Quantitative Analysis

Reference Intensity Ratio (RIR)

Reference Intensity Ratio (RIR)

What is it?

The Reference Intensity Ratio (RIR) is a method used for Quantitative Analysis by Powder Diffraction.

The RIR method is based upon scaling all diffraction data to the diffraction of standard reference materials.

Reference Intensity Ratio (RIR)

Why?

The intensity of a diffraction peak profile is a convolution of many factors, only one of which is the concentration of the analyte (species being measured).

By using the RIR method, ratios scaled to a common reference, are used in the experiment. The assumption is that all the factors, *except concentration,* of the analyte are ratioed and reduced to a constant.

By using ratios and measuring peak areas, the RIR method can be used to determine concentrations.

Reference Intensity Ratio (RIR)

How ?

The RIR method scales all diffraction data to a standard. By convention, corundum is used as the international reference and the scale factor is defined by:

Intensity Analyte / Intensity Corundum = I / Ic

I/Ic can be experimentally derived by adding a known weight fraction of corundum to a pure specimen of the analyte of interest.

I/Ic can also be calculated if the atomic parameters of analyte are known because the atomic parameters of corundum have been determined.

In PDF-4+, I/Ic has been experimentally determined for close to 10,000 materials and has been calculated for >170,000 materials.

Overview of the Method

To understand how to use I/Ic values for quantitative analysis with the PDF-4+ database, a short description of the method is provided in the following slides.

RIR Method

Reference Intensity Ratio (RIR)

What?

RIR Method

- RIR, as used in the Powder Diffraction File, is I/Ic (reference to corundum).
- I/Ic can be determined, experimentally or calculated, from a crystal structure, both methods are used in the PDF-4+ database.
- Experimentally, I/Ic can be determined by taking the ratio of the strongest line of the pattern to the intensity of the strongest line of corundum in a 50/50 weight mixture.
- If we know the crystal structure, we can calculate I/Ic as shown in the following slide.

Reference Intensity Ratio (RIR)

RIR Method

All calculated patterns have I/Ic.

$$I/Ic = \mu\ \gamma\ \rho c\ /\mu c\ \gamma c\ \rho$$

μ = Linear attenuation coefficient
γ = Absolute scale factor
ρ = Density
(Subscript “c” corresponds to corundum)

Single crystal determinations have all the data necessary to calculate the variables in the above equation from atomic parameters and the unit cell parameters with the use of atomic scattering factors and published constants. These are used by the ICDD to calculate I/Ic for these entries.

Reference Intensity Ratio (RIR)

RIR Method

Calculated I/Ic values often significantly differ from experimental I/Ic values.

Natural products, minerals, and biomaterials often contain trace impurities, anion/cation substitution in the lattice, or naturally produced vacancies, and/or defects in the crystalline state. These physical phenomena are well known to influence peak intensities and peak profiles that will change the I/c value. This value can be significantly different from one calculated from a perfect crystalline pure material.

If you are using I/Ic to quantitate a synthetic mixture, you may want to use a calculated value. If you are using I/Ic to quantitate a natural product or mineral sample, you may prefer experimental values.

Quantitative Analysis

RIR Method

Main equation for quantitative analysis

K_{ia} contains structure factor, multiplicity, Lorentz-polarization factor, temperature factor + scale factor for reflection i of phase a

I_{ia} = intensity of reflection i of phase a

$$I_{ia} = \frac{K_{ia} X_a}{\rho_a \mu}$$

X_a = wt fraction of phase a **(want this!!)**

ρ_a is density of phase a

μ = Linear attenuation coefficient

Quantitative Analysis

RIR Method

Measure this!!

$$I_{ia} = \frac{K_{ia} X_a}{\rho_a \mu}$$

X_a = wt fraction of phase a **(want this!!)**

Quantitative Analysis

Reference Intensity Ratios

For analyte $I_a = \dfrac{K_a X_a}{\rho_a \mu}$

For corundum $I_c = \dfrac{K_c X_c}{\rho_c \mu}$

$$\frac{I_a = \dfrac{K_a X_a}{\rho_a \mu}}{I_c = \dfrac{K_c X_c}{\rho_c \mu}} \rightarrow \frac{I_a}{I_c} = \frac{K_a X_a \rho_c}{K_c X_c \rho_a} = K \frac{X_a}{X_c}$$

For 50-50 mixture of analyte with corundum

$$\frac{I_a}{I_c} = K \quad \text{.....denoted } (I/I_c)_a$$

RIR Method

Quantitative Analysis

Reference Intensity Ratios

RIR Method

$$\frac{I_a}{I_c} = \frac{K_a X_a \rho_c}{K_c X_c \rho_a} = K \frac{X_a}{X_c}$$

For any a + b mixture

$$\frac{(I_a/I_c)}{(I_b/I_c)} = \frac{\dfrac{K_a \rho_c}{K_c \rho_a}}{\dfrac{K_b \rho_c}{K_c \rho_b}}$$

$$\frac{I_a}{I_b} = \frac{\dfrac{K_a}{\rho_a}}{\dfrac{K_b}{\rho_b}} \frac{X_a}{X_b} = \frac{(I/I_c)_a}{(I/I_c)_b} \frac{X_a}{X_b}$$

Reference Intensity Ratio (RIR)

Practical Considerations

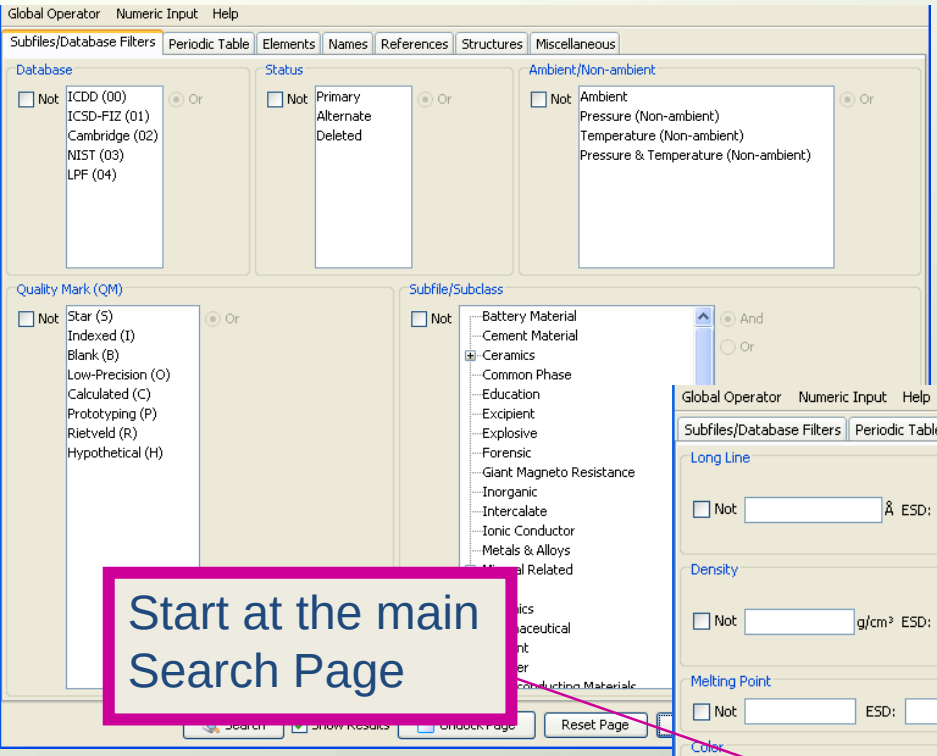
RIR Method

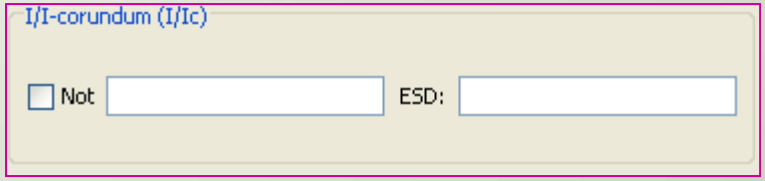
The RIR method uses simultaneous equations to solve analyte concentrations in a multicomponent mixture.

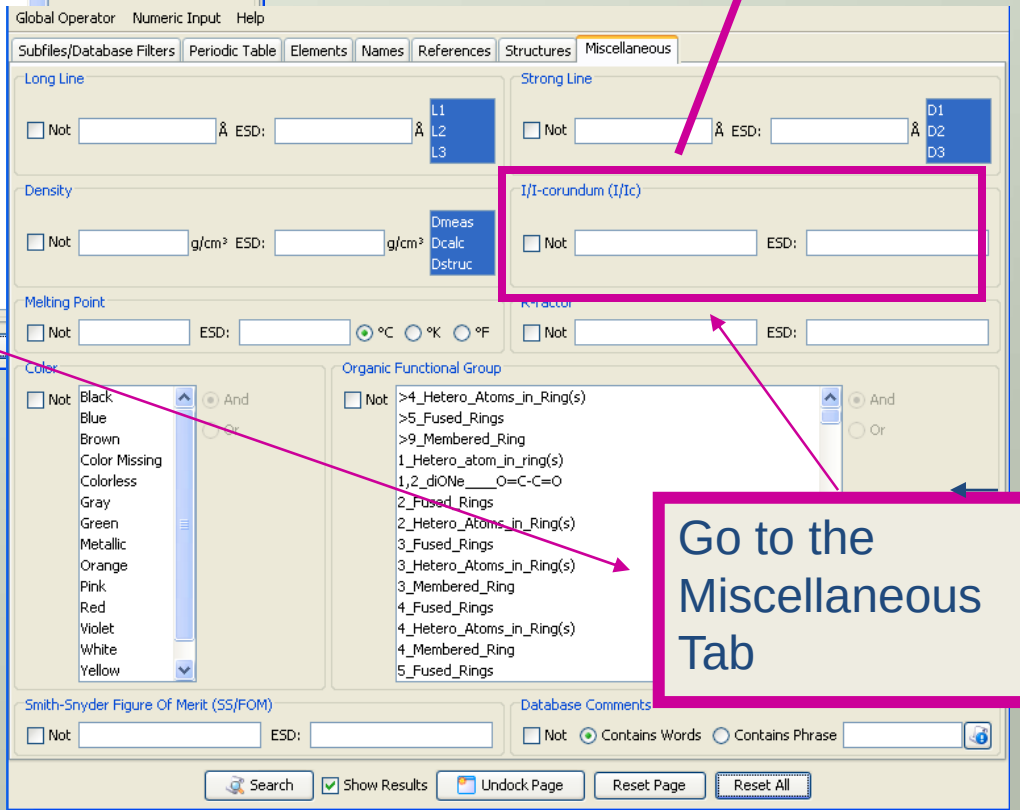
Many vendor programs interface to PDF-4+ to automatically extract I/Ic and peak areas from the experimental data for automated quantitative analysis.

Automated programs assume that the combination of all phases identified account for all observed scattering and 100% of the specimen. Significant errors can occur, if there are non-crystalline phases or unidentified materials present in the specimen.

Finding I/Ic Search



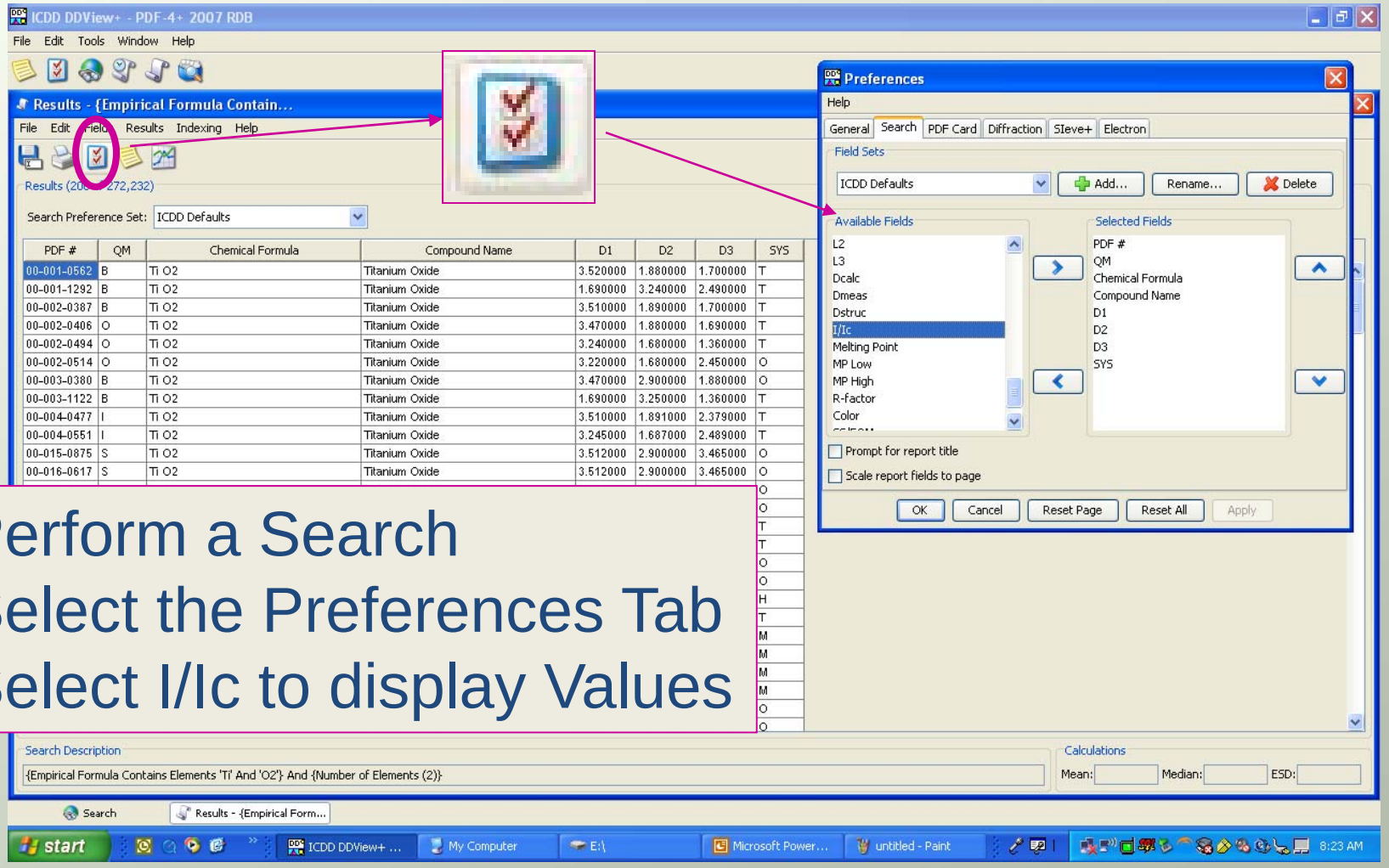




Start at the main Search Page

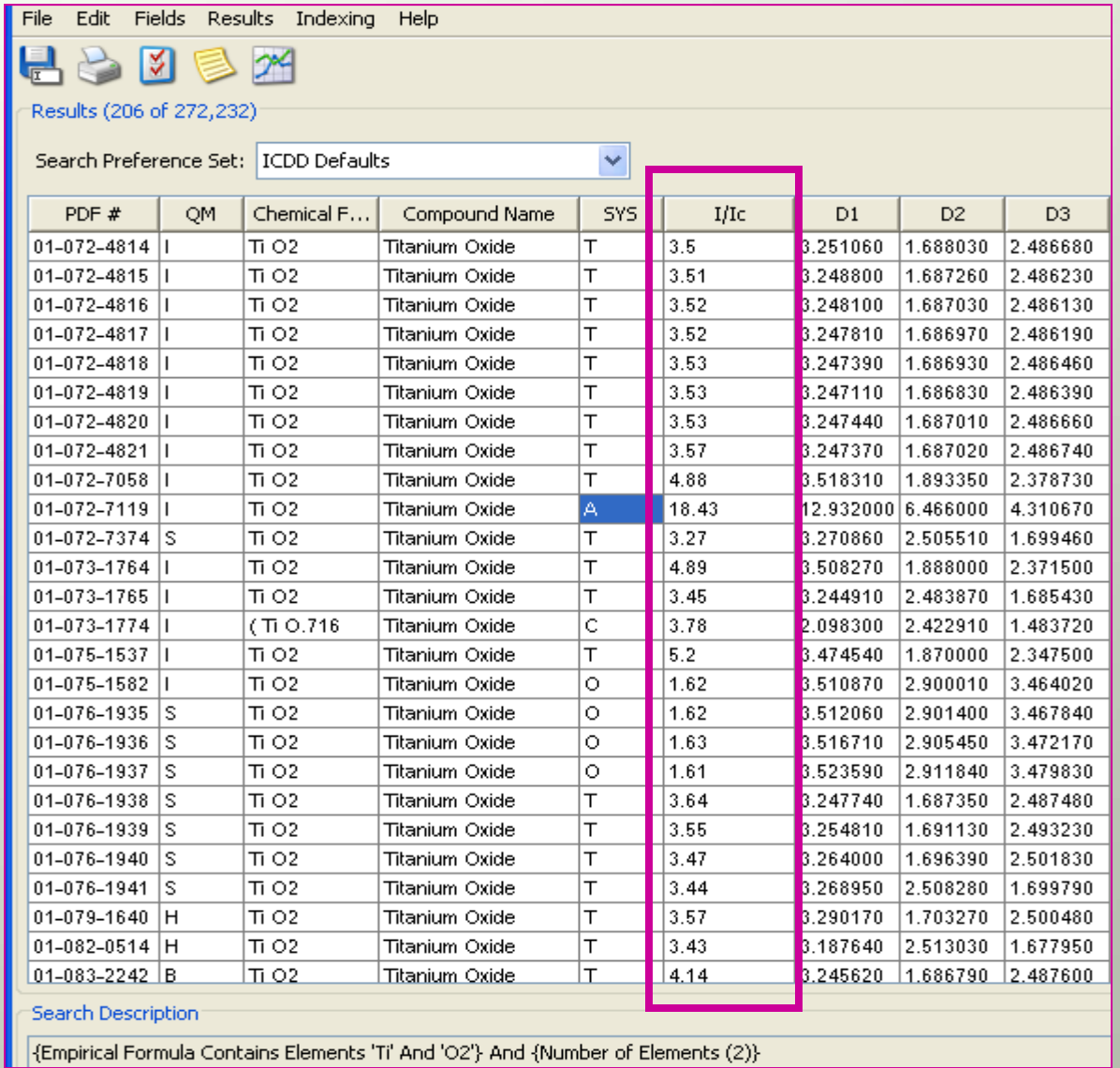
Go to the Miscellaneous Tab

Finding I/Ic for a Material



1) Perform a Search
2) Select the Preferences Tab
3) Select I/Ic to display Values

Finding I/Ic for a Material



File Edit Fields Results Indexing Help

Results (206 of 272,232)

Search Preference Set: ICDD Defaults

PDF #	QM	Chemical F...	Compound Name	SYS	I/Ic	D1	D2	D3
01-072-4814	I	Ti O2	Titanium Oxide	T	3.5	3.251060	1.688030	2.486680
01-072-4815	I	Ti O2	Titanium Oxide	T	3.51	3.248800	1.687260	2.486230
01-072-4816	I	Ti O2	Titanium Oxide	T	3.52	3.248100	1.687030	2.486130
01-072-4817	I	Ti O2	Titanium Oxide	T	3.52	3.247810	1.686970	2.486190
01-072-4818	I	Ti O2	Titanium Oxide	T	3.53	3.247390	1.686930	2.486460
01-072-4819	I	Ti O2	Titanium Oxide	T	3.53	3.247110	1.686830	2.486390
01-072-4820	I	Ti O2	Titanium Oxide	T	3.53	3.247440	1.687010	2.486660
01-072-4821	I	Ti O2	Titanium Oxide	T	3.57	3.247370	1.687020	2.486740
01-072-7058	I	Ti O2	Titanium Oxide	T	4.88	3.518310	1.893350	2.378730
01-072-7119	I	Ti O2	Titanium Oxide	A	18.43	12.932000	6.466000	4.310670
01-072-7374	S	Ti O2	Titanium Oxide	T	3.27	3.270860	2.505510	1.699460
01-073-1764	I	Ti O2	Titanium Oxide	T	4.89	3.508270	1.888000	2.371500
01-073-1765	I	Ti O2	Titanium Oxide	T	3.45	3.244910	2.483870	1.685430
01-073-1774	I	(Ti O.716	Titanium Oxide	C	3.78	2.098300	2.422910	1.483720
01-075-1537	I	Ti O2	Titanium Oxide	T	5.2	3.474540	1.870000	2.347500
01-075-1582	I	Ti O2	Titanium Oxide	O	1.62	3.510870	2.900010	3.464020
01-076-1935	S	Ti O2	Titanium Oxide	O	1.62	3.512060	2.901400	3.467840
01-076-1936	S	Ti O2	Titanium Oxide	O	1.63	3.516710	2.905450	3.472170
01-076-1937	S	Ti O2	Titanium Oxide	O	1.61	3.523590	2.911840	3.479830
01-076-1938	S	Ti O2	Titanium Oxide	T	3.64	3.247740	1.687350	2.487480
01-076-1939	S	Ti O2	Titanium Oxide	T	3.55	3.254810	1.691130	2.493230
01-076-1940	S	Ti O2	Titanium Oxide	T	3.47	3.264000	1.696390	2.501830
01-076-1941	S	Ti O2	Titanium Oxide	T	3.44	3.268950	2.508280	1.699790
01-079-1640	H	Ti O2	Titanium Oxide	T	3.57	3.290170	1.703270	2.500480
01-082-0514	H	Ti O2	Titanium Oxide	T	3.43	3.187640	2.513030	1.677950
01-083-2242	B	Ti O2	Titanium Oxide	T	4.14	3.245620	1.686790	2.487600

Search Description

{Empirical Formula Contains Elements 'Ti' And 'O2'} And {Number of Elements (2)}

TiO2's and I/Ic Displayed

Selecting Appropriate I/Ic Values

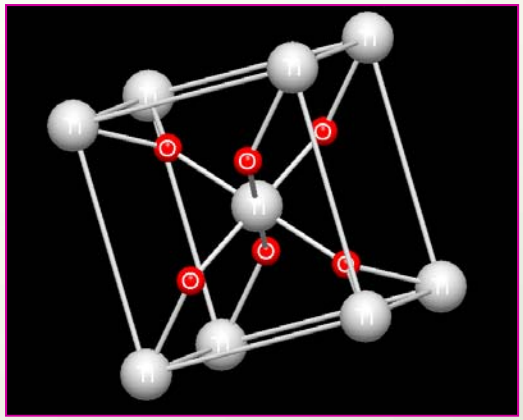
- Choose the appropriate structure.

  Many materials have polymorphs that have the same chemical formula, but different structures. These have different I/Ic's.

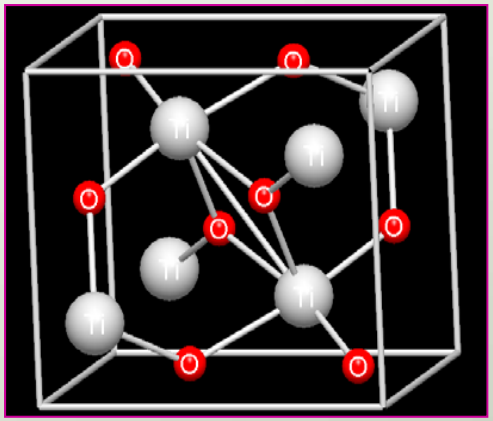
- Match the reference to the specimen as closely as possible.

- Use quality marks and indicators to select the best quality reference.

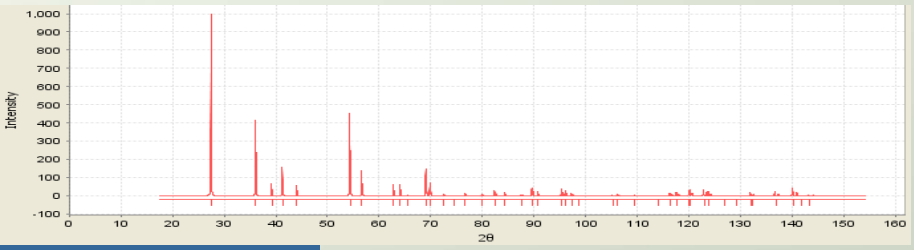
Selecting I/Ic - Structure

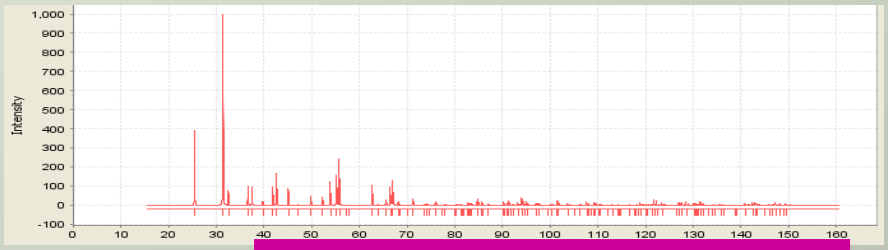


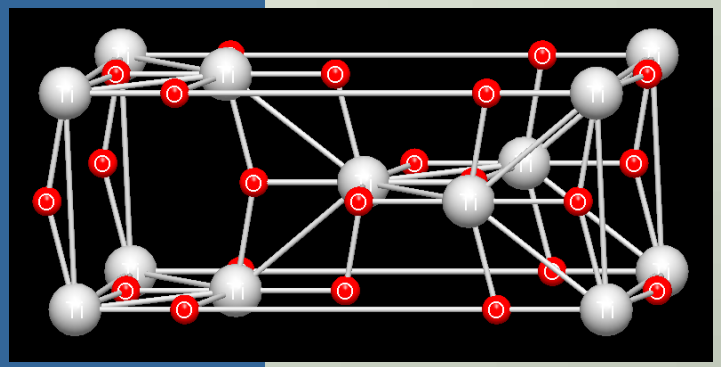
TiO2
Rutile
I/Ic = 3.54



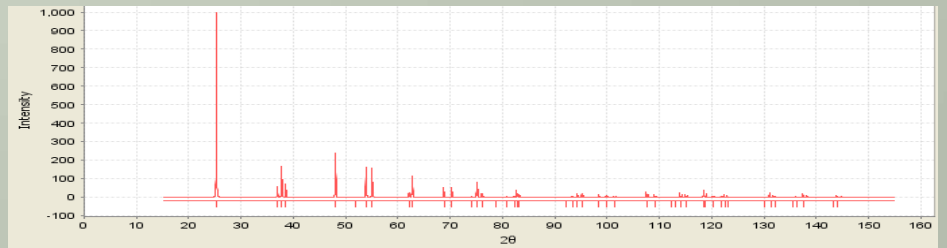
TiO2
Brookite
I/Ic = 3.06







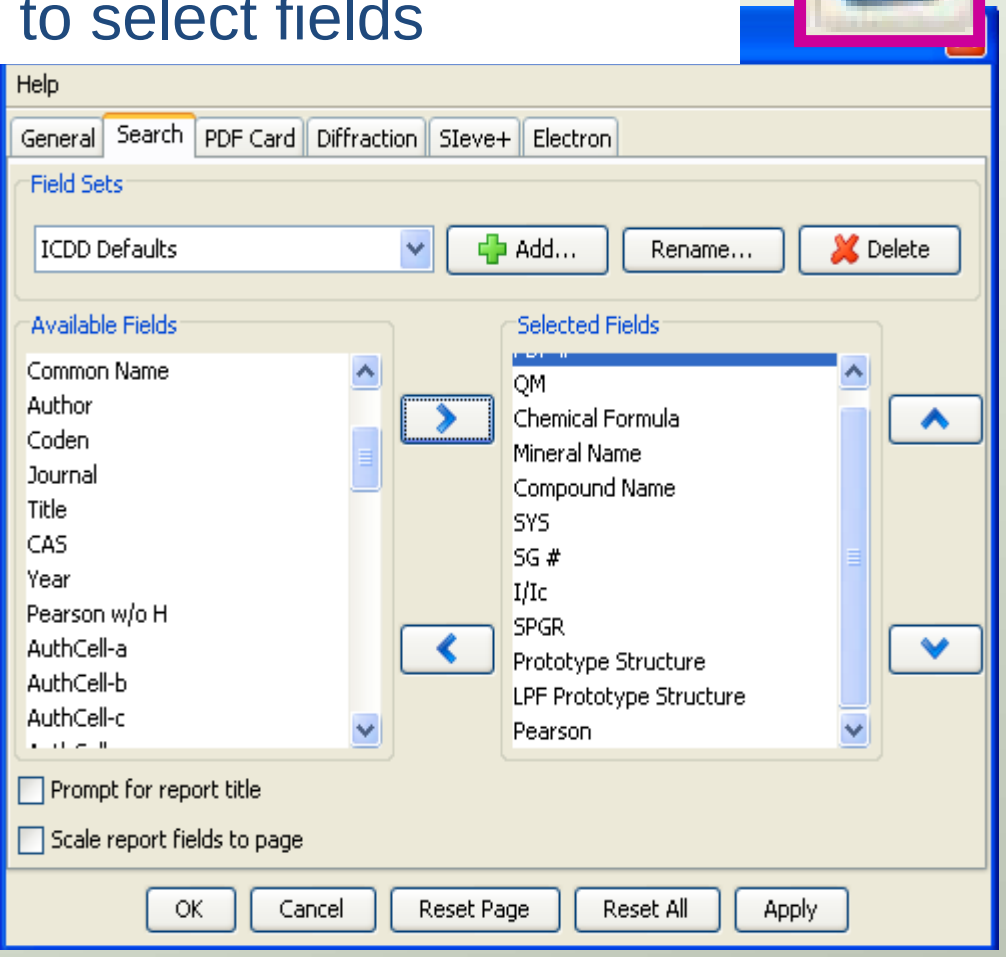
TiO2
Anatase
I/Ic = 5.04



Formulae are the same, pattern, structure and I/Ic are distinctly different

Structure

From Search Results use the Preferences Tab to select fields



You can select many fields that help you determine the structure by matching these data to the experimental data.

<u>These include:</u>

Chemical Name, Mineral Name

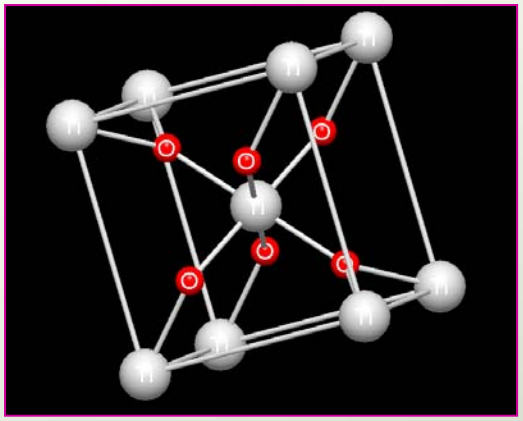
System and Space Group Number (SG#)

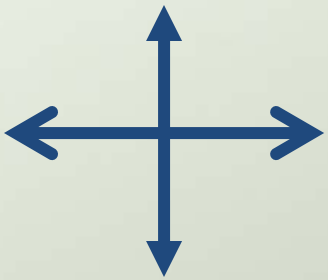
Pearson, Prototype Structure and LPF Prototype Structure

Reduced Cell, Author Cell and Crystal Cell

Strong Line (D1, D2, D3) and Long Line (L1, L2, L3)

Match Reference to Experiment





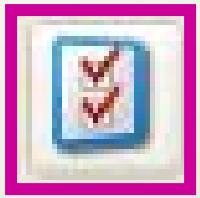
Temperature can expand or contract the unit cell – and change I/Ic.

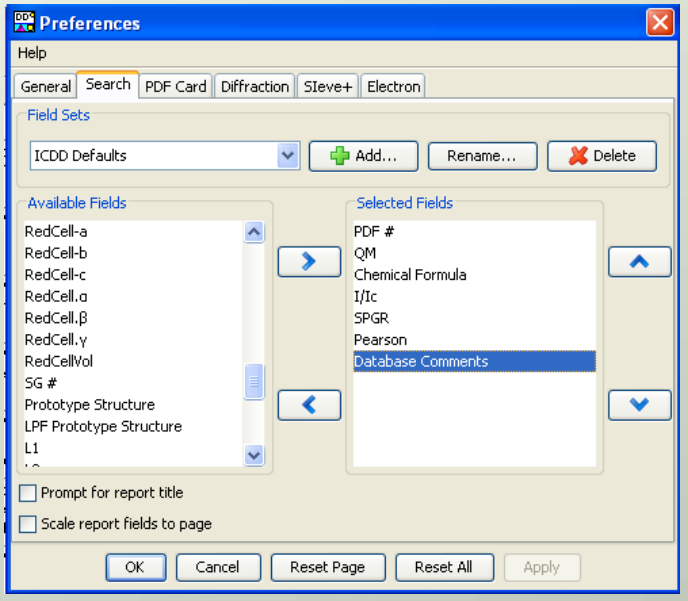
All the known factors that can alter a structure: temperature, pressure, anion or cation substitution, synthesis conditions, vacancies, stress, strain, etc. will change atom positions, electron density distribution, and therefore alter peak intensities and the I/Ic ratio.

The above factors are changes in the **Kia factor** in the equation for quantitative analysis.

Select a reference that most closely matches your experiment!

Matching References





From the Results Form,
select Preferences,
add Database Comments

04-007-5987	P	Ti O2	3.54	P42/mnm	tP6.00	LPF Collection Code: 1403121. Sample Preparation: STARTING MATERIALS:TiO2. Compound Preparation: heated at 1173-1273 K for several hours. Temperature of Data Collection: 298 K. Unit Cell Data Source: Powder Diffraction.
04-007-6246	B	Ti O2	1.82	C2/m	mC24.00	LPF Collection Code: 1403721. Polymorphism/Phase Transition: B. Temperature of Data Collection: 290 K. Significant Warning: Reported temperature factors on non H atoms are outside the range 0.001<U<0.1. Reported temperature factors were ignored and U=0.012 was used in the calculation. Unit Cell Data Source: Powder Diffraction.
04-007-6487	I	Ti O2	3.05	Pbnm	oP12.00	Color: colorless. LPF Collection Code: 1404320. Sample Preparation: STARTING MATERIALS:TiO2. Compound Preparation: heated at 1473 K. Temperature Factor: Reported Anisotropic temperature factors (in Beta) were converted to B. Temperature of Data Collection: 293 K. Minor Warning: LPF Editor Comment: unit for isotropic displacement parameters omitted, assumed to be anstrom 2. Unit Cell Data Source: Single Crystal.

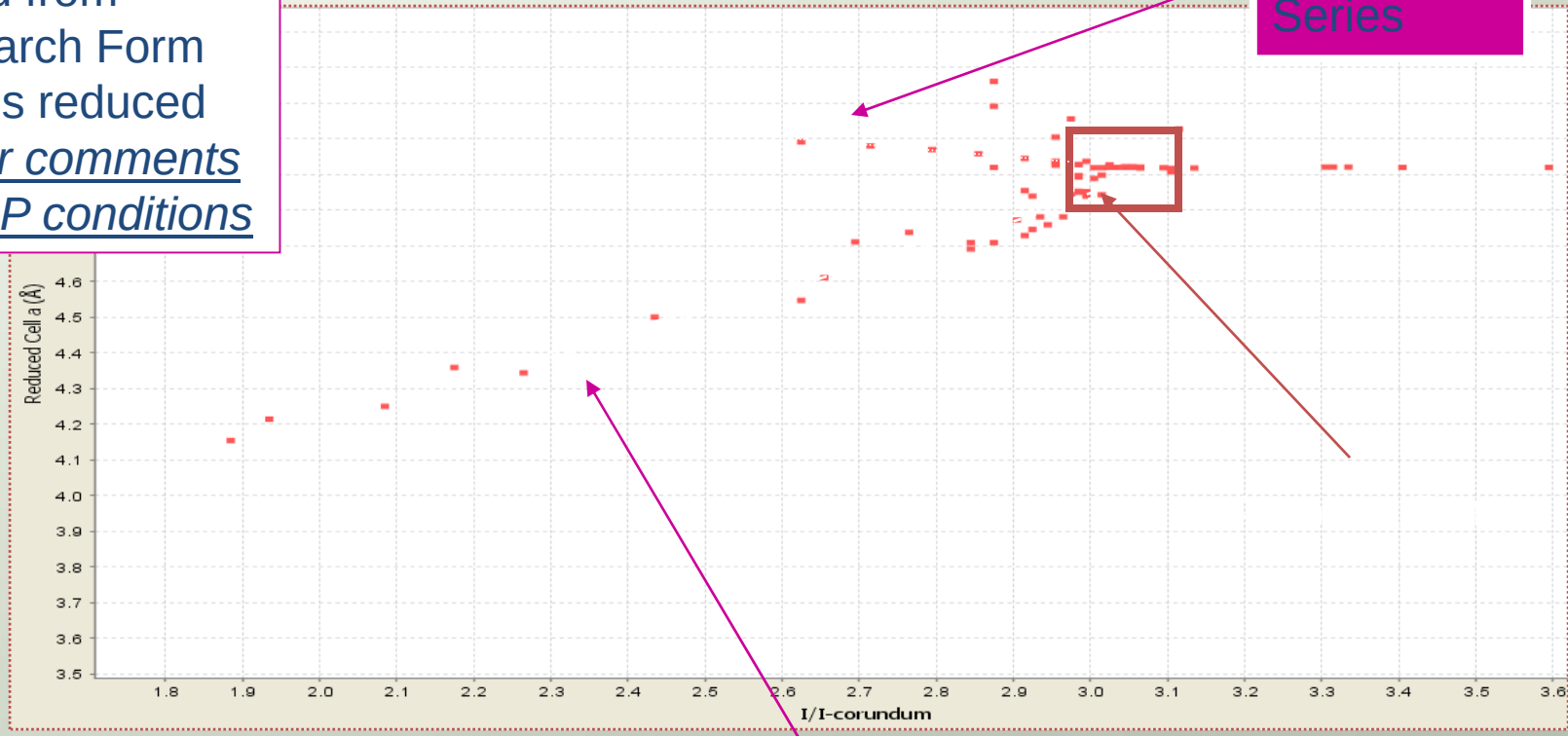
Editor comments contain information on specimen preparation, impurities, temperature of data collection and other factors that can change I/Ic. They can guide you to the appropriate choice.

I/Ic for Quartz

Space Group P3221

75 Determinations

Data plotted from PDF-4+ Search Form of I/Ic versus reduced cell a, *editor comments describe T, P conditions*

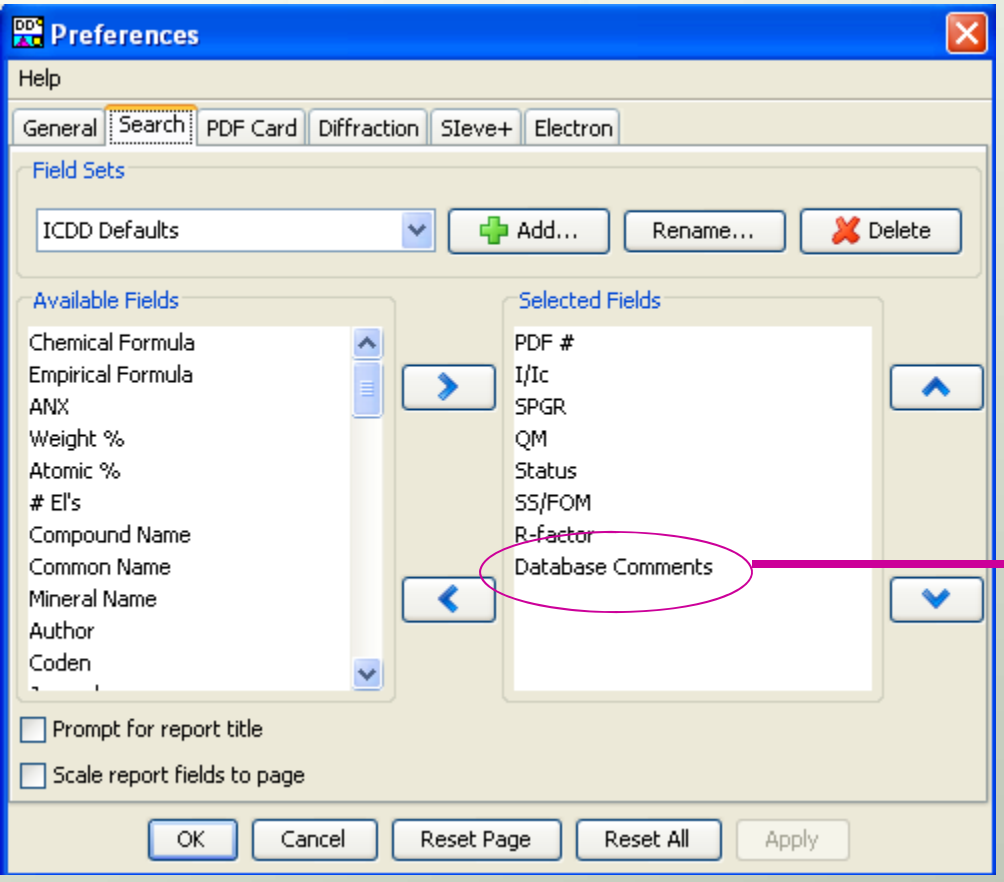


High Temp Series

Effect of Temp and Pressure for Quartz I/Ic

High Pressure Series Synthetic Materials

Using Quality Marks and Indicators



The database contains many quality Indicators. These include:

Indicator	High Quality Value
Quality Mark	S
Status	Primary
SS/FOM	Highest Number
R-Factor	Lowest Number

Database Comments: This includes comments from editors and statistical analyses conducted on the data.

The indicators are defined in the Help documentation in the database.

Use “Preferences” to display quality marks and indicators.

Using Quality Marks and Indicators

Poor Quality

Low Quality Marks are designations B and O
Low Quality Status would be a “Deleted” pattern
R-factors >0.10 (i.e., 10%) and SS/FOM’s below 10 are indications of poor quality

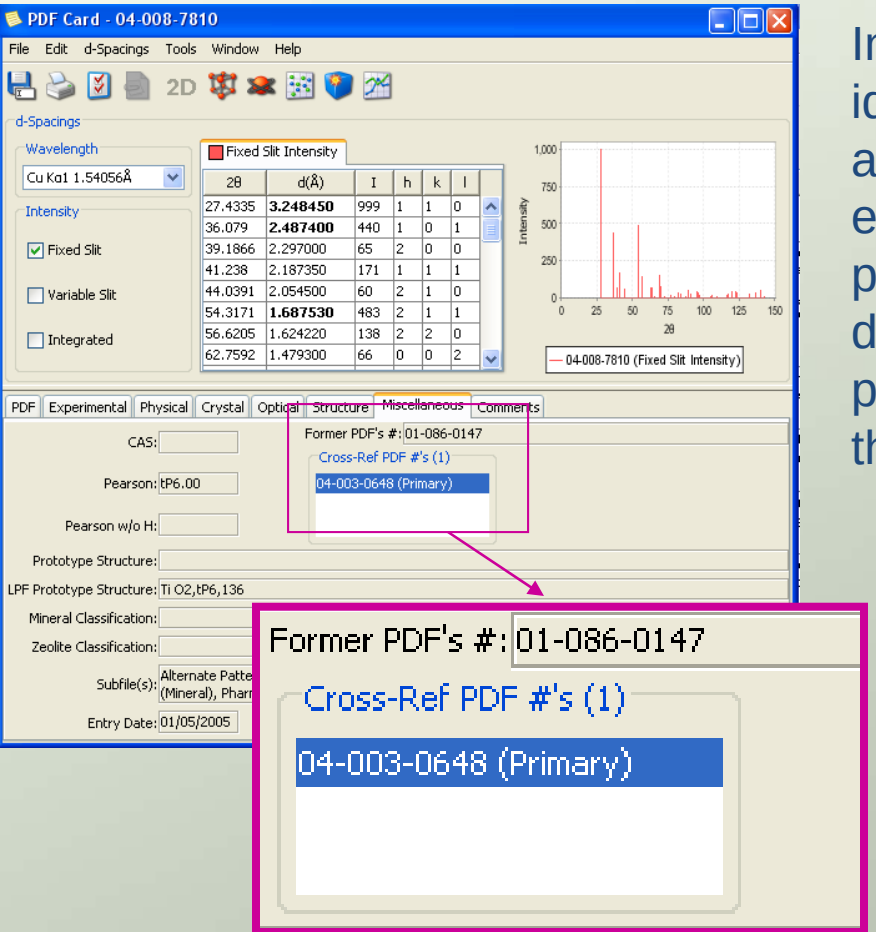
In general, any data meeting the above criteria should not be used in a quantitative analysis calculation as the ICDD’s editorial analysis and review would indicate that the calculation may result in large errors.

The data are included because there may not be better alternative choices for a particular material or the entry may contain other types of unique data (i.e., measured physical properties, novel synthesis, etc.).

Using Cross References

What if a Search/Match program identified an entry with a poor quality mark or poor quality indicator?

- Check the Cross References



In this example, a Search/Match program identified entry PDF 04-08-7810, which has an I/Ic of 3.6 and a “B” Quality Mark. The editors’ comments mention that the atomic parameters were derived (not experimentally determined or calculated) from the original publication. This results in low precision for the cell parameters and I/Ic values.

Solution: The entry contains cross-references identified in the “Miscellaneous Tab” of the entry. The primary (high quality) entry is highlighted and is an active link in the database. The primary entry has an I/Ic of 3.61 and is an “S” quality entry.

Application
Examples

- Using ICDD's SIeve and SIeve+ programs, materials are identified, peak intensities of each phase are calculated and I/Ic values are displayed – allowing the user to calculate concentrations by the RIR method.
- Many software distributors have RIR calculation modules, which can perform multiple, simultaneous calculations for complex mixtures, use integrated intensities and correct for absorption – all in a matter of seconds!

Examples are shown for the above.

Sleve+

Input experimental data.

Two phase identification in the analysis of an unknown.

GOM	PDF #	Compound Name ▲	Chemical Formula	D1	D2	D3	D4	D5	D6	D7	D8
1254	04-007-6692	Cerium Titanium Oxide	Ce2 Ti2 O7	2.976300	2.982970	4.186270	3.215220	2.699360	2.757500	2.707670	2.777650
624	01-071-7093	Cerium Yttrium	(Ce0.98 Y0.02)	2.979130	2.580000	1.555800	1.824340	1.183790	1.153810	1.489560	0.872199
862	04-006-7962	Cerium Zirconium Oxide	Ce0.15 Zr0.85 O2	2.983250	1.832240	1.551350	1.816240	2.568560	1.571400	2.614390	1.188360
768	04-006-7961	Cerium Zirconium Oxide	Ce0.12 Zr0.88 O2	2.980390	1.830300	1.550080	1.814850	2.566590	1.569450	2.610850	1.187120
580	04-006-7959	Cerium Zirconium Oxide	Ce0.1 Zr0.9 O2	2.978710	1.828770	1.549810	1.814800	2.566510	1.567310	2.606500	1.186180
542	01-071-3203	Cesium Ammine Phosphide	(Cs3 P11) (N H3)3	2.989480	8.007960	3.130050	3.366560	4.097300	4.639240	4.156330	3.538360
1223	04-009-5795	Cesium Antimony Iodide	Cs3 Sb2 I9	2.983960	3.440150	3.462000	2.105000	2.114990	5.967910	1.798620	1.795530

Matches Filter

Filter Description

Select...

Experiment

Search Line(s): 2.98220 Å D1 Range: 2.968 - 2.997 Å Rotation: 1 of 3

Preferences

Search Window: 0.15 ° Match Window: 0.15 °

Search Method: Hanawalt Lowest Allowable GOM: 500

Wavelength: Cu Ka1 1.54056Å

Phases (2)

# ▲	Accepted	PDF #	Compound Name	Int. Ratio	Int. %	I/Ic	Time
1	☑	01-089-1487	Magnesium Aluminum Silicate	1.11	78	1.41	47.6s
2	☐	04-006-7962	Cerium Zirconium Oxide	0.311	22	10.88	68.3s

Lines (14 of 20)

Ex d(Å) ▼	Ex I	P1 d(Å)	P1 I	P2 d(Å)	P2 I
11.30794	2				
8.44311	100	8.438780	100		
5.16004	9				
4.90437	15	4.904160	18		
4.85981	8	4.856350	9		
4.66904	11	4.665900	9		
4.08603	38	4.083300	38		
3.52993	6				
3.43370	6				
3.38019	27	3.380380	26		
3.34271	5				
3.14912	13	3.146490	14		
3.13282	33	3.129540	35		
3.09371	4				
3.03184	39	3.029500	26		
3.01178	40	3.010620	23		
2.98220	29			2.983250	100
2.64354	11	2.640670	11		
2.33576	5	2.332950	7		
1.83616	12	1.838080	1	1.832240	32

$$\frac{I_a}{I_b} = \frac{(I/I_c)_a}{(I/I_c)_b} \frac{X_a}{X_b}$$

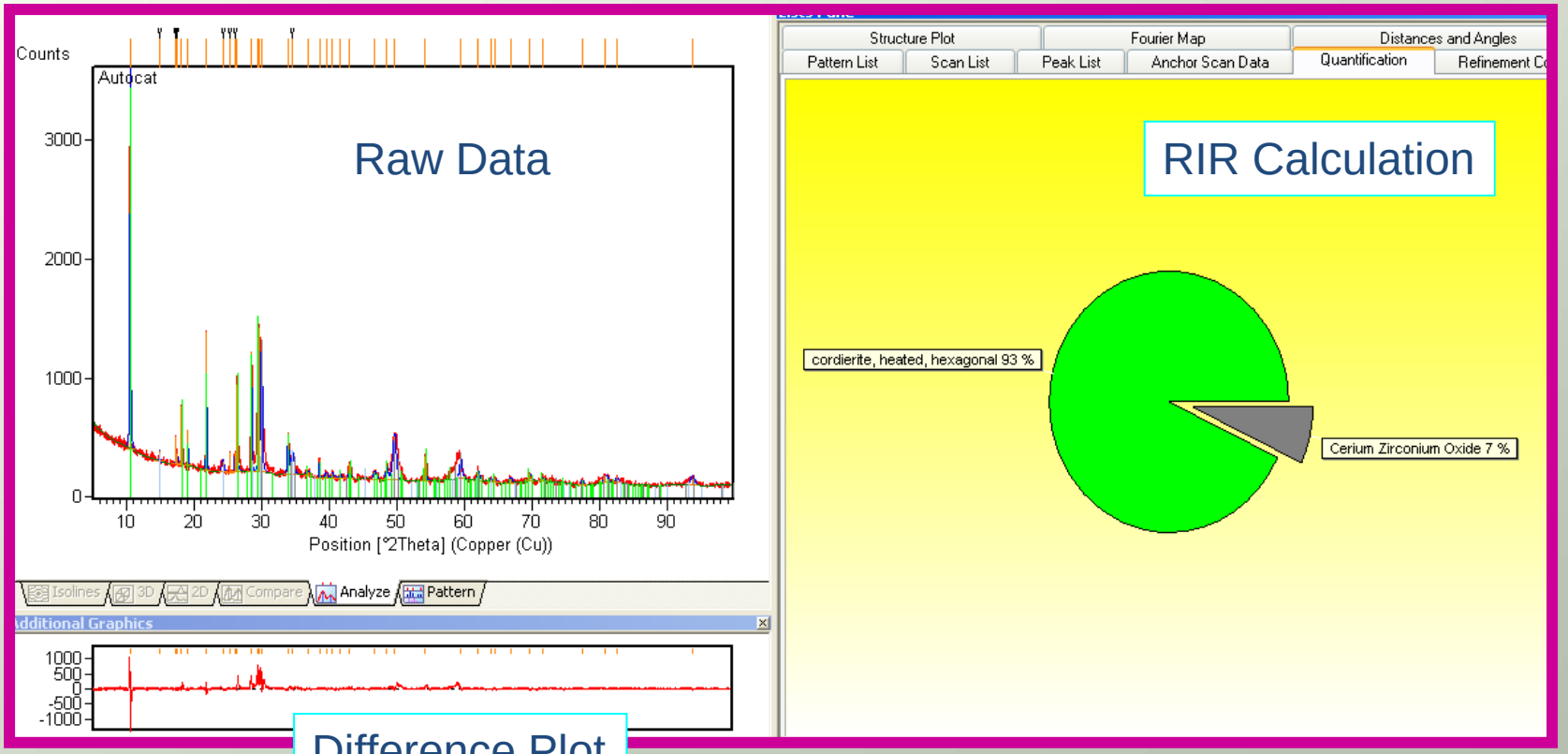
Results summary

Compound Name	Int. Ratio	Int. %	I/Ic
Magnesium Aluminum Silicate	1.11	78	1.41
Cerium Zirconium Oxide	0.311	22	10.88

This results in 96% magnesium aluminum silicate and 4% cerium zirconium oxide and uses peak intensities.

Automated RIR Analysis

Vendor Software – Same Example



This software calculated 92% magnesium aluminum silicate and 7% cerium zirconium oxide using integrated intensities.

Thank you for viewing our tutorial.
Additional tutorials are available at the ICDD website
(www.icdd.com).

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