Online Full Profile Search Match and the Crystallography Open Database

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The air quality is one of the major concerns for health. There is a need for continuous monitoring of the particulate especially in the submicron range. XRD is one of the principal techniques for the analysis of powders and fundamental to identify dangerous products. An European project named Nanoair has been concluded successfully which aim was to develop a mobile instrument for qualitative and quantitative analysis of breathable particles. The instrument uses XRD and SAXS for the characterization of the automatically collected samples.

Goal of the project and general idea

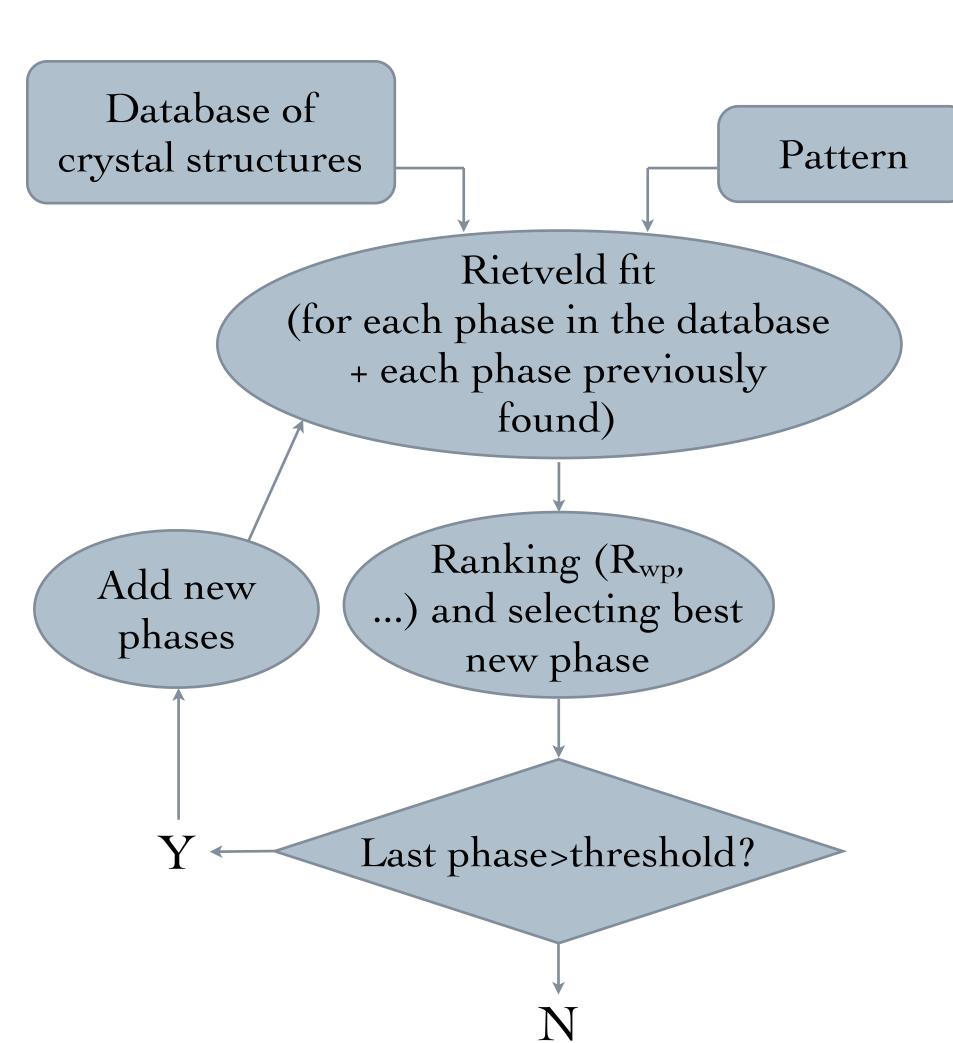
Build a complete portable system that collect the dust, analyses it in automatic to obtain particle sizes (by SAXS), phase identification and quantification along with crystallites/microstrains (by XRD) and finally store all data and results online and the samples locally for reference. For the XRD automatic analysis objective, we recognized:

- Actual search-match softwares require still human intervention to judge which phases are to be accepted or rejected after identification
- The only quantification method easily automatizable and reliable for such task is the Rietveld method but we are limited to the phases with a structure already refined (and deposited in one of the databases) unless also the PONKS method is used
- The idea is to use the Rietveld (+ PONKS) also for the search-match step (as we are in any case limited to phases usable in the Rietveld). A Full Pattern Search-Match method has been built and tested using the COD archive (imported to a local database) plus we can add specific phases missing if necessary. <u>COD: www.crystallography.net</u>

The method has been extended also to neutron and electron diffraction. A TOF neutron version is under testing.

The FPSM (Full Pattern Search-Match method)

Developed inside the Nanoair project



Pro:

- No user intervention, automatic analysis
- No peaks identification required (works with nano materials/particles
- Full Rietveld quantitative analysis provided
- Works for neutron and electron diffraction Cons:
- Only phases with know crystal structure are ready to be used (unknown structures require a list of peaks and calibrated intensities, PONKS)
- Available databases are still uncompleted
- If no elemental composition provided \rightarrow
- requires > 20 minutes on 12 cores computer
- Good ranking algorithm required for very small

	by L. Lutterotti using
	Zinc oxide, vol: 17.5
1	Zind Suda, Velt 43.9 Calcium fluoride, vol: 43.9 Aluminium oxide - alpha, vol: 38.5
	The "FPSM method" uses a Rietveld like fitting procedure to test all possible crystal structures
	from a Database, rank them and find the ones that more probable are present in your and the second second second diffraction pattern. In the end a quantification is done also with the phases identified. Be
	aware that if the phase is not present in the database (<u>COD</u> is used here), it cannot be found
	nor quantify; so this method is limited to only the phase for which a crystal structure has been determine and that has been uploaded to the <u>COD database</u> . This page has been constructed
	to permit other people to use the method and test it on their data. To use it you need to upload a datafile in proper format (use <u>.prn</u> , a double column format with no title line, first column
	contains the 2theta coordinate, the second column the intensity) . You need also to specify
	some additional instrument characteristics (wavelength, geometry etc.). If a proper instrumental broadening function is supplied (same format and specification as in the Maud
1	program), then a reasonable analysis of crystallite sizes and microstrain is reported.
	See paper: L. Lutterotti, H. Pilliere, C. Fontugne, P. Boullay, D. Chateigner (2012), in preparation.
1	
Diffr	action pattern and sample composition
-	d diffraction pattern: Choose File no file selected
Atomi	c elements in the sample: O AI Ca F Zn
🗆 San	nple nanocrystalline
Expe	rriment details
Radia	
	ay tube: Cu ≑ er ✓ x-ray Wavelength (Å): 1.540598
_	neutron
	gg-вленнано (meta-2theta)
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	nsmission
Instru	ment broadening function: Medium +
	Search and quantify
DISC	LAIMER
	ploaded file will not be stored locally in our server and is only kept in memory during the
Your	itation. We have nor space, nor interest on keeping your experimental data or results!
compu	
compu The Fl the da	PSM method will not be able to find a phase if it is not present in the database. At the moment tabase is constructed using all phases in the <u>COD</u> . So it is extremely important to contribute and e/upload crystal structures to the <u>COD</u> to make it more complete.



End: Final Rietveld quantification

phase amount

Further improvements:

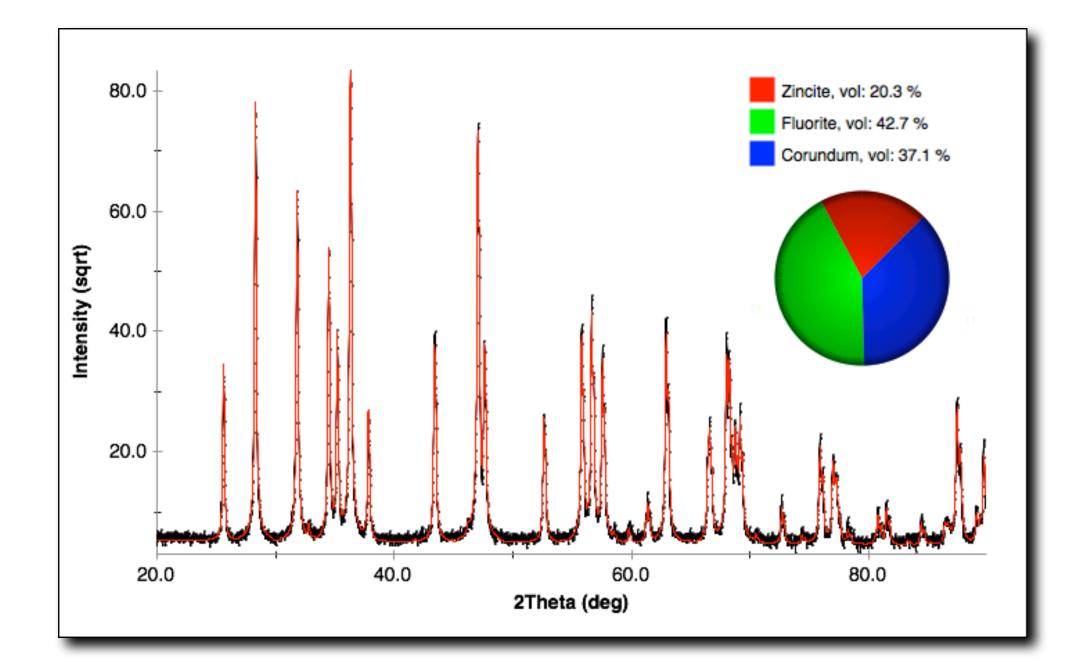
• Combination with fluorescence to remove

manual composition restriction

Two trial web pages have been setup online at: http://nanoair.ing.unitn.it:8080/sfpm http://cod.iutcaen.unicaen.fr/sfpm search and quantification is limited by proxy connection timelimit (few minutes) so it should be used restricting the composition as much as possible to speed up computation.

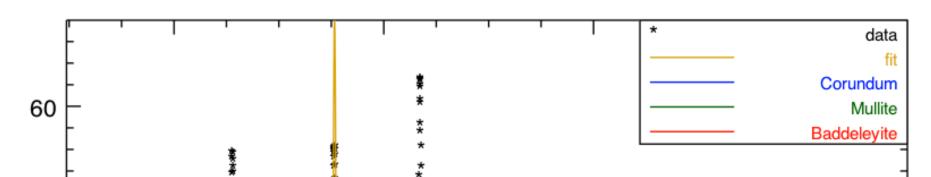
Testing FPSM using the COD

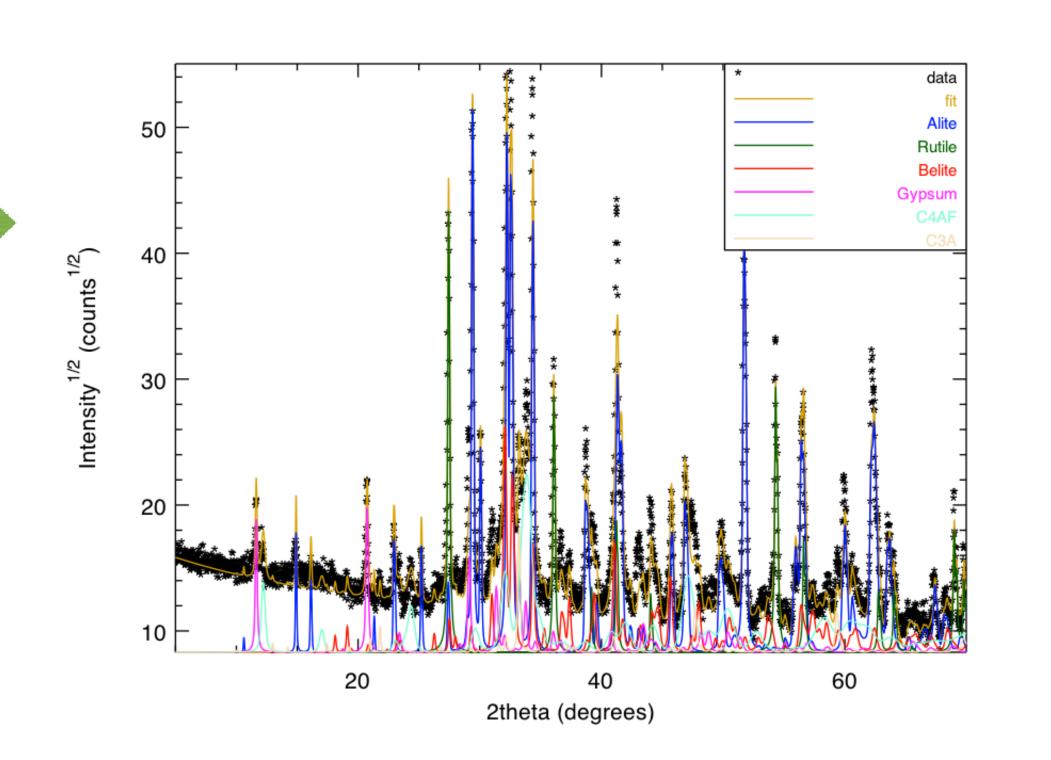
Sample cpd1h of Round-Robin on quantitative analysis http://www.iucr.org/resources/commissions/powder-diffraction/projects/qarr



Some additional phases (cement phases) has been added to the database as not present in the COD

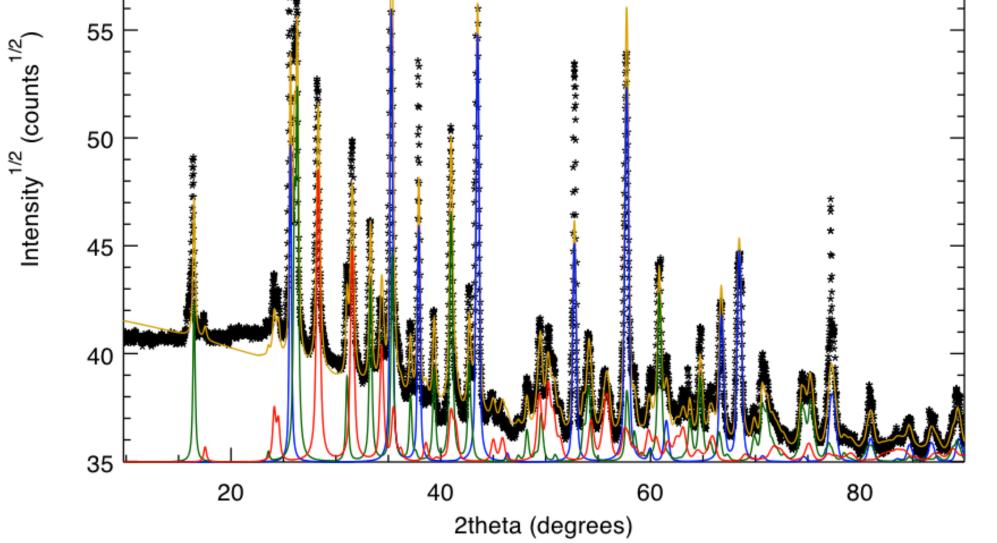
name	vol. (%)	wt. (%)	crystallites (Å)	microstrain	
	52.3359			0.000913623	
Rutile	8.7909	11.3199	1382.41	4.9784e-05	
Belite	14.6584	14.8578	1014.1	0.00145265	
Gypsum	7.28186	5.03503	881.992	0.00175863	
C4AF	14.4548	16.3939	485.795	0.00705494	
C3A	2.47814	2.27862	1426.2	0.00125916	





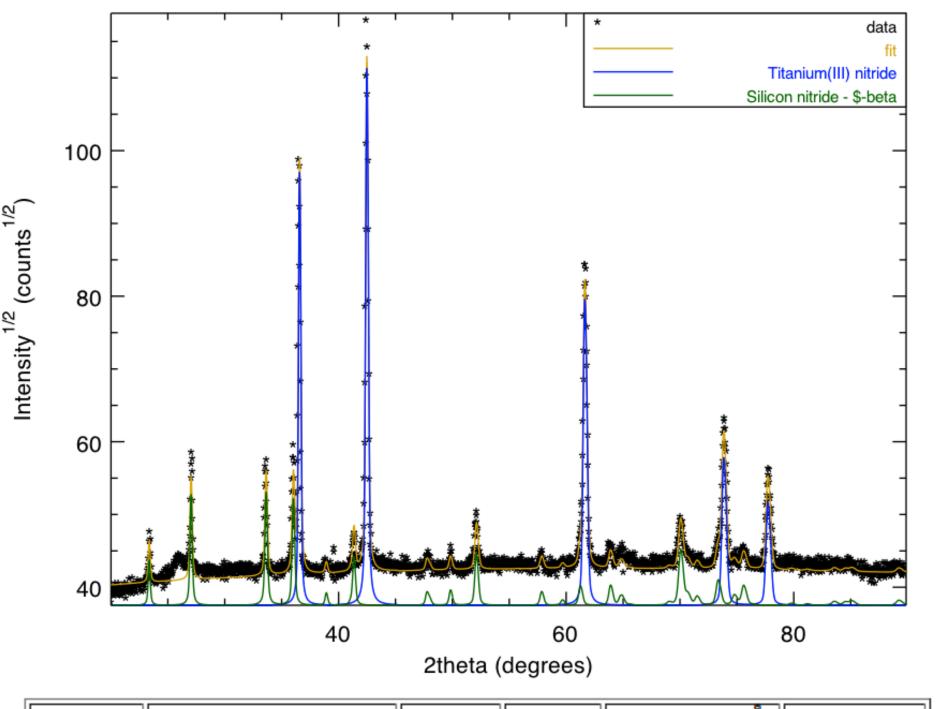
Phase (wt%)	FPSM	Round-Robin
ZnO	29.0	29.6
CaF	33.9	34.3
Al_2O_3	37.1	36.1

- Total computation time (12 cores, 2.93GHz, COD, inorganic):
- No composition restriction: 565 secs
- Only Al, Ca, F, Zn, O, Mg, Na, Si, Cl: 19 secs



Phase ID	name	vol. (%)	wt. (%)	crystallites (Å)	microstrain
<u>9009672</u>	Corundum	41.0726	45.1467	730.664	0.00137145
9005502	Mullite	53.5784	46.2318	515.483	0.000527227
9005833	Baddeleyite	5.34905	8.62151	371.805	0.00203445

Final Rietveld analysis, Rw: 0.0455532, GofF: 1.79502



Phase ID	name	vol. (%)	wt. (%)	crystallites (Å)	microstrain
1101045	Titanium(III) nitride	50.0729	62.8891	1682.09	0.00122093
1001246	Silicon nitride - \$-beta	49.9271	37.1109	800.99	0.00129495

Final Rietveld analysis, Rw: 0.0601521, GofF: 2.66024