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APPLICATION NOTE

# Identification of unknown powders

## INTRODUCTION

Unknown contaminants such as powders, particles and residues can cause issues in various manufacturing processes. In order to determine the composition of unknown materials, it is often useful to employ several analytical techniques. This paper describes identification of two unknown powders using Raman spectroscopy, combined with two X-ray techniques: X-ray fluorescence spectroscopy (XRF), and X-ray diffraction (XRD). Whereas Raman uses vibrational spectroscopy to determine the bonding environments in organic and inorganic compounds, XRF provides elemental composition. XRD can be utilized to determine phase identification and quantification of crystalline materials based on their unique crystal structure.

## ANALYSIS

The two powders of interest in this had a red and black appearance (see Figure 1) and are referred to as Red and Black samples.

Raman spectroscopy is an excellent choice for analyzing unknown powders because it can determine the composition of many inorganic species and is particularly sensitive to iron-based compounds. It is also very applicable to samples that are very black in appearance and may contain large amounts of non-organic carbon. Furthermore, Raman's small spot size makes it possible to detect rust from particles on the order of a few microns in size.

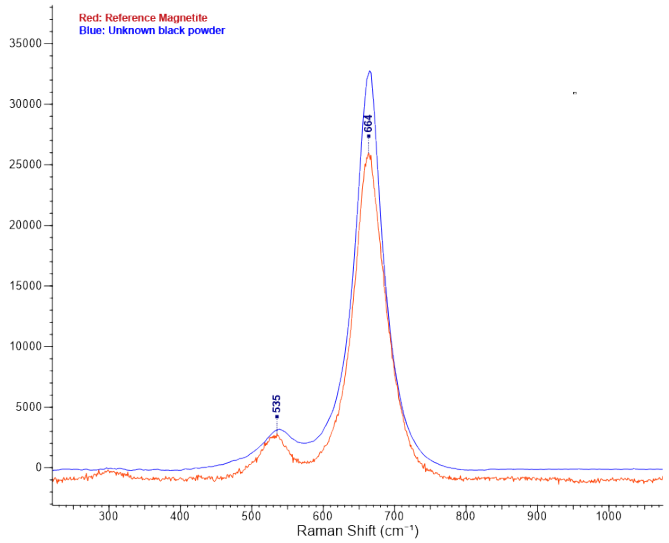
The Raman spectrum of the black powder is shown in Spectrum 1. The spectrum is consistent with Magnetite ($Fe_3O_4$) in the spinel structure with a signature peak at 660 $cm^{-1}$. The red powder Raman results are shown in Spectrum 2. In this case, Hematite ($Fe_2O_3$) appears to be the main component, although a weak peak at 654 $cm^{1}$ suggests that some $Fe_3O_4$ may be present.

To further elucidate the composition, XRF was performed on the two powders. Based on the Raman results, the black powder was likely a magnetite, which means it should have ~ 70 wt% Fe and 30 wt% O. As shown in Table 1, XRF detected 63.5 % Fe and 35% oxygen. The reason for this discrepancy is likely due to the trace contaminants detected in the black powder: Si, Mg, Al, Ti and V were all detected above 0.1 wt%. The combined amount of impurities in the black powder was found to be ~ 1.57 wt%. It should also be noted that whereas Mg, Al and Ti have one oxide form, V and Mn have a range of potential oxide forms with different O content. Thus, the latter are expected to significantly increase the oxygen concentration measured, if they were present.

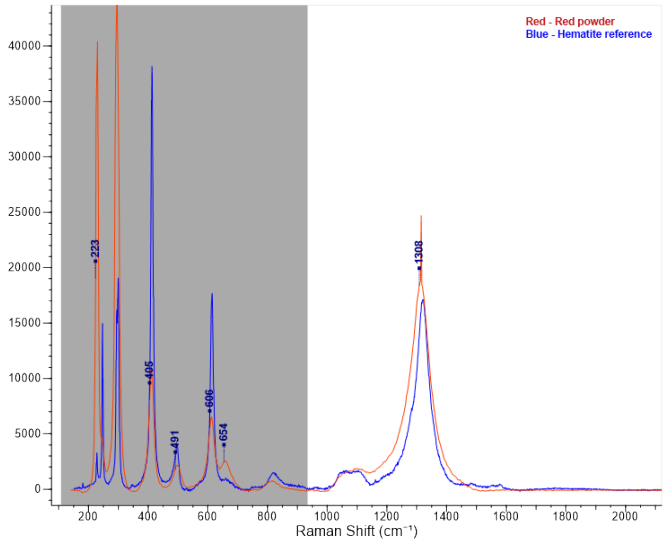
Similarly, the red powder was found to be primarily hematite with an expected Fe and O content of 72.4 and 27.6 wt%, respectively. The XRF results for the red powder show an even larger increase

**Figure 1. Optical images of two unknown powders**

# Identification of unknown powders




**Raman Spectrum 1. Unknown black powder**




**Raman Spectrum 2. Unknown red powder**

in oxygen content compared to the expected value. However, this sample only contained 0.68% impurities so the elevated oxygen levels cannot be explained by impurities alone. As suggested by the Raman results, the red powder may not be purely composed of $Fe_3O_4$ and may contain some $Fe_2O_3$, which would increase the oxygen content.

**Table 1. XRF results for select major elements**

| | Black Powder | $Fe_2O_3$ | Red Powder | $Fe_3O_4$ |
|---|---|---|---|---|
| Fe | 63.5 | 69.9 | 62.6 | 72.4 |
| O | 35.0 | 30.1 | 36.7 | 27.6 |
| Si | 0.44 | 0 | 0.24 | |
| Mg | 0.27 | | 0.011 | |
| Al | 0.21 | | 0.030 | |
| Ti | 0.16 | | 0.004 | |
| V | 0.12 | | - | |
| Ca | 0.093 | | | |
| Na | 0.052 | | 0.044 | |
| Mn | 0.048 | | 0.15 | |
| Other elements | 0.16 | | 0.14 | |

To determine how much of each iron oxide species is present in the two powders, XRD analysis was performed and the results are shown in Table 2. The reason for discrepancies between the expected and observed Fe:O ratios can be explained by the presence of hematite in the black powder (~7.5 wt%) and a larger amount of magnetite in the red powder (~14 wt%). The detection limit for XRD is roughly ~1 wt%, any contaminants that may be present are likely below this limit.

**Table 2. Phase identification and quantitative analysis results**

| Sample ID | Phases Identified | Concentration (± 5 wt%) |
|---|---|---|
| Black Powder | $Fe_3O_4$ – Magnetite<br>Cubic, S.G.: Fd-3m (227)<br>PDF# 04-009-8424 | 92.5 |
| | $Fe_2O_3$ – Hematite<br>Hexagonal, S.G.: R-3c (167)<br>PDF# 01-087-1164 | 7.5 |
| Red Powder | $Fe_2O_3$ – Hematite<br>Hexagonal, S.G.: R-3c (167)<br>PDF# 01-087-1164 | 86.2 |
| | $Fe_3O_4$ – Magnetite<br>Cubic, S.G.: Fd-3m (227)<br>PDF# 04-009-8424 | 13.8 |

Semi-quantitative analysis was performed using WPF (whole pattern fitting), which is a subset of Rietveld Refinement that accounts for all intensity above background. This technique requires that either the structure factors and atomic locations or the reference intensity ratio (a way of comparing the diffracting power of different phases) are known for all phases identified. During this process, the structure factor (related to concentration), lattice parameters (which relate to peak position), peak width and peak shape are refined for each phase to minimize the R value, which is an an estimate of the agreement between the model and

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the experimental data over the entire pattern.

The WPF results are shown in Figure 3 and Figure 5 for the Black and Red samples respectively. The concentrations of the phases are listed in Table 1. The R values are ~2% indicating an excellent model fit.

## SUMMARY

Thus, while Raman correctly identified the major composition of the two powders, XRF and XRD provided additional details by identifying a mixture of phases in each powder as well as a number of contaminants. This paper demonstrates the synergy of applying multiple analytical techniques to fully understand the chemical makeup of unknown materials.

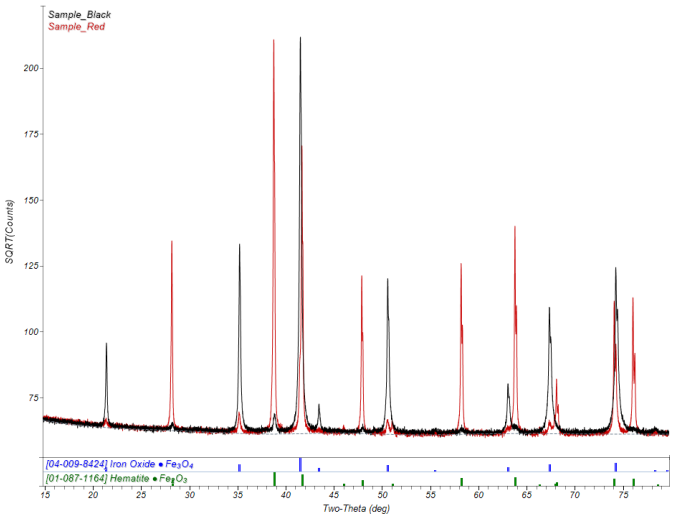



**Figure 1: Comparison of diffraction patterns from both powders**

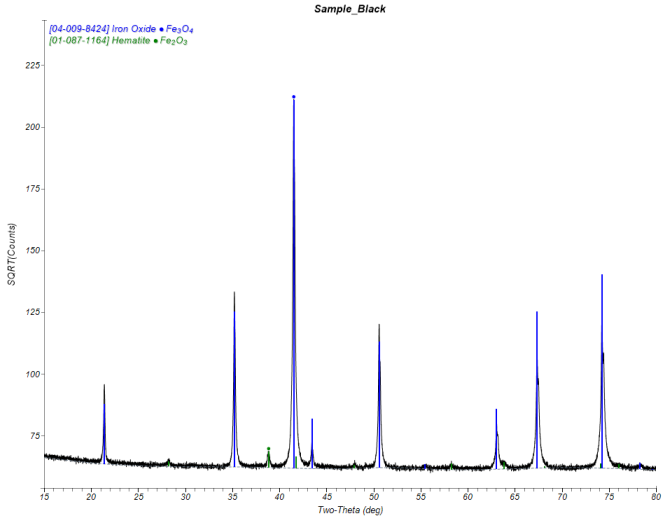



**Figure 2: Sample identification for the black powder**

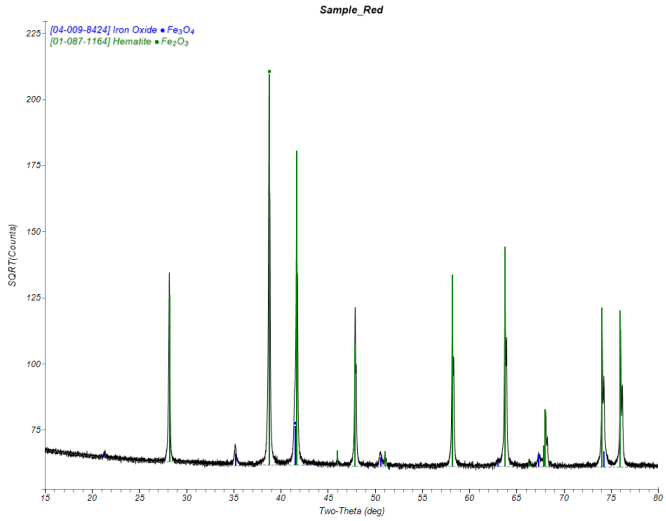



**Figure 3: Sample identification for the red powder**

# Identification of unknown powders

Sample_Black | WPF Report

**Scan ID:** GU215_Black.xrdml • GU215_Black

**Scan Parameters:** 5.004°/100.004°/0.00836°/40.005(s), I(p)=44907/3584, Co(40kV,40mA), Wednesday, November 25, 2020, 5:01

**Control File:** U:\IJM\Yanike App Note_C0LGU215\GU215_Black_WPF.wrk.xml

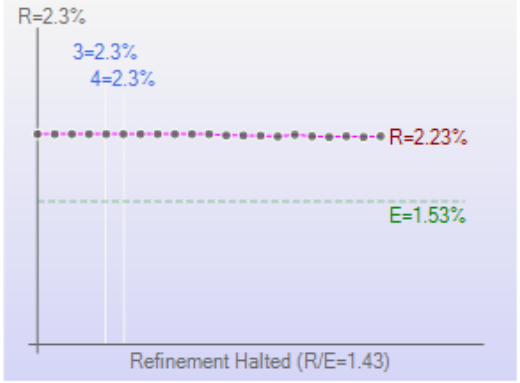
| | | |
|---|---|---|
| ☐ Zero Offset = 0.0 | ☑ Displacement = 0.0746 (0.0004) | ☐ Beam Spill-Off below 0.0° |
| ☑ Kα2 Peaks Present | ☐ Kα2/Kα1 Ratio = 0.5 | ☐ X-Ray Polarization = 1.0 |

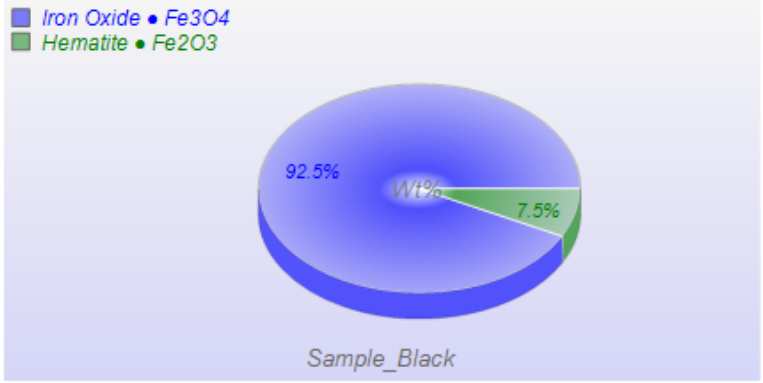
**Geometry:** Diffractometer Lp **Fitted-Range:** 15.0° - 100.0° **BG-Model:** Fixed-Curve (13) λ: 1.78899Å (Co)

**PSF:** pseudo-Voigt **Broadening:** Individual FWHM Curve **Instrument:** Alpha LaB6_Co radiation 013019

| Phase ID (2) | Chemical Formula | PDF-# | Space Group | Wt% | RIR |
|---|---|---|---|---|---|
| Iron Oxide | $Fe_3O_4$ | 04-009-8424 | cFd-3m² (227) | 92.5 | 3.60 |
| Hematite | $Fe_2O_3$ | 01-087-1164 | hR-3c (167) | 7.5 | 3.26 |

Refinement Halted (R/E=1.43), ♣ Round=4, Iter=6, P=46, R=2.19% (E=1.53%, EPS=0.5)



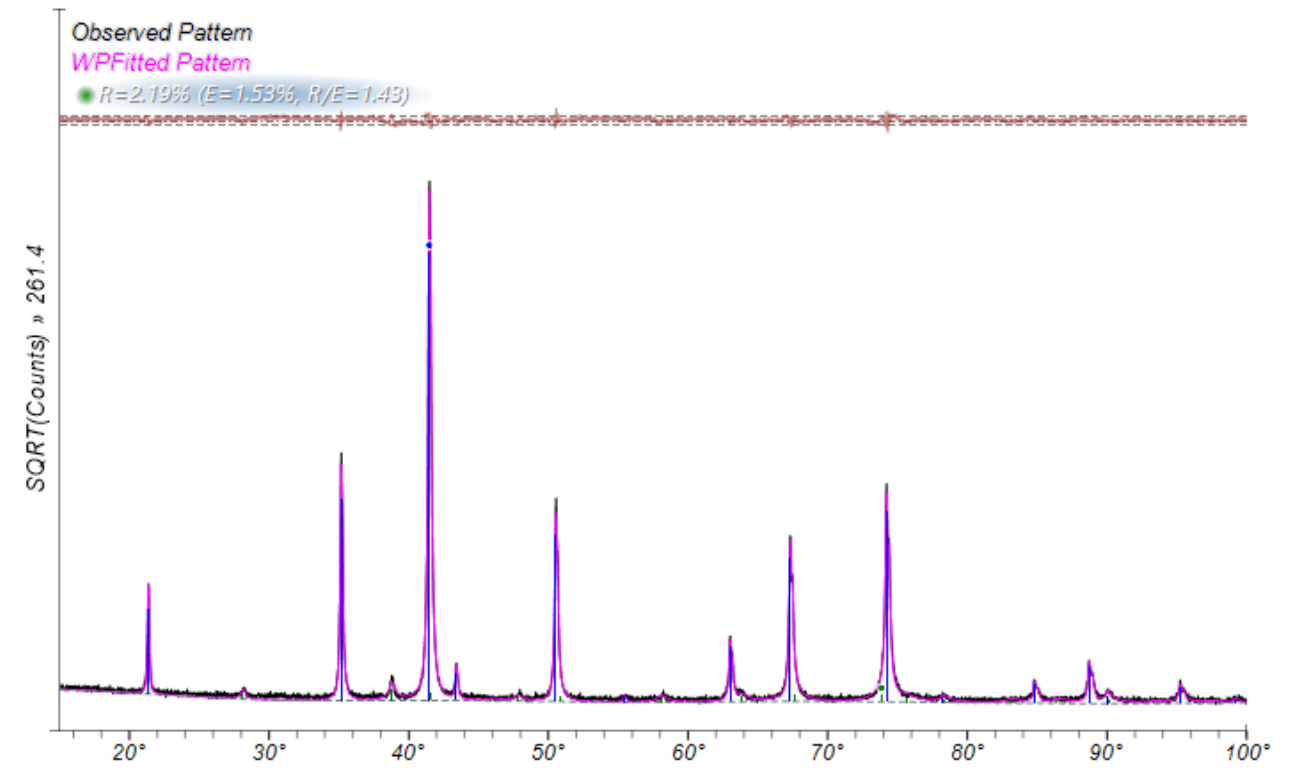




**Figure 4: Whole pattern fitting results for black powder**

# Identification of unknown powders

Sample_Red | WPF Report

**Scan ID:** GU215_Red.xrdml • GU215_Red

**Scan Parameters:** 3.505°/100.0°/0.00836°/40.005(s), I(p)=44506/3588, Co(40kV,40mA), Wednesday, November 25, 2020, 3:44 PM

**Control File:** U:\IJM\Yanike App Note_C0LGU215\GU215_Red_WPF.wrk.xml

☐ Zero Offset = 0.0 ☑ Displacement = 0.0194 (0.0004) ☐ Beam Spill-Off below 0.0°

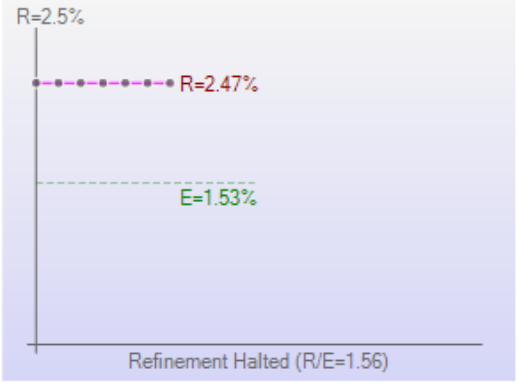
☑ Kα2 Peaks Present ☐ Kα2/Kα1 Ratio = 0.5 ☐ X-Ray Polarization = 1.0

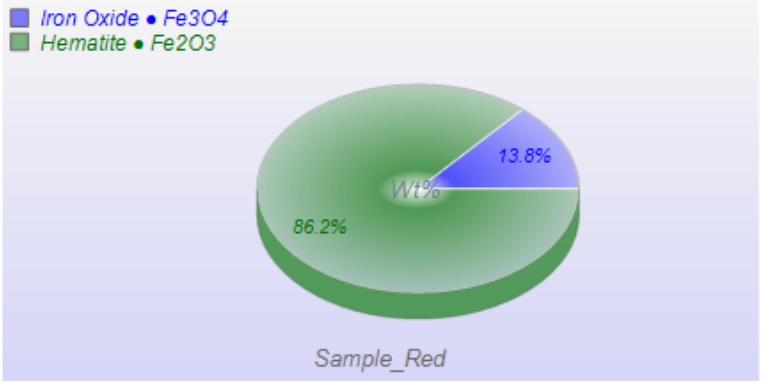
**Geometry:** Diffractometer Lp **Fitted-Range:** 15.0° - 100.0° **BG-Model:** Fixed-Curve (16) λ: 1.78899Å (Co)

**PSF:** pseudo-Voigt **Broadening:** Individual FWHM Curve **Instrument:** Alpha LaB6_Co radiation 013019

| Phase ID (2) | Chemical Formula | PDF-# | Space Group | Wt% | RIR |
|---|---|---|---|---|---|
| Iron Oxide (PO) | $Fe_3O_4$ | 04-009-8424 | cFd-3m² (227) | 13.8 | 3.60 |
| Hematite | $Fe_2O_3$ | 01-087-1164 | hR-3c (167) | 86.2 | 3.26 |

Refinement Halted (R/E=1.56), ♣ Round=3, Iter=6, P=48, R=2.39% (E=1.53%, EPS=0.5)



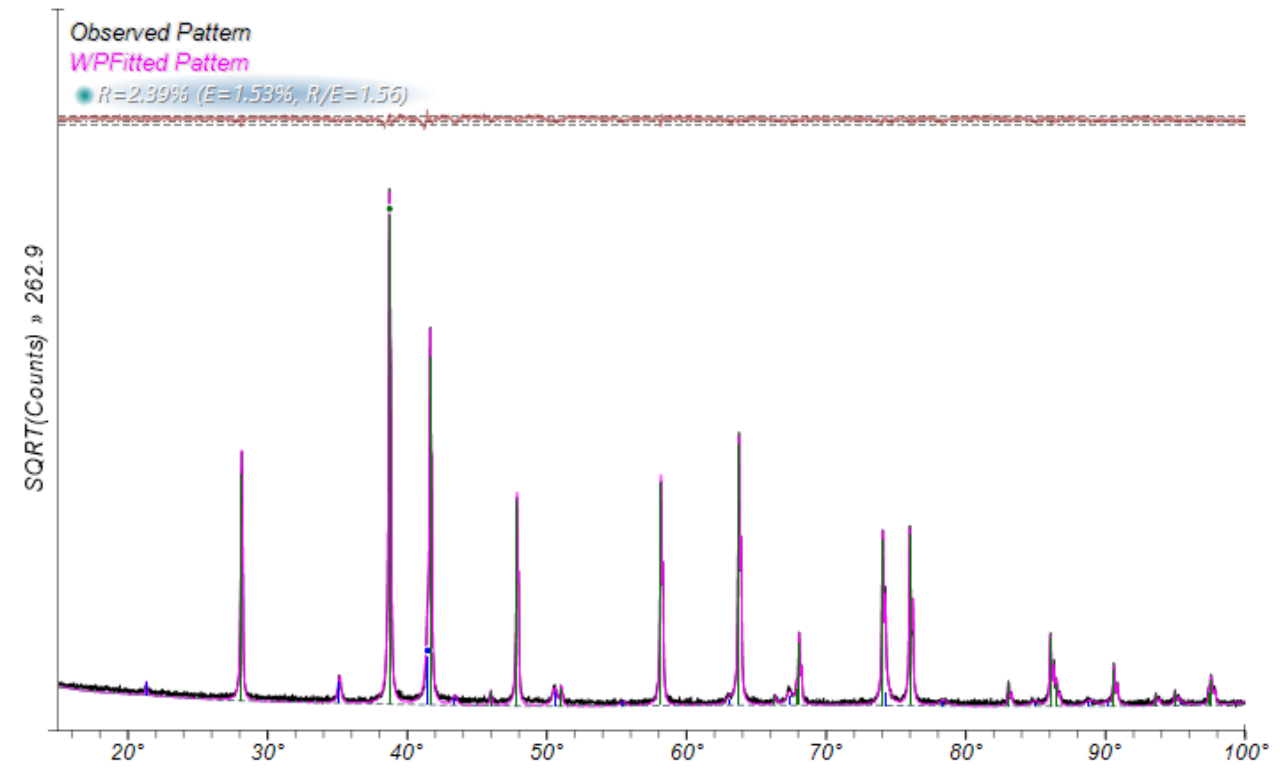




**Figure 5: Whole pattern fitting results for red powder**