of XPS and cleaning with argon ion gas clusters does determine that the surface possesses the correct stoichiometry and is free of contamination, thereby allowing Raman spectra to be acquired with absolute confidence in the elemental and chemical composition of the region of interest.

Figure 5 shows the Raman spectra obtained from the two different crystalline forms of  $\text{CaCO}_3$ . The higher shifted peaks correspond to what are referred to as internal modes associated with the carbonate anion. While a slight shift can be observed in some of these peaks, they are similar in both polymorphs.

The peaks in the lower shifted region are due to lattice modes and depend on the way the carbonate anions are arranged in relationship to each other in the crystal structures. The lower symmetry in the aragonite structure leads to many more peaks in this region of the Raman spectrum. The exact assignments of these different vibrational modes have been addressed elsewhere.<sup>3</sup>

It is also possible to determine the ratio of polymorphs in mixed samples using Raman spectroscopy. By using polymorphically pure samples of titanium dioxide ( $\text{TiO}_2$ ) as references, it is possible to develop a method for determining the percentage of each polymorph present. A total of five powders were analyzed using coincident XPS-Raman: pure anatase- $\text{TiO}_2$ , pure rutile- $\text{TiO}_2$  and three mixed powders.

Survey spectra, high-resolution C 1s, O 1s, Ti 2p and valence band photoemission spectra were repeatedly acquired from all the TiO<sub>2</sub> powders while performing cleaning cycles with Ar<sub>2000</sub><sup>+</sup> gas clusters at 4 kV to remove surface carbon contamination. The use of argon ion gas clusters allows surface contamination to be removed without damaging the chemistry of the underlying substrate, as evidenced by the lack of a metallized titanium peak at 455 eV, this emerges when etching with monatomic argon due to the preferential sputtering of oxygen, forming sub-stoichiometric TiO<sub>2-x</sub>.

Slight differences can be observed in the valence band spectral shapes acquired from the pure anatase-TiO<sub>2</sub> and rutile-TiO<sub>2</sub> powders using XPS (Figure 6); however, the differences are subtle, making determination of the relative proportion of each polymorph difficult (Figure 7). However, the markedly different Raman shift peak positions observed in the pure anatase-TiO<sub>2</sub> and rutile-TiO<sub>2</sub> powder spectra allow you to easily distinguish between the anatase and rutile polymorphs (Figure 8). Furthermore, the spectral profiles can be used as references for non-linear least squares fitting of the Raman spectra acquired from the mixed powders (Figure 9), enabling quick and straightforward determination of the anatase:rutile ratio of the three mixed powder samples. It is also possible to use the 142 cm<sup>-1</sup> peak in the Raman spectrum of anatase as the basis of a quantitative method for determining the percentage of anatase in a mixture of anatase and rutile. The Thermo Scientific™ TQ Analyst™ Software provides a convenient way to develop these types of quantitative methods.

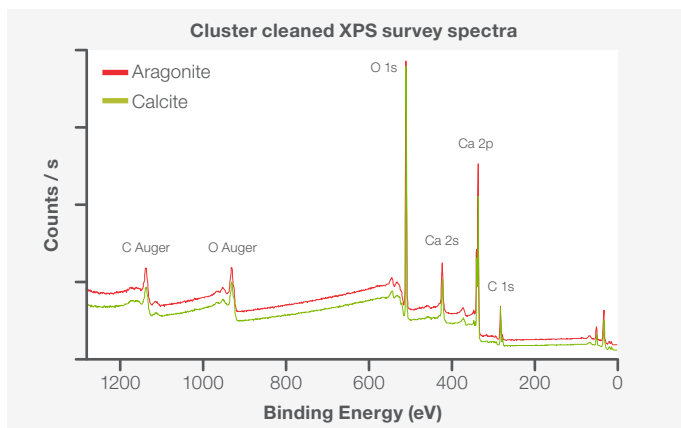


Figure 4: XPS spectral overlay (cluster-cleaned).

Emission peak	Aragonite as received	Calcite as received	Aragonite cluster cleaned	Calcite cluster cleaned
C 1s	46.1	54.2	19.5	23.2
Ca 2p	10.1	10.2	21.2	19.3
Na 1s	0.7	0.4	n/a	n/a
O 1s	40.5	34.6	59.3	57.5
Si 2p	2.6	0.6	n/a	n/a

Table 1: Elemental composition for aragonite and calcite samples measured by XPS before and after gas cluster ion cleaning.

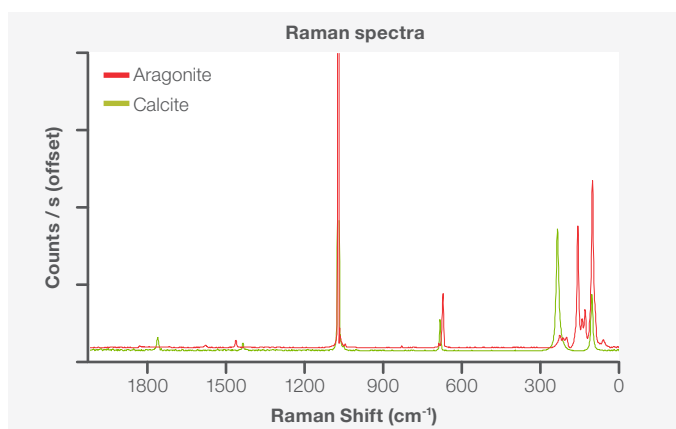


Figure 5: Overlay of the Raman spectra obtained from the CaCO<sub>3</sub> crystals.

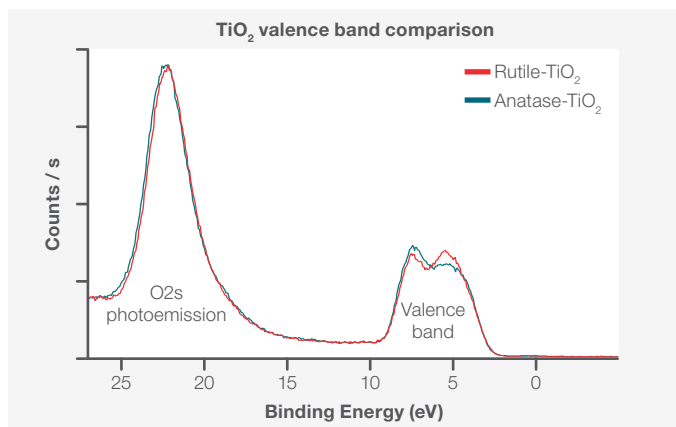


Figure 6: XPS valence band comparison of pure TiO<sub>2</sub> powders.

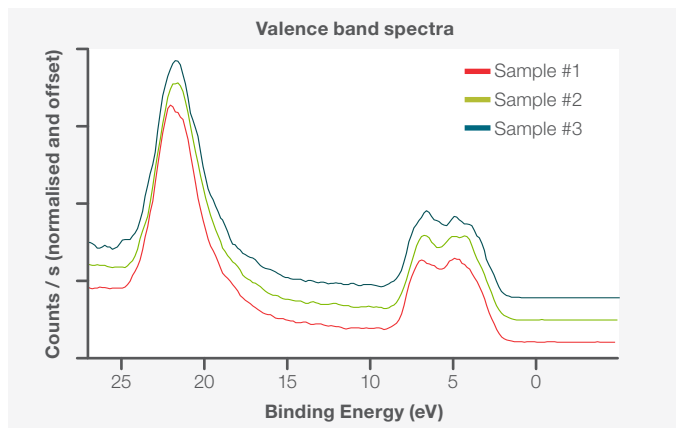


Figure 7: XPS valence band comparison of mixed TiO<sub>2</sub> powders.

Sample	Anatase:Rutile Ratio
1	9:91
2	49:51
3	71:29

Table 2: Measurement of the anatase:rutile ratio in the TiO<sub>2</sub> powders from the Raman data shown in figure 9.

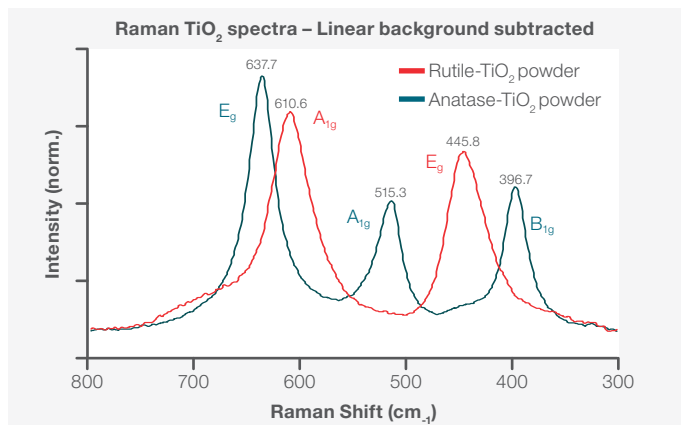


Figure 8: Comparison of the Raman spectra of the pure TiO<sub>2</sub> powders.

### Summary

In conclusion, XPS is used for quantitative determination of both elemental and chemical composition for any solid material compatible with ultra-high vacuum, whereas Raman spectroscopy is used for identification of referenced compounds by careful spectral matching employing searching algorithms and spectral databases. The combination of XPS and Raman on a single instrument, the Nexsa and iXR Spectrometers, allows more powerful analysis of a material than either technique in isolation, with the cleanliness, purity and stoichiometry of a sample determined using XPS, and identification and quantification of molecular structures to be determined using Raman spectroscopy. As both techniques are aligned to the same position within the vacuum system, all the time-consuming aspects of locating the same analysis point when transferring between instruments is removed, giving absolutely certainty that the information acquired has all come from the same region of the sample, which is particularly useful when studying non-uniform samples.

### Keywords

XPS, Raman spectroscopy, material characterisation, surface analysis, minerals, multitechnique, Nexsa, iXR

### References

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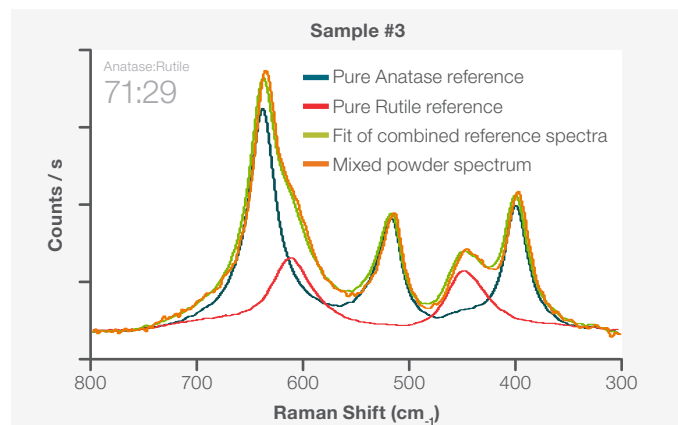
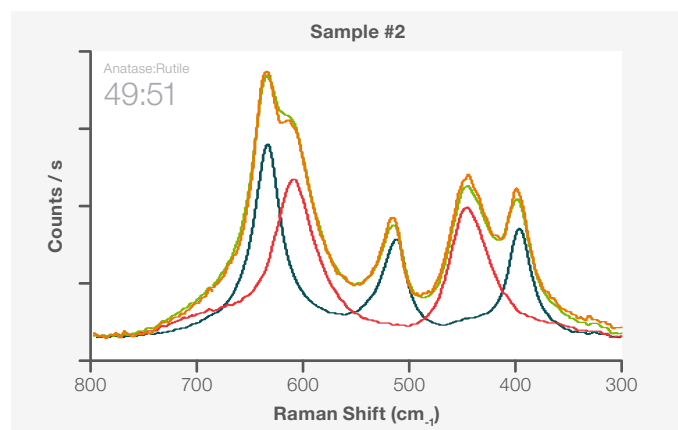
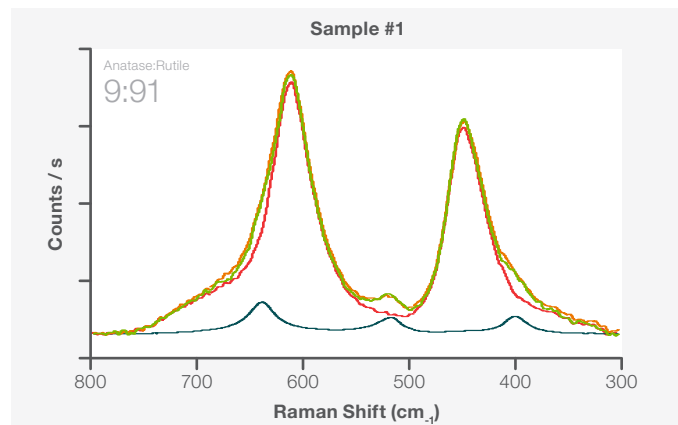


Figure 9: Comparison of the Raman spectra of the mixed TiO<sub>2</sub> powders.

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