XRF and SEM-EDS

- Using the PDF for material identification using elemental data from XRF and SEM-EDS.

XRF and SEM-EDS

What?

The Powder Diffraction File contains data on pure solid state compounds of well defined elemental composition.

XRF and SEM-EDS methods can provide an experimental determination of a specimen’s elemental composition.

By matching experimental composition data to the database entries, materials can be identified. The more elements positively identified in the XRF or SEM-EDS experiment, the more narrow the selection of candidate phases will be.

If additional data are used, such as physical properties (color, density) or chemical properties, a unique solution can often be identified.

XRF and SEM-EDS

Why?

Scientists have long recognized that using multiple observations of a specimen increases the probability of a successful identification.

The Powder Diffraction File is designed as a database for material identification. While characteristic diffraction and crystallographic data are a primary tool used in the database, other characteristics of a material are input into the database or calculated to increase the chances of a successful identification.

Elemental composition has been experimentally determined or calculated for all entries in the Powder Diffraction File.

Elemental data, from an XRF or SEM-EDS, are often available in global analysis and materials characterization facilities.

XRF and SEM-EDS

How?

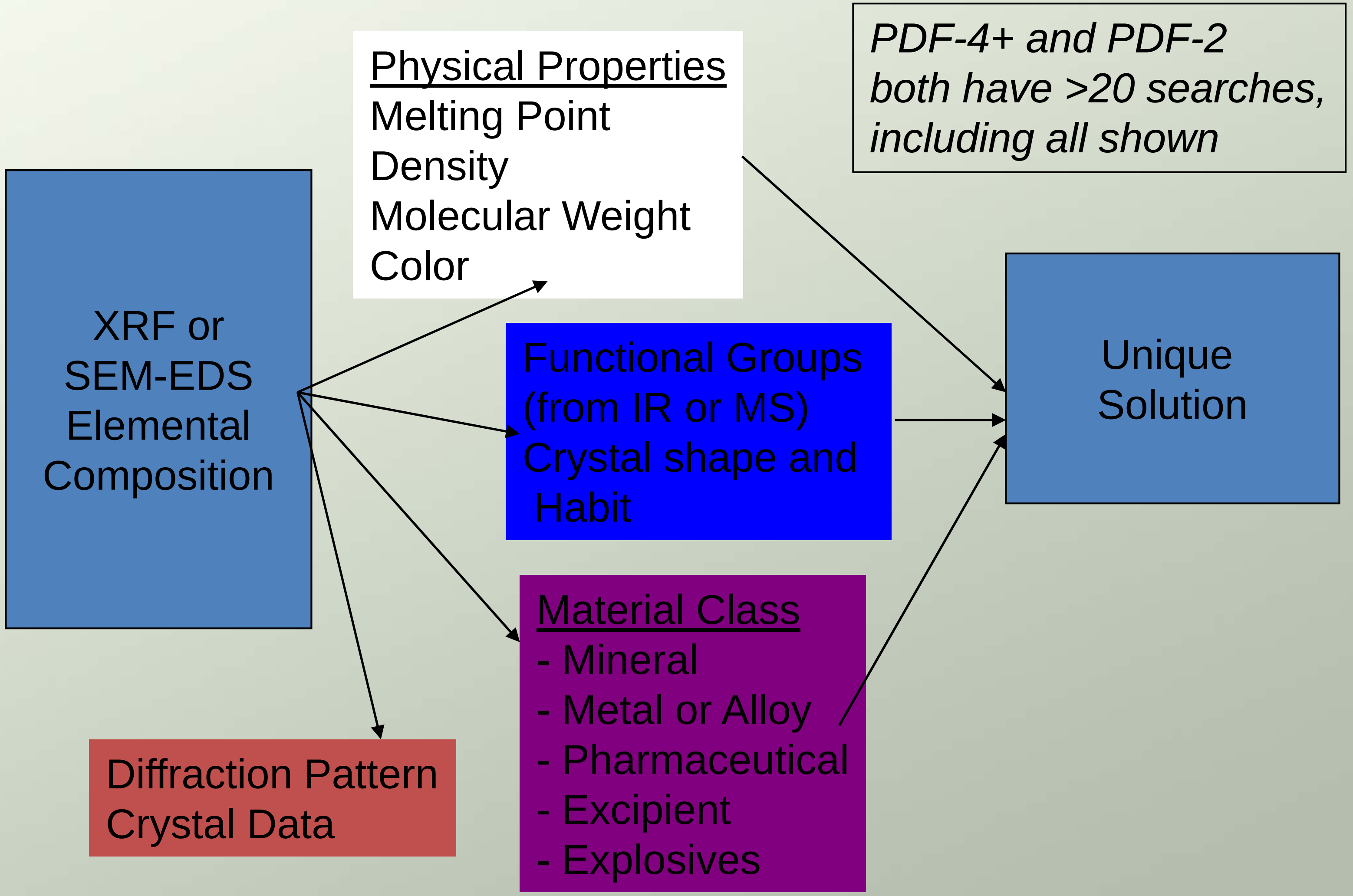
All entries in the PDF have calculated atomic and weight percent compositions. The former was designed for use with EDS data and the latter with XRF analyses.

The PDF has composition searches so that experimental data can be compared to the references in the database. ESD’s and elemental ranges can be applied to the search.

XRF and SEM-EDS

How?

The more you know, the more efficient the search.



Material Identification

Case 1 - Meteor

A specimen of a commercial meteorite was examined.
The task was to evaluate the composition and verify the authenticity.

What do you know ?

Elemental composition determined by XRF –
Do a composition search.
The specimen is a meteorite –
Use the metal and alloy subfile and/or the mineral subfile.

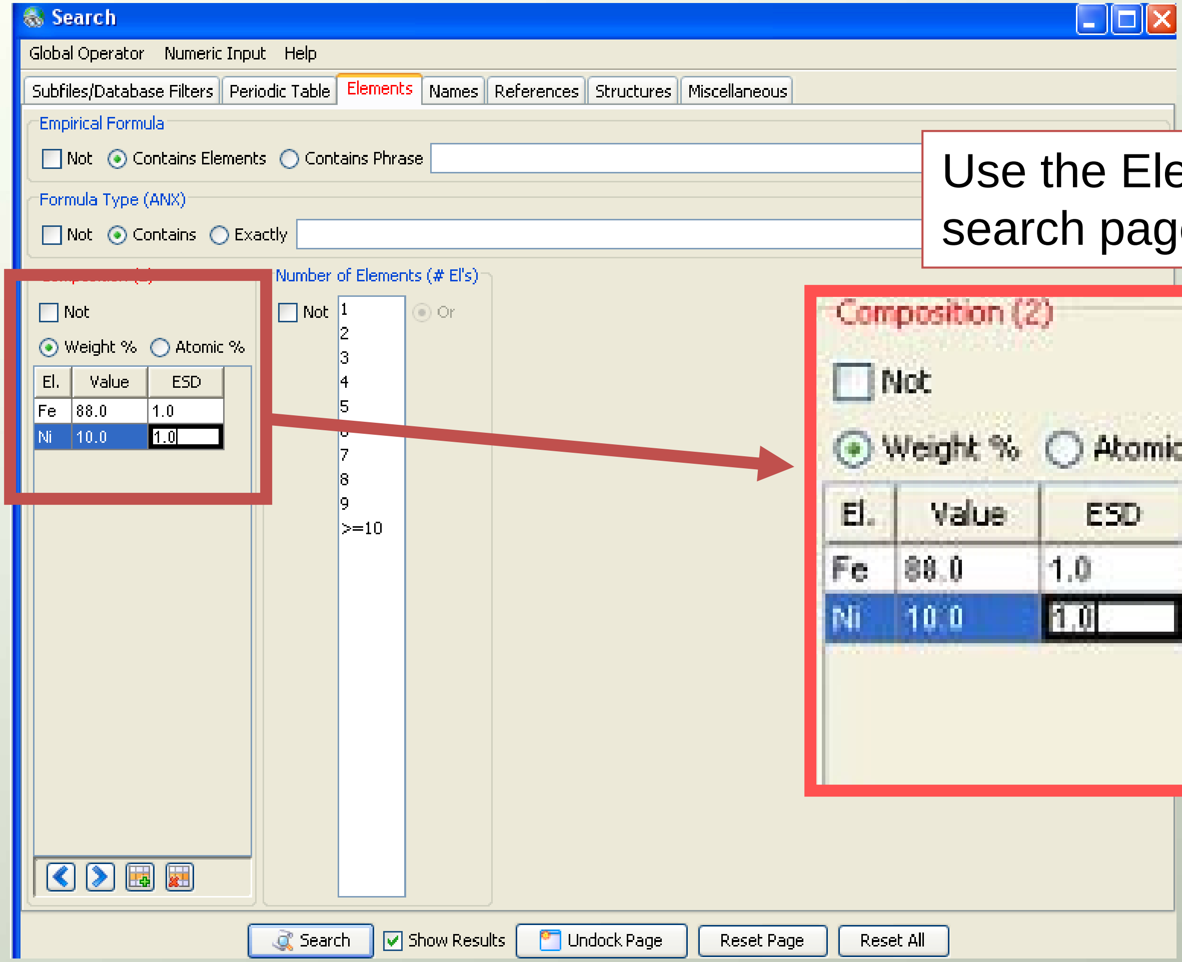
The specimen was also be examined visually. It appeared metallic, with minor surface corrosion and metallic gray underneath the surface layer. The specimen was heavy.

Data From the XRF Analysis of the Meteor

Compound Formula	nZ	Conc (wt-%)	Stat. Dev. (wt-%)	Line	Peak Int (kCPS)	Bkg Int (kCPS)	Net Int (kCPS)
Na	11	0.27	0.022	Na KA1-HS-Min	0.207	0.035	0.172
Mg	12	0.071	0.0079	Mg KA1-HS-Min	0.250	0.099	0.151
Al	13	0.1	0.011	Al KA1-HS-Min	0.182	0.020	0.162
Si	14	0.23	0.015	Si KA1-HS-Min	0.451	0.025	0.426
P	15	0.47	0.018	P KA1-HS-Min	1.219	0.045	1.174
S	16	0.07	0.0057	S KA1-HS-Min	0.375	0.054	0.321
Cl	17	0.1	0.0099	Cl KA1-HR-Min	0.281	0.047	0.234
K	19	0.042	0.0042	K KA1-HS-Min	0.305	0.062	0.243
Ca	20	0.033	0.0041	Ca KA1-HS-Min	0.292	0.091	0.201
Cr	24	0.017	0.0022	Cr KA1-HS-Min	0.456	0.201	0.255
Fe	26	88.05	0.1	Fe KA1-HS-Min	1167.631	0.514	1167.117
Co	27	0.568	0.0063	Co KA1-HS-Min	14.569	0.556	14.013
Ni	28	9.98	0.1	Ni KA1-HS-Min	15.133	0.074	15.059
Total		100.00					

Composition Search

Meteor

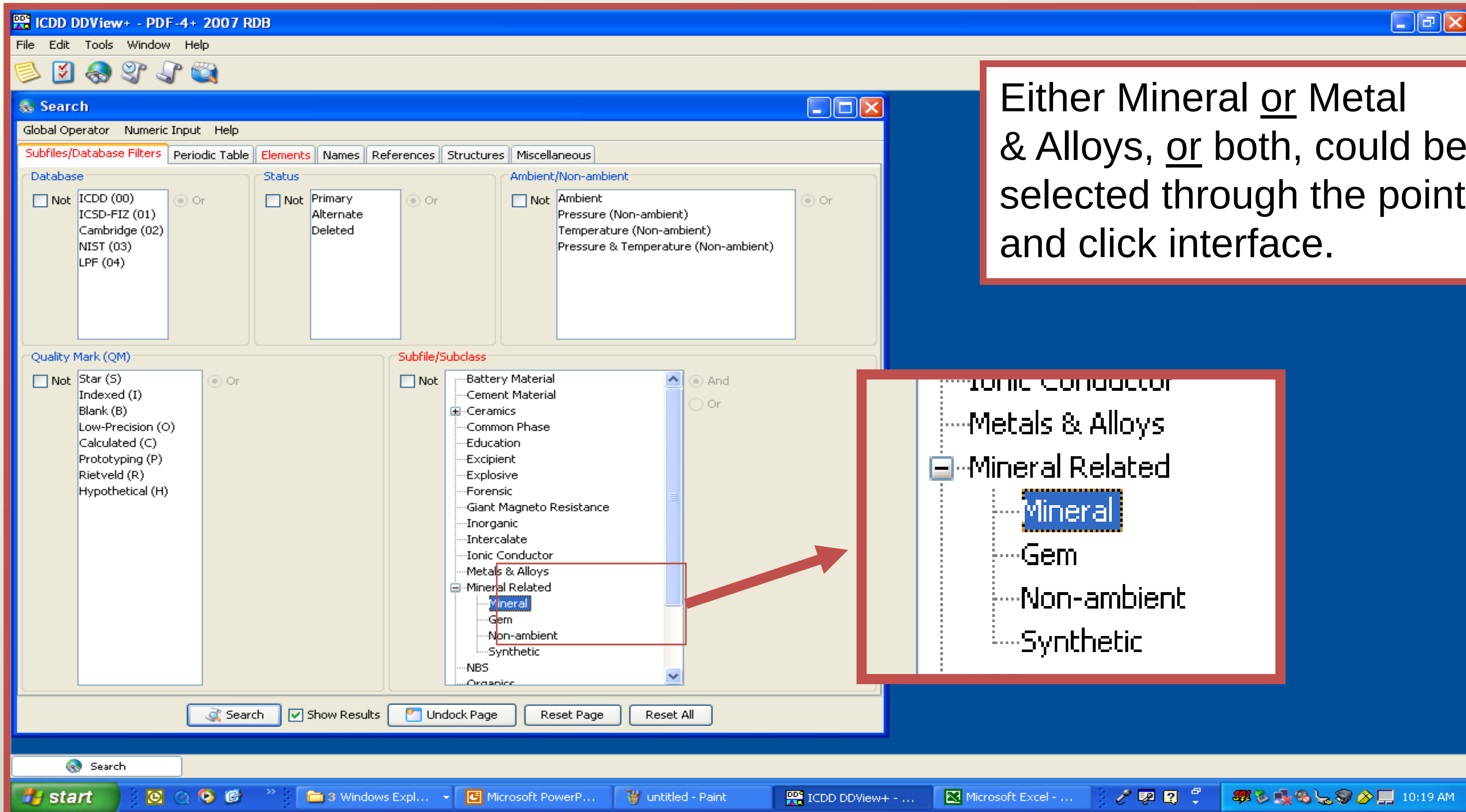


Use the Elements search page in PDF-4+

Input major elements from the XRF analysis. Click on a search using weight percents.

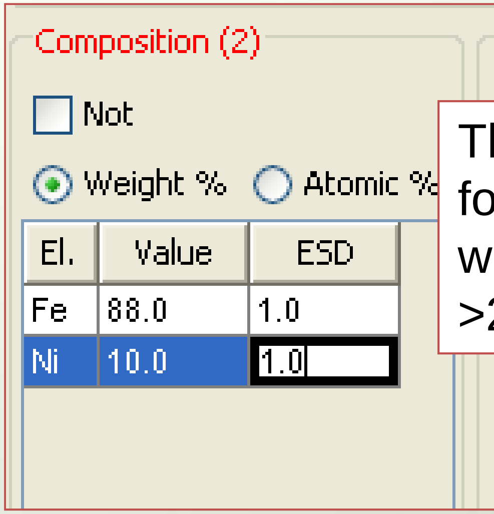
Subfile Search

Meteor



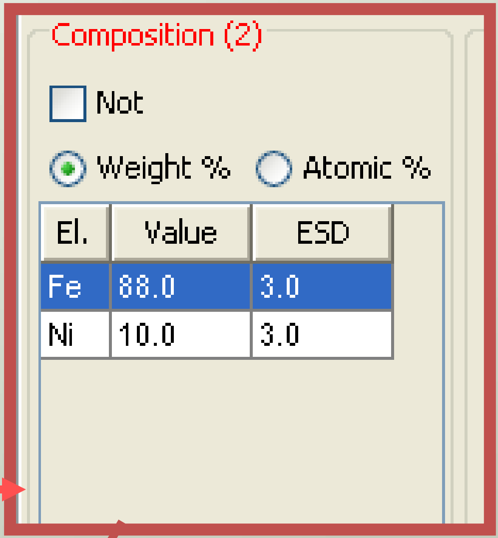
Either Mineral or Metal & Alloys, or both, could be selected through the point and click interface.

Results

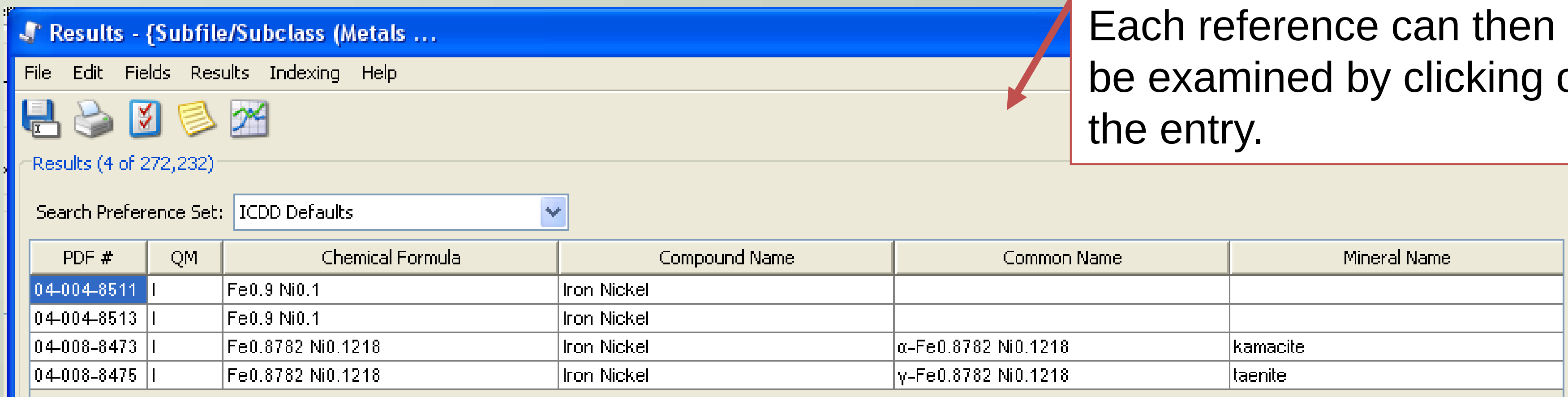


This composition found 0 results when compared to >270,000 entries.

Search broaden by increasing ESD ranges



4 compositions identified. Each reference can then be examined by clicking on the entry.



PDF #	QM	Chemical Formula	Compound Name	Common Name	Mineral Name
04-004-8511	I	Fe0.9 Ni0.1	Iron Nickel		
04-004-8513	I	Fe0.9 Ni0.1	Iron Nickel		
04-008-8473	I	Fe0.8782 Ni0.1218	Iron Nickel	α-Fe0.8782 Ni0.1218	kamacite
04-008-8475	I	Fe0.8782 Ni0.1218	Iron Nickel	γ-Fe0.8782 Ni0.1218	taenite

Results

PDF #	QM	Chemical Formula	Compound Name	Common Name	Mineral Name
04-004-8511	I	$Fe_{0.9} Ni_{0.1}$	Iron Nickel		
04-004-8513	I	$Fe_{0.9} Ni_{0.1}$	Iron Nickel		
04-008-8473	I	$Fe_{0.8782} Ni_{0.1218}$	Iron Nickel	α-$Fe_{0.8782} Ni_{0.1218}$	kamacite
04-008-8475	I	$Fe_{0.8782} Ni_{0.1218}$	Iron Nickel	γ-$Fe_{0.8782} Ni_{0.1218}$	taenite

- 2 Entries have a composition of 90% Fe and 10% Nickel and are man-made alloys.
- 2 Entries have a composition of 88% Fe and 12% Nickel, have an identified mineral names, and were found in a meteorite.

The specimen contains 88.1(1)% Fe and 10.0(1)% Ni with many trace elements.

Results

PDF Card - 04-008-8475

File Edit d-Spacings Tools Window Help

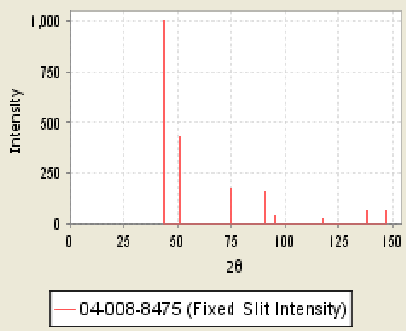
d-Spacings

Wavelength: Cu Kα1 1.54056Å

Intensity
- [x] Fixed Slit
- [ ] Variable Slit
- [ ] Integrated

Fixed Slit Intensity

2θ	d(Å)	I	h	k	l
43.5691	**2.075570**	999	1	1	1
50.7484	**1.797500**	425	2	0	0
74.6064	**1.271020**	174	2	2	0
90.5734	1.083930	161	3	1	1
95.8436	1.037790	44	2	2	2
117.9755	0.898750	20	4	0	0
138.1202	0.824750	66	3	3	1
146.7586	0.803866	63	4	2	0



PDF | Experimental | Physical | Crystal | Optical | Structure | Miscellaneous | Comments

Author's Reported Data

Radiation: CuKα1 λ: 1.5406 Filter:

Wavelength

d-Spacing: Calculated Cutoff: Intensity: Calculated

I/Ic: 7.84 Camera Diameter:

Reference: "KAMACITE AND TAENITE SUPERSTRUCTURES AND A METASTABLE TETRAGONAL PHASE IN IRON METEORITES". Ramsden A.R., Cameron E.N. Am. Mineral. 51, 37 (1966). Calculated from LPF using POWD-12++.

The reference and editors' comment sections for the two mineral phases, Kamacite and Taenite, mention that they are Fe-Ni alloy polymorphs, and were analyzed from the Carlton meteorite in Hamilton, Texas.

The two minerals have different morphologies and crystal habits.

Verification

Meteor

The commercial vendor of the meteorite claimed that the meteor was from the Tambo Quemada meteorite in Peru. Furthermore, it is classified as an Iron, Medium Octahedrite (IIIB) meteor with an 8.7% Nickel content.

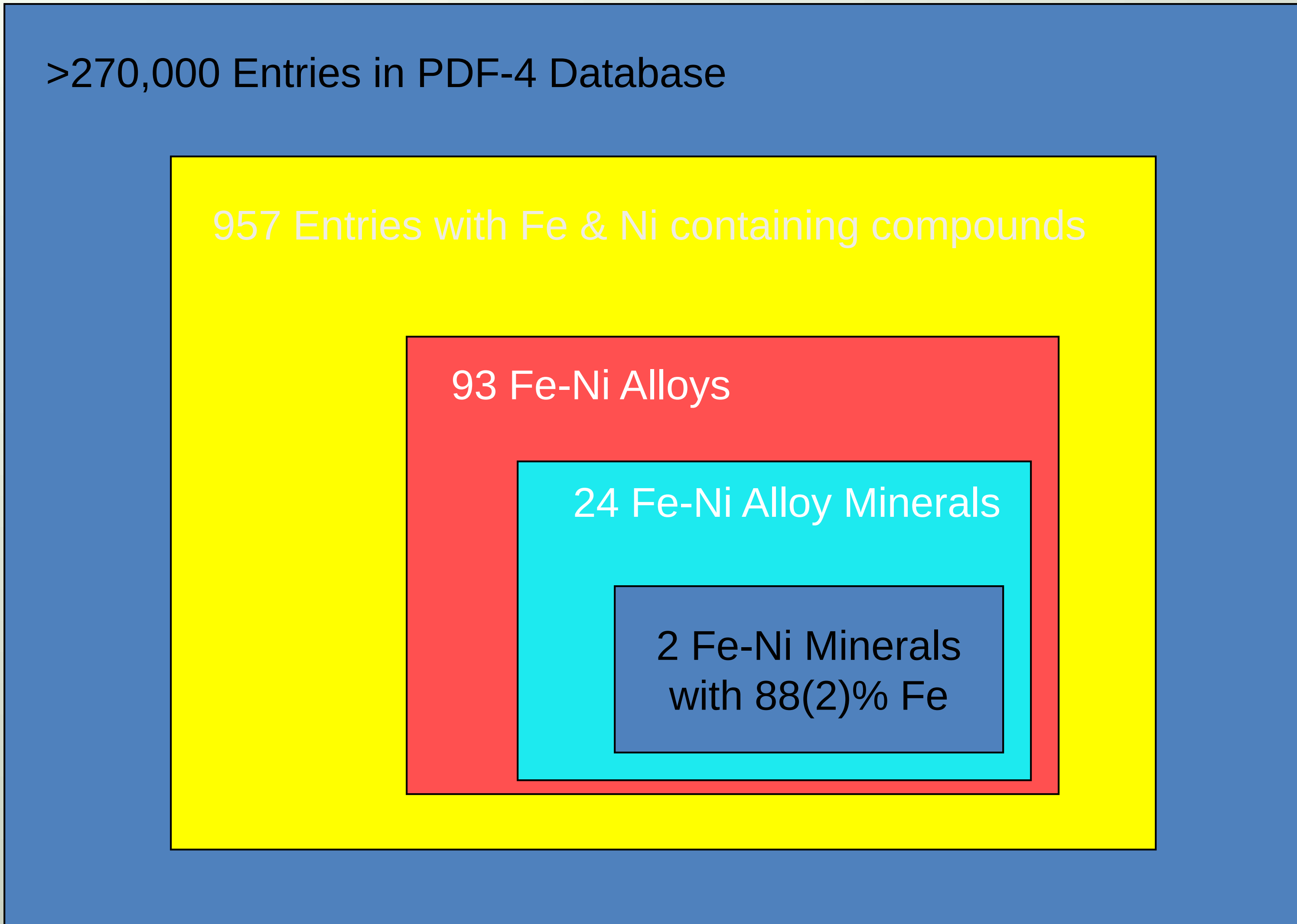
(Note: This class of meteorites commonly has taenite and kamacite Fe-Ni Minerals. Furthermore, taenites are often Ni rich, even though the reference from the Carlton meteorite was not.)

Once the references point to taenite and kamacite, each of which has a specific crystal habit, the original specimen was reexamined. Visual examination showed evidence of the habit and color described for these minerals. Two different morphologies are clearly observed.

Conclusion

- The commercial vendor claims were verified. XRF data directed the user to specific minerals contained in the PDF database.
- References in the PDF direct the user to cross confirm visual evidence on color and habit.
- The Ni content in the specimen was slightly higher than that of reference Carlton meteorites, and that claimed by the vendors’ bulk analysis of the Tambo Quemada meteorite.
- The Ni variation can be easily explained by differences in concentrations of kamacite and taenite, which are both observed in the specimen.

How Searches Reduce the Candidate Lists



Alternate Search Strategy

Simplier

>270,000 Entries in PDF-4 Database

24 Minerals containing Ni and Fe

3 Fe-Ni Minerals with 88(2)% Fe

In this case, the third mineral is Haxonite, an Fe-Ni-Co carbide.

This mineral is found in meteorites and has 0.5 wt% Co, and is often mixed with the other 2 minerals.

Since the specimen contains Co, this phase may be also be present.

Mineral Sample

Case 2

In this experiment, the specimen was a commercial raw material intended for a manufacturing process.

The objective was to verify purity and Composition, claimed by the producer.

Mineral Specimen

Case 2

Compound Formula	nZ	Concentration	Line 1	Concentr. 1	Stat. Dev. 1	Depth 1
Al2O3	13	56.81	Al KA1-HS-Min	56.81	0.32	29 um
SiO2	14	41.5	Si KA1-HS-Min	41.5	0.28	39 um
P2O5	15	0.15	P KA1-HS-Min	0.15	0.018	53 um
K2O	19	0.043	K KA1-HS-Min	0.043	0.0064	0.22 mm
CaO	20	0.042	Ca KA1-HS-Min	0.042	0.0071	0.30 mm
TiO2	22	1.13	Ti KA1-HS-Min	1.13	0.019	0.53 mm
Cr2O3	24	0.038	Cr KA1-HS-Min	0.038	0.0042	0.90 mm
Fe2O3	26	0.635	Fe KA1-HS-Min	0.635	0.0071	1.5 mm
SrO	38	0.029	Sr KA1-HS-Min	0.029	0.0036	17 mm
ZrO2	40	0.0405	Zr KA1-HS-Min	0.0405	0.0015	24 mm

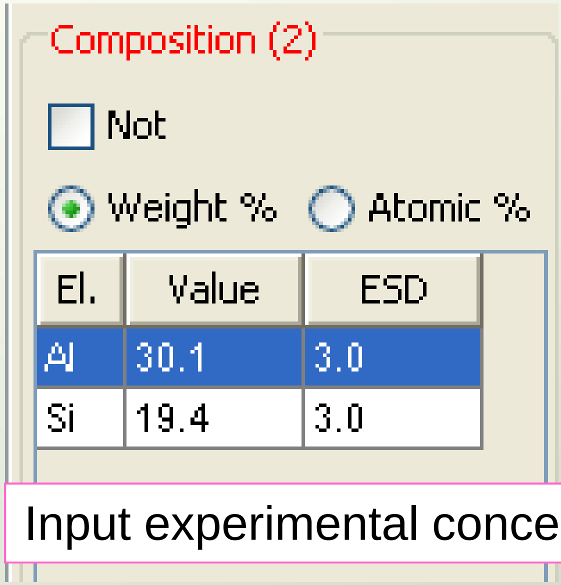
XRF analysis of a mineral specimen – *all data expressed as oxides.*

Convert to Element Concentration

Experimental Data	Calculated Data*
56.8% Al_2O_3	30.06% Al
41.5% SiO_2	19.39% Si

*Can use MW's provided in the ICDD database.

Use a Composition Search



Input experimental concentrations

This composition only matches 1 entry, and that entry ($Si_6Al_{10}O_{21}N_4$) is not a Mineral, but a synthetic ceramic!

No Success
Try a New Search

Broaden composition range –
put ESD’s at 5 wt%.

Restrict to minerals (eliminates synthetic ceramics)

New Search

Case 2

5 Minerals identified as candidates

PDF #	QM	Chemical Formula	Compound Name	Mineral Name
00-007-0330	O	K - Al4 (Si Al)8 O20 (O H)4 ·x H2 O	Potassium Aluminum Silicate Hydroxide	Illite-Montmorillonite, regular
00-012-0625	B	Mg2 (Al , Fe)6 (Si O4)4 O2 (O H)2	Magnesium Aluminum Iron Silicate	Yoderite
00-042-0374	O	K - Na - Al2 - Si - O - H2 O	Potassium Sodium Aluminum Silicate	Erionite-Na, syn
00-047-0356	B	Na39.8 Al70.4 Si41.2 O207.9	Sodium Aluminum Silicate	Chabazite-Na, syn
01-074-1394	I	Mg3 Al6 (Si.8 Al.2)5 O21 (O H)	Magnesium Aluminum Silicate Hydroxide	Kornerupine

None match manufacturer’s label.

Verification

The manufacturer's mineral does have several reference compounds in the database. Composition data for these references are shown below.

Database References

Al33.30 O49.37 Si17.33
Al33.30 O49.37 Si17.33
Al33.30 O49.37 Si17.33
Al33.30 O49.37 Si17.33
Al33.30 O49.37 Si17.33
Al33.30 O49.37 Si17.33

Al / Si = 1.92

<u>XRF Analysis</u>

30.1% Al
19.4% Si

Al / Si = 1.55

The Al and Si concentrations, as well as the Al/Si concentration ratio, indicate that the specimen is not pure. The mineral is often found with SiO_2. The lack of additional elements in the XRF would rule out many other minerals. The Al analysis would indicate ~90% purity.

Conclusion

Case 2

- In this case, the analysis indicates that the specimen is not pure.
- Comparison of the data with standards in the database, suggests impurities, which could be verified with some simple additional testing (i.e. light microscopy examination).

XRF Analysis of the Liberty Bell

Copper	64.95–73.10
Tin	24.00–30.16
Lead	1.30–5.47
Zinc	0.25–1.65
Iron	0.00–0.87
Silver	0.14–0.26
Antimony	0.08–0.18
Arsenic	0.19–0.42
Gold	0.02–0.06
Nickel	0.00–0.28

Range reflects 10 specimens taken from the bell in 1960.
Analysis taken from the Liberty Bell Internet site.

Liberty Bell

Case 3

Composition (2)

Not

Weight % Atomic %

El.	Value	ESD
Cu	69.0	5.0
Sn	27.0	4.0

Input Composition (prior slide)

There are 59 references of the Cu-Znalloy system – bronze.

PDF #	QM ▲	Weight %	Chemical Formula	Compound Name	SYS	Author	Journal
00-034-1092	I	Cu64.00 Mg6.12 Sn29.88	Cu4 Mg Sn	Copper Magnesium Tin	C	Osamura, K., Murakami.	J. Less-Common Met.
04-001-5604	I	Cu64.00 Mg6.12 Sn29.88	Mg Cu4 Sn	Magnesium Copper Tin	C	Osamura K., Murakami Y.	J. Less-Common Met.
00-006-0650	B	Cu64.00 Mg6.12 Sn29.88	Cu4 Mg Sn	Copper Magnesium Tin	C	Gladyszewsky, E. et al.	Dokl. Akad. Nauk SSSR
01-071-0094	B	Cu69.63 Sn30.37	Cu51.68 Sn12.07	Copper Tin	C	Arnberg, L., Jonsson, A., Westman, S.	Acta Chem. Scand., Ser.

Four alloy matches.

Cu64.00 Mg6.12 Sn29.88
Cu64.00 Mg6.12 Sn29.88
Cu64.00 Mg6.12 Sn29.88
Cu69.63 Sn30.37

Liberty Bell

Case 3

Bronze References

04-007-2188	I	Cu61.63 Sn38.37	Cu3 Sn	Copper Tin
04-007-9969	I	Cu61.63 Sn38.37	Cu6.75 Sn2.25	Copper Tin
01-071-7871	I	Cu62.26 Sn37.74	Cu3.02 Sn0.98	Copper Tin
00-026-0564	B	Cu64.09 Sn35.91	Cu10 Sn3	Copper Tin
01-071-7873	B	Cu64.09 Sn35.91	Cu10 Sn3	Copper Tin
04-007-2013	I	Cu64.09 Sn35.91	Cu10 Sn3	Copper Tin
01-071-0122	B	Cu65.50 Sn34.50	Sn11 Cu39	Copper Tin
04-003-1647	P	Cu65.50 Sn34.50	Cu3.12 Sn0.88	Copper Tin
04-007-1295	S	Cu66.29 Sn33.71	Cu40.4 Sn11	Copper Tin
00-031-0485	C	Cu66.34 Sn33.66	Cu40.5 Sn11	Copper Tin
00-031-0486	C	Cu66.34 Sn33.66	Cu81 Sn22	Copper Tin
01-071-0121	B	Cu66.34 Sn33.66	Sn11 Cu40.5	Copper Tin
00-030-0511	C	Cu66.59 Sn33.41	Cu327.92 Sn88.08	Copper Tin
00-030-0510	C	Cu66.62 Sn33.38	Cu41 Sn11	Copper Tin
01-071-7876	S	Cu66.62 Sn33.38	Cu41 Sn11	Copper Tin
01-071-7877	B	Cu66.62 Sn33.38	Cu41 Sn11	Copper Tin
04-004-2878	S	Cu67.91 Sn32.09	Cu41.5 Sn10.5	Copper Tin
01-071-0094	B	Cu69.63 Sn30.37	Cu51.68 Sn12.07	Copper Tin
00-017-0865	B	Cu74.99 Sn25.01	Cu5.6 Sn	Copper Tin
00-031-0487	B	Cu74.99 Sn25.01	Cu5.6 Sn	Copper Tin
01-071-7875	I	Cu75.21 Sn24.79	(Cu0.85 Sn0.15)	Copper Tin
04-007-3939	B	Cu76.68 Sn23.32	Cu0.86 Sn0.14	Copper Tin
04-001-1512	I	Cu82.81 Sn17.19	Cu0.9 Sn0.1	Copper Tin
04-007-7996	I	Cu84.41 Sn15.59	Cu0.91 Sn0.09	Copper Tin
04-003-2428	I	Cu86.03 Sn13.97	Cu0.92 Sn0.08	Copper Tin

There are several bronze phases, (alpha, beta, gamma) of similar composition within the Sn ranges, found in the Liberty Bell. This shows a few of them.

Closest Match (→ 01-071-0094)

From Cambridge University

Google Search:
http://www.msm.cam.ac.uk/phase-trans/2005/bell/bell.html

Metallurgy of Bronze Bells and Castings
H. K. D. H. Bhadeshia

Bronze used for making bells and gongs is essentially an alloy of copper and tin. Copper, containing about 22-24 wt% of tin, is often known as *bell metal,* because it has a pleasing sound quality when struck.

(Note: This citation was not in reference to the Liberty Bell, but elemental analyses of ancient gongs in Korea).

General Searches

Strategies

The prior examples assume that the user has a quantitative elemental analysis, so the preferred search mechanism is the composition search.

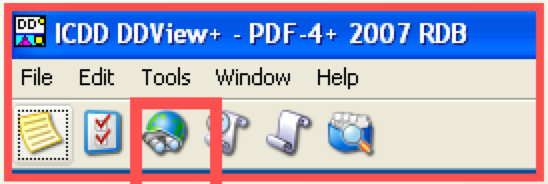
Qualitative analyses can also be used. In these cases, a general periodic table search is effective.

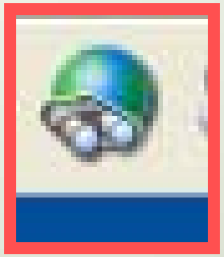
Semi-quantitative results might use combinations of the composition search with wide ESD's and a periodic table search and/or an elements search.

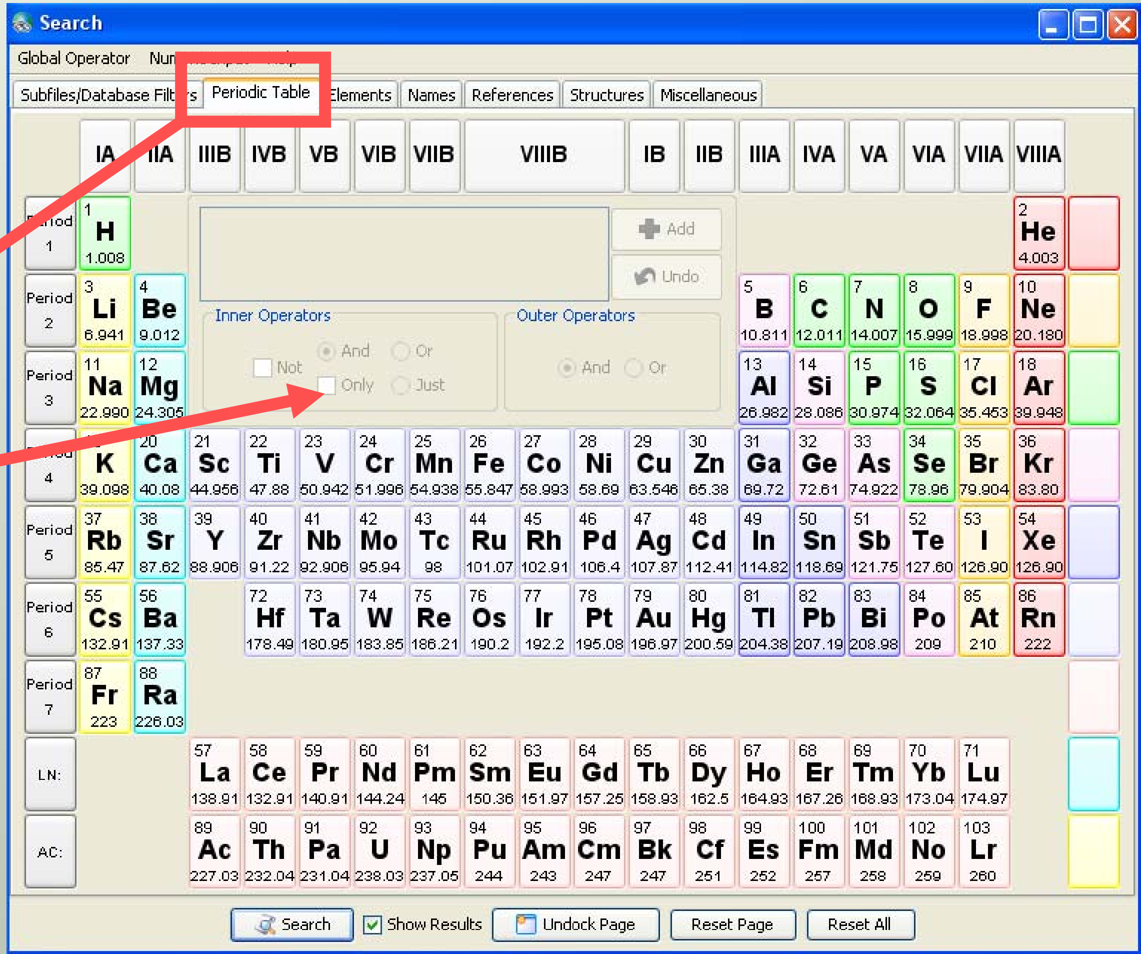
Any of the above searches can be combined with diffraction data for dramatically improved results – see the Advanced Identification Tutorial for details. The results of any elemental analysis search can be directly fed into the identification Programs, SIeve or SIeve+, as shown in the tutorial.

Periodic Table Search

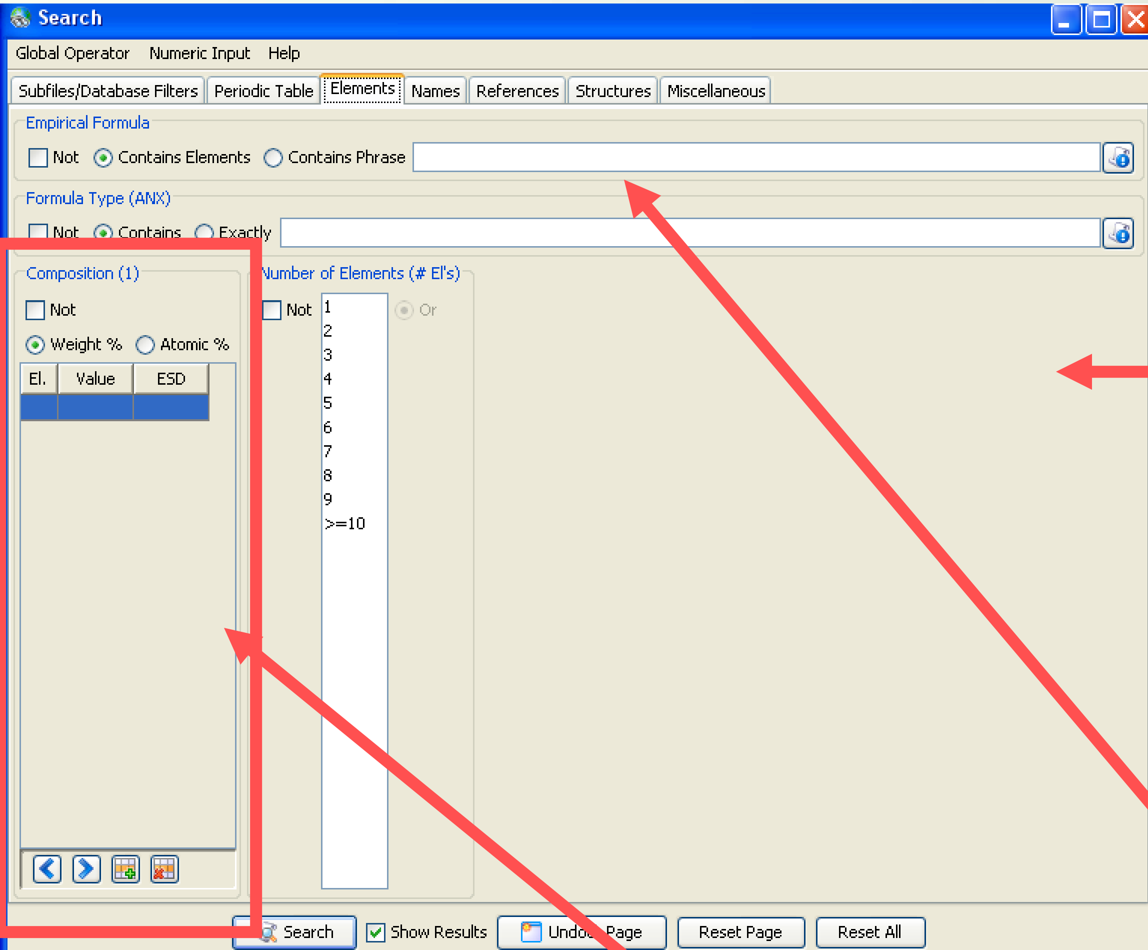
Click Search Icon From the Toolbar.
Click Periodic Table.







Elements Search



The number of elements selected for the search. For example, in Case 1 (meteor), 2 elements account for 98 wt% of the specimen. If 1 element was selected, only single elements would be considered. If 2 elements were selected, all binary alloys would be searched. If both 1 and 2 were selected, all combinations of elements and binary alloys would be searched.

If you have a candidate formula, as in Case 2, it can be searched here.

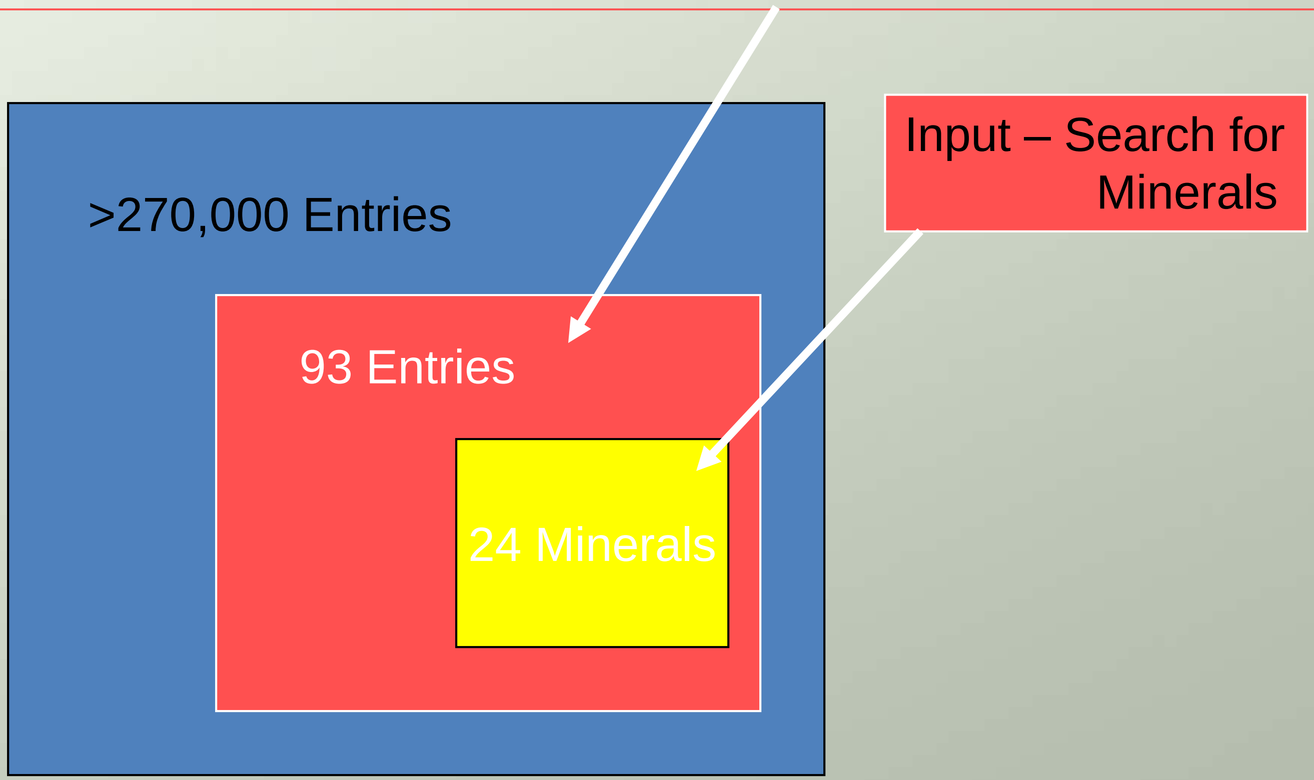
Composition Search – Shown in all 3 cases.

Case 1 Revisited

Assume Qualitative XRF Data

Input – Fe and Ni into the Periodic Table Search by point and clicking the elements

Input – All 1 and 2 element combinations (elements and binaries)



Case 1 Revisted

Qualitative XRF Data

QM	Weight %	Mineral Name ▲	SPGR
B	Ni100.00	Awaruite	Fm-3m
B	Fe24.08 Ni75.92	Awaruite	Pm-3m
I	Fe24.08 Ni75.92	Awaruite	Pm-3m
B	Fe48.76 Ni51.24	Kamacite	
O	Fe48.76 Ni51.24	Kamacite	P
S	Fe93.71 Ni6.29	Kamacite	Im-3m
B	Fe48.76 Ni51.24	Taenite	
O	Fe82.63 Ni17.37	Taenite	P4132
B	Fe60.82 Ni39.18	Taenite, syn	Fm-3m
B	Fe100.00	Taenite, syn	Fm-3m
S	Fe48.76 Ni51.24	Tetrataenite	Pm
I	Fe48.76 Ni51.24	Tetrataenite	Pm
O	Fe94.34 Ni5.66	Unnamed mineral (NR)	P
B	Fe94.37 Ni5.63	kamacite	Im-3m
B	Fe94.32 Ni5.68	kamacite	Im-3m
B	Fe94.14 Ni5.86	kamacite	Im-3m
B	Fe94.02 Ni5.98	kamacite	Im-3m
B	Fe93.52 Ni6.48	kamacite	Im-3m
I	Fe87.28 Ni12.72	kamacite	Im-3m
I	Fe83.67 Ni16.33	kamacite	Im-3m
I	Fe87.28 Ni12.72	taenite	Fm-3m
I	Fe83.67 Ni16.33	taenite	Fm-3m
I	Fe70.10 Ni29.90	taenite	Fm-3m
B	Fe48.76 Ni51.24	tetrataenite	P4/mmm

You now have 24 candidate materials in 8 mineral families (mineral name)

However, we also know the specimen is claimed to be from a meteorite!

Search for meteorites!

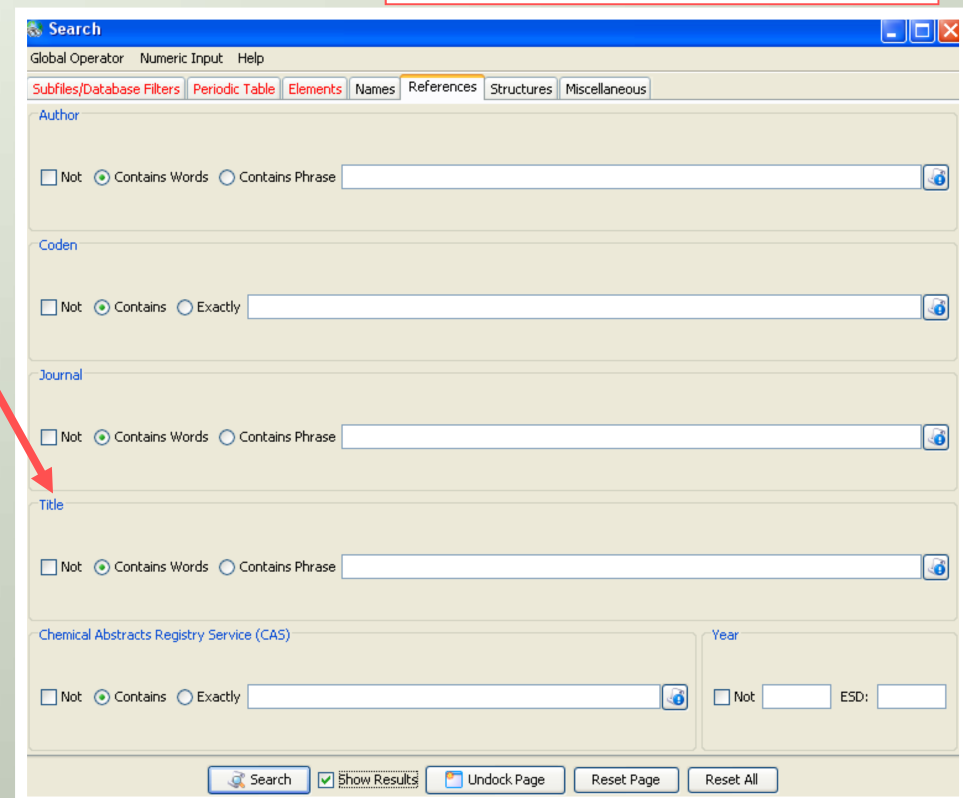
Case 1 Revisited

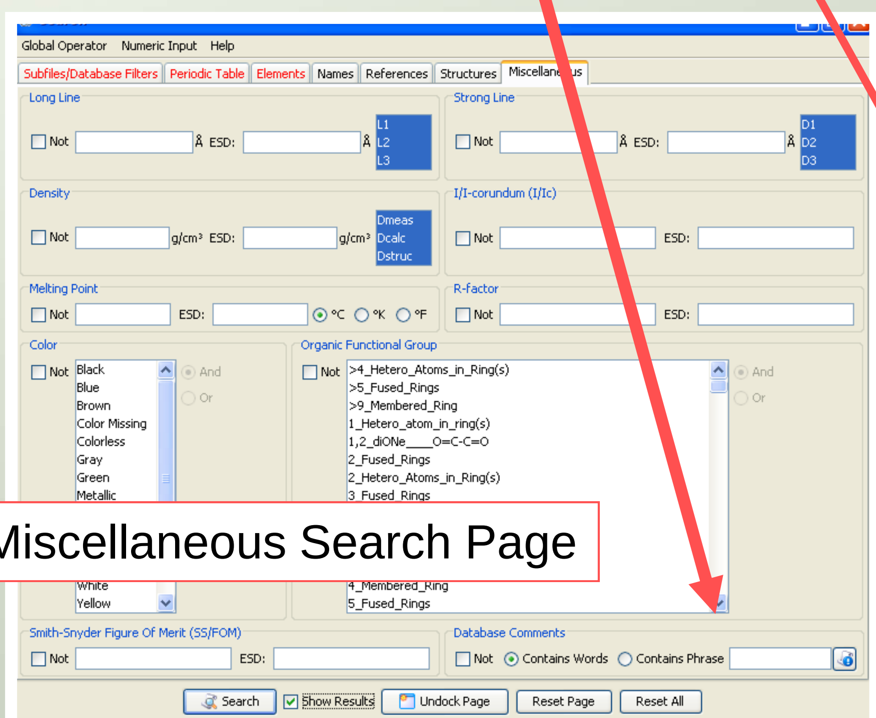
Qualitative XRF Data

Two good places to search for "meteorites":

- The title of the references
- The editors' comments (includes specimen details)

Reference Search Page





Miscellaneous Search Page

Case 1 Revisited

Qualitative XRF Data

- Searching “meteor” in the comment section finds 18 entries of Fe-Ni composition – and four minerals.
- Searching “meteor” in the title finds 13 entries of Fe-Ni composition and three mineral types – including taenite and kamacite.

Conclusions

Since the PDF is a collection of pure single phase materials, identification is enhanced when the specimen is phase pure. This means that this application improves with either XRF or SEM-EDS microanalysis.

The literature citations, reference histories, physical and chemical properties in the database, can all be used to cross reference with experimental elemental data to assist in material identification.

Thank you for viewing our tutorial.

Additional tutorials are available at the ICDD web site (www.icdd.com).

International Centre for Diffraction Data

12 Campus Boulevard

Newtown Square, PA 19073

Phone: 610.325.9814

Fax: 610.325.9823