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Application News

Infrared Raman Microscope AIRsight™
Energy-Dispersive X-Ray Fluorescence Spectrometer EDX-8100

Rust Analysis —Using Infrared Raman Microscopes and Energy-Dispersive X-Ray Fluorescence Spectrometers—

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User Benefits

- Raman analysis can determine the functional groups of metallic oxides for qualitative analysis (identification) of types of rust.
- Fluorescent X-ray analysis detects each element as signal peaks at different energy levels, offering a versatile tool for the evaluation of metal samples.

■ Introduction

Rust from metal corrosion consists of metal oxides and hydroxides that are formed by reactions between the metal, substances adhered to the metal, and air. Inorganic compounds such as metal oxides and hydroxides that contain high mass atoms exhibit molecular vibrations in a lower frequency region than organic compounds. The analysis of these low frequency regions by infrared spectroscopy is complex and requires beam splitters designed for far-infrared analysis and dry air or nitrogen purging. However, Raman spectroscopy can analyze these low frequency regions using standard equipment, making it effective for the qualitative analysis of metal oxides and other inorganic compounds. Inorganic substances can also be characterized by energy-dispersive X-ray fluorescence spectrometer (EDX). EDX works by irradiating a sample with X-rays and detecting the fluorescent X-rays produced. Because the energy of the fluorescent X-rays is unique to each element, we use them to perform qualitative analysis, including single element substances such as metals. This approach allows EDX to be used for the qualitative analysis of single-element substances, such as metals. Raman spectroscopy irradiates the sample with a laser, measures the resulting Raman scattered light that is unique to each sample molecule, and performs qualitative analysis that is based on the difference in wavelength (Raman shift) between the incident laser light and the Raman scattered light. Because Raman spectroscopy measures bonds between inorganic elements and oxygen, nitrogen, and sulfur (functional group analysis), single-element metals do not produce peaks in Raman spectra.

This Application News describes an example analysis of standard metal oxides and a real-world rust sample that was performed using an AIRsight infrared Raman microscope (Fig. 1, left). An example analysis of the real-world rust sample was also performed using an EDX-8100 (Fig. 1, right).

Fig. 1 IRTracer™-100 with AIRsight™ (left) and EDX-8100 (right)

■ Example Raman Analysis of Iron Oxides and Iron Oxyhydroxides

Powdered samples of the following four main components of rust were analyzed: Fe_2O_3, Fe_3O_4, α-FeO(OH), and γ-FeO(OH). The analyzed samples are shown in Fig. 2. Raman spectroscopy was performed using the conditions shown in Table 1.

Table 2 Samples from Left to Right: Fe_2O_3, Fe_3O_4, α-FeO(OH), and γ-FeO(OH)

Table 1 Measurement Conditions

Instruments:	IRTracer™-100, AIRsight
Number of Scan:	10 (Fe_2O_3), 50 (other samples)
Exposure Time:	5 sec
Objective Lens:	100 times (standard metal oxides), 50 times (rust)
Excitation Wavelength:	785 nm
Detector:	CCD

Fig. 3 shows the Raman spectrum obtained from Fe_2O_3. There are multiple sharp peaks in the wavenumber region between 600 and 200 cm^{-1} and another peak near 1300 cm^{-1}.

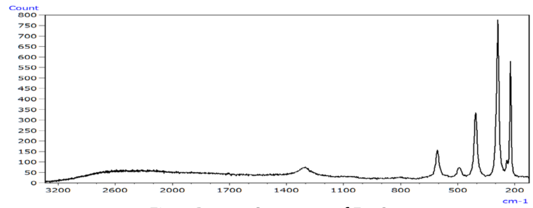

Fig. 3 Raman Spectrum of Fe_2O_3

Fig. 4 shows the Raman spectrum obtained from Fe_3O_4. The signal intensity is lower than Fe_2O_3, and there is a single peak near 660 cm^{-1}.

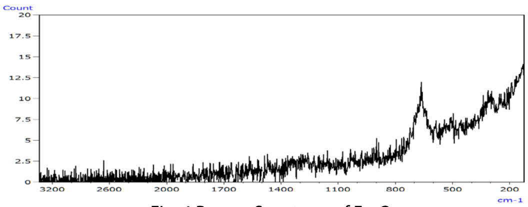

Fig. 4 Raman Spectrum of Fe_3O_4

Fig. 5 shows the Raman spectrum obtained from α-FeO(OH). There are multiple sharp peaks in the wavenumber region between 700 and 150 cm^{-1}.

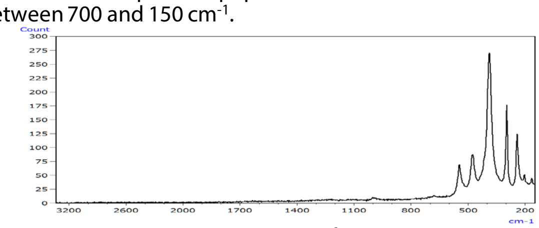

Fig. 5 Raman Spectrum of α-FeO(OH)

Fig. 6 shows the Raman spectrum obtained from γ-FeO(OH). The Raman spectrum shows that the peaks were detected in a similar wavenumber region to α-FeO(OH), but each peak has a different signal intensity.

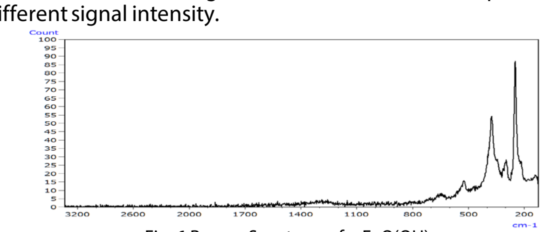

Fig. 6 Raman Spectrum of γ-FeO(OH)

Lastly, Fig. 7 shows a superimposed view of the four Raman spectra after autoscaling was applied and after enlarging the wavenumber region between 1100 and 150 cm^{-1}. The positions of the peaks detected by Raman spectroscopy provide information about the functional groups in the sample and allow an accurate qualitative analysis of the sample by comparing measured peaks against a spectral database.

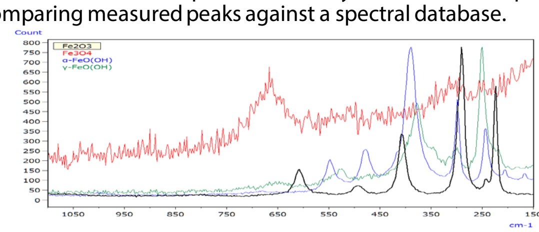

Fig. 7 Superimposed View of Figs. 3 to 6 after Applying Autoscaling

■ Laser Light-Induced Reduction Reactions during Analysis of Inorganic Substance

The intensity of the spectrum measured by Raman analysis is dependent on the intensity of the irradiated laser light, with stronger laser light typically producing data with less noise. However, if the laser light is too strong, it can burn organic samples, and it can cause unintended reduction reactions to occur in inorganic samples. Fig. 8 shows the Raman spectrum of Fe_3O_4 measured with a high-intensity laser superimposed with the Raman spectrum of Fe_2O_3 measured with a normal laser. Examining the spectra suggests the high-intensity laser caused a reduction reaction in the Fe_3O_4 sample that converted the Fe_3O_4 into Fe_2O_3. Fig. 9 shows photographs of the Fe_3O_4 sample before and after the Raman analysis. The photographs show that the Fe_3O_4 sample was black before analysis and turned a red color similar to Fe_2O_3 after analysis (Fig. 2). Both the spectral data and the visual inspection of the sample suggest a reduction reaction occurred that was induced by the laser. This experiment shows how the intensity of the laser light must be carefully considered when performing Raman analysis.

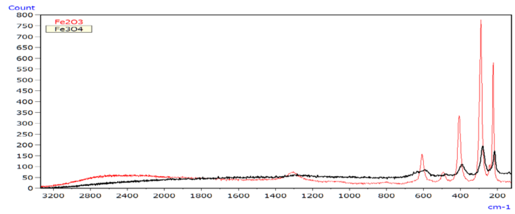

Fig. 8 Raman Spectra of Fe_3O_4 (Black Line) Measured with High-Intensity Laser Light and Fe_2O_3 (Red Line) Measured with Normal Laser

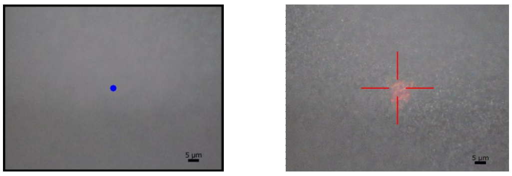

Fig. 9 Photograph of Fe_3O_4 Sample before (Left) and after Analysis (Right)

■ Raman Analysis of Rust Patch (Discolored Area) on Tool

A patch of rust (the discolored area) on a spanner was analyzed. The analyzed samples are shown in Fig. 10. In Fig. 11, the Raman spectrum of the patch of rust obtained with the analysis conditions shown in Table 1 are superimposed with the Raman spectra of α-FeO(OH) (Fig. 5) and Fe_2O_3 (Fig. 3). Fig. 12 shows an enlarged view of Fig. 11 for the wavenumber range between 1050 and 150 cm^{-1}. Comparing the spectra suggests that the rust on the spanner was composed of α-FeO(OH) and Fe_2O_3. Also, Raman analysis (the data is not shown here) of a patch of the spanner with no rust produced a Raman spectrum with no peaks. As already mentioned, this is because Raman spectroscopy does not produce peaks from single-element metals.

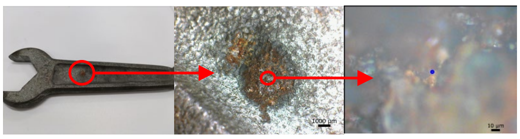

Fig. 10 Tool with Patch of Rust

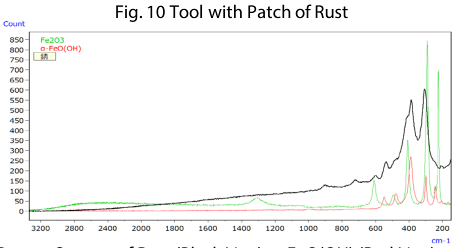

Fig. 11 Raman Spectra of Rust (Black Line), α-FeO(OH) (Red Line), and Fe_2O_3 (Green Line)

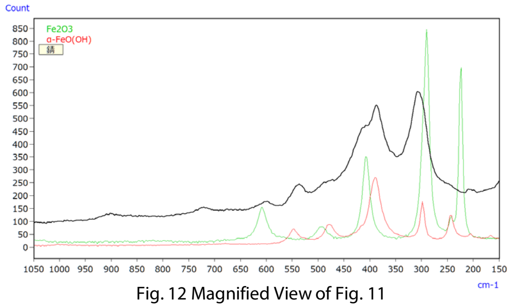

Fig. 12 Magnified View of Fig. 11

■ EDX Analysis of Rust Patch (Discolored Area) on Tool

A patch of rust (the discolored area) and a normal part of a tool (Fig. 10) were analyzed by EDX spectroscopy using the conditions shown in Table 2. The profiles obtained from the rust patch and a normal part are shown superimposed in Fig. 13. The greater Fe signal intensity in the rust patch and the greater Zn signal intensity in the normal part indicate the tool is made of an Fe-based metal and is plated with Zn. The results also show larger amounts of Cl, Ca, and other elements in the rust patch. As this analysis shows, EDX analysis detects each element as an individual peak. This enables qualitative analysis of the elemental compositions of samples. EDX spectroscopy can also analyze samples regardless of their composition, whether they are single-element materials or oxides.

Table 2 Analytical Conditions

Instrument:	EDX-8100
X-Ray Tube Target:	Rh
Voltage/Current:	15 kV (C-Sc, S-Ca), 50 kV (Ti-U) /Auto
Atmosphere:	Vacuum
Collimator:	1 mmΦ
Primary filters:	None (C-Sc, Ti-U), #2 (S-Ca)
Integration Time:	60 sec. (Ti-U, S-Ca), 120 sec. (S-Ca)

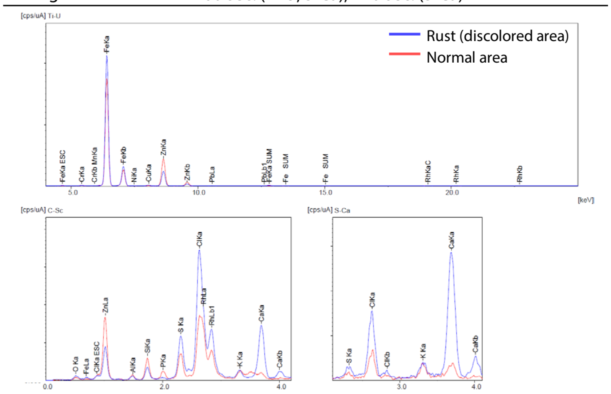

Fig. 13 Superimposed EDX Profiles of Rust Patch and Normal Part of Tool

■ Conclusion

An AIRsight infrared Raman microscope was used to analyze iron oxides and iron oxyhydroxides, which are the main components of rust. The analysis showed that Raman spectroscopy can produce spectral profiles from inorganic compounds that cannot ordinarily be readily analyzed by infrared spectroscopy. It also showed that high-intensity laser light can cause reduction reactions in inorganic compounds that change the measured Raman spectrum.

The composition of a real-world rust patch was also determined by Raman spectroscopy by comparing the Raman spectrum of the rust patch with the Raman spectra of candidate compounds. (When candidate compounds are not known, comparing against a spectral database is effective.) The EDX analysis also provided information on metals that were not detected by either infrared or Raman spectroscopy, and it detected elements that were present at very low levels.

<References>

1) Case Examples of Raman Spectral Data Analysis, Technical Information Institute Co., Ltd. (2022)

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