Fundamental Parameters Initiative
International Initiative on X-ray Fundamental Parameters

Status updates and next steps

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And All Partners of The International Initiative on X-ray Fundamental Parameters

EXRS 2022 - June 27, 2022

www.EXSA.hu/fpi.php

Outlook

1. Summary of the FP initiative

2. DXC 2018

3. Eleventh FP workshop at U NOVA Lisbon, May 16-17, 2019

4. Virtual FP workshop, November 5-6, 2020

5. Virtual FP workshop, June 24, 2021

6. Future works

1. Summary of the Fundamental Parameters Initiative

Achievements & challenges

- ✓ **11 international workshops since 2008 (Europe/ USA/ Japan) (+ 2 in virtual format)**
- ✓ **> 100 participants (national metrology institutes, academic partners, industrial partners)**
- ✓ **joint generation of a comprehensive FP roadmap (updated in 2017)**

  literature database hosted by EXSA
- ✓ **> 25 Publications**
- ✓ **mutual cooperations in various joint projects (e.g. academic, EURAMET and industry)**
- ✓ **Web page: https://www.exsa.hu/news/?page_id=13**

- ✓ **validation of recent FP values (determined by either theory or experiments)**
- ✓ **establishment of a joint FP database**

1. Summary of the Fundamental Parameters Initiative
MOTIVATION

- **Fundamental parameters crucial for quantitative x-ray analysis**

✓ **Strong demand of users/companies from many application fields : innovative materials, environment, chemistry, etc.**

✓ **Data bases (tables) – reliability – uncertainties ?**

✓ **Lack of recent experimental values (few measurements performed > 30 years ago)**

- **Improvement of experimental facilities and methods**

✓ **Synchrotron radiation, high resolution detectors, improved electronics, improvement of calculation speed, ultra-thin free-standing foils**

1. Summary of the Fundamental Parameters Initiative

METHODOLOGICAL APPROACH

- **Initiate new measurements taking advantage of technical improvements**
- **Perform similar measurements in different institutes to establish reliabilty (mutual validation) and associated uncertainties of the experimental values**
- **Perform calculations for selected cases (use calculations for interpolations and validation purposes)**
- **Compare calculations to experiments**
- **Provide reliable practical tables to users**

Roadmap document on atomic Fundamental Parameters for X-ray methodologies

Version 2.0

December 2017

www.exsa.hu/news/wp-content/uploads/IIFP_Roadmap_V2.pdf

http://www.lnhb.fr/pdf/IIFP_Roadmap_V2.pdf

Contents

Expert group No.	1.	Starting event:	Nov. 2010
Topic title	Prioritisation of FP requirements		
Expert group leader	Chris Jeynes		
Contributing co-authors	Burkhard Beckhoff	Marie-Christine Lépy	
	Peter Brouwer	*and others*	

Detailed description of topic:
Fundamental parameters are insufficiently well-known across the whole range of the physical processes involved; progress in any (preferably all) of the following areas would be welcomed from various parts of the community : 1. Mass Absorption Coefficients 2. Fluorescence Yields 3. Relative Line Intensities 4. Chemical Effects 5. Electron Ionisation Cross-sections 6. Benchmarks

Description of status:
##1-3 are highest priority, then ##4-5 are also important. Benchmarks (#6) are highlighted as a way forward for establishing results 1. Absorption is fairly well-known for ~3-50 keV X-rays in many materials, but the database for soft X-rays is limited and the database is heavily extrapolated. 2. Fluorescence yields for soft X-rays (BeK-CaK and SiL-ZnL) are particularly problematical 3. Relative line intensities for soft X-rays (100eV - ~3keV) problematic. These are heavily affected by transition probabilities of both diagram and satellite lines, and cascade and Auger effects. M & N lines relatively (or completely) unknown. 4. Chemical effects are not known well at all and a survey is needed to indicate their importance. 5. Electron ionisations cross-sections are not known sufficiently well and are important both for secondary effects in photon and particle excitation. These are particularly important for treating tube spectra correctly. 6. We suggest that a "Benchmarking" approach may encourage an efficient validation of new results. These depend on the simulated and observed spectra from certified standards of various kinds being directly compared.

*4.3 **Summary** (needs to be discussed and reorganized)*

Detector type	Energy range	Energy resolution	Counting rate (s^{-1})	Advantages	Drawbacks
Ionization chamber	>8 keV	No	$>10^6$	transmission mode	weak linearity
Photodiode	1 eV to 60 keV	No	$>10^6$	can be calibrated, high stability, high linearity	No energy resolution, hence high order and stray light can disturb flux measurements
Proportional counter		Poor			
Flow and sealed detectors.					
Scintillator detector					
Si(Li) detector	1 to 30 keV	~140 eV @Mn-Kα	$<10^3$		Require cooling with liquid N2
SDD	1 to 30 keV	~130 eV @Mn-Kα	$<10^5$	No liquid nitrogen	Poor efficiency above 20 keV
CdTe					
HPGe					
Cryogenic detector	1 to 20 keV	1.2% at 1 keV and decreasing to 0.3 % at 20 keV	Less than 100 Hz to obtain good quality spectra.	High resolution in a wide range, ideal to study line ratios. Peaks are clean without tails.	Low count rate.

selected snapshots from the FP roadmap

www.exsa.hu/news/wp-content/uploads/IIFP_Roadmap_V2.pdf

'Prioritisation of FP requirements (energies, elements, uncertainties)'
Input generation for this topic section of a FP related road map,
C. Jeynes, U Surrey

FP priorities from different international X-ray instrument manufacturers:

We believe that the main requirement is a new and more accurate database of mass absorption coefficients. Currently our knowledge of these comes from published literature, with a nominal accuracy of:

- 2-5% in the range 2-3 keV
- 5-15% in the range 0.3-2 keV
- 15%+ in the range 0.1-0.3 keV

and higher errors likely in the vicinity of absorption edges.

We would like to see work on the energy range 100 eV – 3 keV, starting with Al and Si and continuing with Mg, P, S, then each element in turn, where it exists in a form which can be used at the experimental facilities.

At the last workshop the importance of a self-consistent database with wide range of energies and atomic numbers (but not necessarily very accurate data for special elements) was stressed. It is essential that blind samples can be analysed: for these a comprehensive database is needed to support an FP approach.

1. Set of data for L-shell excitation:
   - fluorescence yields for L1, L2 and L3 shell
   - Coster Kronig yields f12, f23, f13
   - jump ratios for L1, L2 and L3 shell
   - photoelectric cross sections (or photon mass attenuation coefficients) in the energy range between the L-l line and 1keV above the L1-shell excitation energy getting two values between L3 and L2 and between L2 and L1.

priority	item	range of interest		Desired uncertainty	Comments and some examples:
		atom (Z), shells	energy (keV)		
1	Mass absorption coefficients	All (1 - 83 (hopefully up to 95))	0.1- 60	< 1%	* For bulk sample analysis, relative mass absorption coefficients among elements are important in major element analysis and desired relative uncertainty is < 0.1%. * For thin film analysis using bulk standards, absolute values directly affect to the result and desired uncertainty is <1% in this case. * Chemical state dependency
2	Photo-electric cross section for each sub shell	ibid.	0.1- 60	<several percent	* Desired uncertainties for photoelectric cross sections and transition probabilities may be rather loose as far as calibrating line intensities empirically with actual instruments and pure (or known) specimens and line intensities can be taken as chemical-state-independent. * These are important for precise calculations of secondary excitation * Relatively large discrepancies between experimental and calculated intensities appeared in minor L and M lines. These discrepancy can be caused by both photo-electric cross sections and transition probabilities including radiative and C.-K. * Low energy lines strongly depend on chemical states (e.g. no intensity of Si-L line from SiO_2)

selected snapshots from the FP roadmap

www.exsa.hu/news/wp-content/uploads/IIFP_Roadmap_V2.pdf

International initiative on x-ray fundamental parameters

Tenth FP workshop - Round table discussion on FPs → input to FP roadmap

Are there any recommendations for the most reliable data bases ?

- **ionisation cross sections**

  (including sub-shell values) – *best:* recent experiments

  second-best: Scofield (Cullen) data

- **fluorescence yields and CK**

  transition probabilities – *best:* recent experiments, second-best: Krause data

- **line energies** – *best:* recent experiments, second-best: NIST phys. ref. data

Literature database (https://www.exsa.hu/?inh=636)

Fundamental Parameter Initiative
literature database

filter by keyword | filter by element | filter by author

Fundamental Parameters Related to Selenium Kα and Kβ Emission X-ray Spectra

M. Guerra, J.M. Sampaio, G.R. Vília, C.A. Godinho, D. Pinheiro, P. Amaro, J.P. Marques, J. Machado, P. Indelicato, F. Parente, J.P. Santos

Atoms **9**(1), 8, 2021

Overview and calculation of X-ray K-shell transition yields for comprehensive data libraries

L. Martins, P. Amaro, S. Pessanha, M. Guerra, J. Machado, M.L. Carvalho, J.P. Santos, P. Indelicato

X-Ray Spectrometry **49**(3), 398-423, 2020

Experimental determination of L fluorescence yields of gadolinium

Y. Ménesguen, M.-C. Lépy

X-Ray Spectrometry **49**(5), 596-602, 2020

Valence-to-core X-ray emission spectroscopy of titanium compounds using energy dispersive detectors

L. Miaja-Avila, G.C. O'Neil, Y.I. Joe, K.M. Morgan, J.W. Fowler, W.B. Doriese, B. Ganly, D. Lu, B.D. Ravel, D.S. Swetz, J.N. Ullom

X-Ray Spectrometry , 1-12, 2020

Diagram, valence-to-core, and hypersatellite K β X-ray transitions in metallic chromium

F. Zeeshan, J. Hoszowska, J.-C. Dousse, D. Sokaras, T.-C. Weng, R. Alonso-Mori, M. Kavčič, M. Guerra, J.M. Sampaio, F. Parente, P. Indelicato, J.P. Marques, J.P. Santos

X-Ray Spectrometry **48**, 351– 359, 2019

Fundamental Parameter Initiative
literature database

filter by keyword | filter by author

Gd - Gadolinium ✕

Experimental determination of L fluorescence yields of gadolinium

Y. Ménesguen, M.-C. Lépy

X-Ray Spectrometry **49**(5), 596-602, 2020

Precise x-ray energies of gadolinium determined by a combined experimental and theoretical approach

Y. Ménesguen, M.-C. Lépy, Y. Ito, M. Yamashita, S. Fukushima, M. Polasik, K. Słabkowska, Ł. Syrocki, E. Węder, P. Indelicato, J.P. Marques, J.M. Sampaio, M. Guerra, F. Parente, J.P. Santos

Journal of Quantitative Spectroscopy and Radiative Transfer **236**, 106585, 2019

Experimental determination of line energies, line widths and relative transition probabilities of the Gadolinium L x-ray emission spectrum

M.L. Wansleben, Y. Kayser, P. Hönicke, I. Holfelder, A. Wählisch, R. Unterumsberger, B. Beckhoff

Metrologia **56**(6), 065007, 2019

Examplary survey of new FP measurements: MAC values and Fluorescence yields

Z	Element	100→300 eV	300→1000 eV	1.0→3.0 keV	3.0→10 keV	10→30 keV	Fluorescence yield K	Fluorescence yield L	Intensity ratio Kβ/Kα	Intensity ratio L	μ, δ, β sur LNHB.fr		
1	H												
2	He												
3	Li												
4	Be												
5	B												
6	C						P						
7	N						P						
8	O						P						
9	F												
10	Ne												
11	Na												
12	Mg						P		F				
13	Al						P		F				
14	Si								F				
15	P												
16	S								S				
17	Cl								S				
18	Ar												
19	K								F				
20	Ca						P		P				
21	Sc								F				
22	Ti						L, P		L, P				
23	V						L, P		L, P, F				
24	Cr						P		P				
25	Mn												
26	Fe						L, P	(P)	L, P, F				
27	Co						L, P		L, P				
28	Ni						(L), P	P	P, F				
29	Cu						L, P		L, P, F				
30	Zn						L, P	(P)	L, P, F				
31	Ga						P	P	P				
32	Ge						L		F	F			
33	As												
34	Se												
35	Br												
36	Kr												
37	Rb												
38	Sr												
39	Y												
40	Zr							P					
41	Nb						L						
42	Mo							P					
43	Tc												

Z	Element	100→300	300→1000	1.0→3.0	3.0→10	10→30	Fluorescence yield		Intensity ratio		μ, δ, β sur LNHB.fr		
44	Ru												
45	Rh						L						
46	Pd							P					
47	Ag						P	P					
48	Cd												
49	In							P					
50	Sn							P (L)					
51	Sb												
52	Te												
53	I												
54	Xe												
55	Cs												
56	Ba												
57	La							P					
58	Ce												
59	Pr												
60	Nd												
61	Pm												
62	Sm												
63	Eu												
64	Gd							P					
65	Tb												
66	Dy												
67	Ho												
68	Er												
69	Tm												
70	Yb												
71	Lu												
72	Hf							P		F			
73	Ta												
74	W												
75	Re												
76	Os												
77	Ir												
78	Pt							P		F			
79	Au												
80	Hg												

PTB Data	LNHB data	On-going processing

F: Univ. Friburg, L= LNHB, P= PTB

Since EXRS 2018 ….

2. DXC 2018

3. Eleventh FP workshop at U NOVA Lisbon, May 16-17, 2019

4. Virtual FP workshop, November 5-6, 2020

5. Virtual FP workshop, June 24, 2021

The 67th annual Denver X-ray Conference will be held at the Westin Westminster Hotel, Westminster, Colorado, U.S.A. the week of 6 – 10 August 2018.

Attendees and exhibitors > 400 X-ray scientists, with 70% from USA

Included was a special session and open group discussion on *Advanced Fundamental Parameters*, which served as the annual meeting for the International Initiative on X-ray Fundamental Parameters.
Joel Ullom of NIST, USA served as Chair for the special interest group.

Exchanges with US experts and users

3. Summary of the Eleventh FP workshop at U NOVA Lisbon May 16 and 17, 2019

- **Joint session in the frame of QUANT'19 under the auspices of EXSA**
- **Dedicated FP workshop issues on May, 16-17**
  - **Session 4 - Scientific contributions**
  - **Round table (including presentations of the workshop participants)**
  - **Session 5 - Scientific contributions**
  - **Report on 2018 FP workshop at DXC (USA)**
  - **Objectives of the FP initiatives - Update of EG activities**
  - **Discussion on joint FP projects and fund raising**

4. Summary of the 2020 virtual workshop

Agenda (November 5-6, 2020)

- **2 sessions from 13:00 to 17:00 CET**
- **45-48 on-line participants (> 50 registered)**
- **15 20'talks of FPI partners**
- **Splitting into separate discussion groups:**
  - **- FP validation with reference to theoretical works**
  - **- FP validation with reference to experimental works**
  - **- FP validation with reference to application fields**
- **Joint discussion on IIFP perspectives and upcoming workshops**

→ online survey on proposals for joint collaborative activities after the workshop

5. Summary of the 2021 virtual FP workshop

Objectives of the 2021 virtual FP workshop

- **enhanced dissemination as part of the EXSA 2021 virtual conference**
- **updates on recent achievements in FP determinations**
- **special FP issue**
- **joint discussion on optimal strategies to validate recent FP values**
- **implementation of joint collaboration activities on FP validations**
- **strategies for the implementation of validated FP values in a database**
- **future activities and FP workshops**

5.2 Survey for future works

The **online survey** was open between the 2020 and the 2021 virtual FP workshops

5 proposals in different categories (1. theory, 2. experiments & 3. applications / CRM) were received to initiate joint collaborative works among FP initiative members

Workshop's goal:

- joint discussion of these 5 proposals
- identification of potential partners interested to contribute to these proposals
- definition of first working steps towards collaborative FP validation efforts

5.3 Action points to collaborative works proposal no. 1

proposer: **Marie-Christine Lépy, CEA-LNHB**

Priorities on methodologies: ***(1. ref. to theory ; 2. ref. to experiments ; 3. ref to applications or CRMs)***

1. **X-ray absorption, X-ray fluorescence, Radionuclide decay**
2. **X-ray fluorescence on same samples (fully characterized) – comparison / assessment of uncertainties**
3. **Quantification by XRF using standards - comparison with standardless methods**

Priorities on FPs to be validated:

1. **mass attenuation coefficients, fluorescence yields, Coster Kronig factors**
2. **K fluorescence yields of transition elements**
3. **assessment of fluorescence yields for transition metals (priority : 22<Z<29, Ti, Cr)**

Collaboration partners interested: **University NOVA Lisbon, PTB, and others**

5.4 Action points to collaborative works proposal no. 2

proposer: **Mauro Guerra, LIBPhys-UNL, Nova School of Science and Technology**

Priorities on methodologies: ***(1. ref. to theory ; 2. ref. to experiments ; 3. ref to applications or CRMs)***

1. **use of large scale Multiconfiguration Dirac Fock calculations for simulation of spectral profiles of high-resolution x-ray spectrometry.**

Priorities on FPs to be validated:

1. **line energies, widths, shapes, intensity ratios**

Collaboration partners interested: **NIST - Maryland and Boulder**

5.5 Action points to collaborative works proposal no. 3

proposer: Peter Brouwer, Malvern Panalytical, The Netherlands

Priorities on methodologies: ***(1. ref. to theory ; 2. ref. to experiments ; 3. ref to applications or CRMs)***

2. / 3. It would be very valuable to have a set of benchmark measurements on 'industrial' samples.

A set of samples is irradiated with a set of well defined monochromatic X-Ray beams and the spectra are recorded with calibrated detectors or intensities of specified spectral lines are recorded.

Priorities on FPs to be validated:

2. / 3. These measurements can be used to verify the combination of code and various FP parameters.

Collaboration partners interested: to be defined

5.6 Action points to collaborative works proposal no. 4

proposer: Csilla Szabo-Foster, NIST

Priorities on methodologies: ***(1. ref. to theory ; 2. ref. to experiments ; 3. ref to applications or CRMs)***

1. **MCDF calculations**
2. **Wavelength-dispersive spectroscopy (double crystal method) methods**
3. **Comparison of spectra of x-ray transitions acquired with different methods**

Priorities on FPs to be validated:

1. & 2. transition energies

3. x-ray transition energies

Collaboration partners interested: **University NOVA Lisbon, Laboratoire Kastler Brossel, NIST Boulder, University of Melbourne, University of Fribourg, and others**

5.7 Action points to collaborative works proposal no. 5

proposer: **Burkhard Beckhoff, PTB**

Priorities on methodologies: ***(1. ref. to theory ; 2. ref. to experiments ; 3. ref to applications or CRMs)***

1. **comparing theoretical calculation results with those achieved by reference-free X-ray spectrometry**
2. **reference-free (high-resolution) X-ray spectrometry based upon calibrated instrumentation**
3. **investigation of certified reference materials or well-known samples by means of reference-free XRF**

Priorities on FPs to be validated:

1. & 2. ionization and scattering cross sections, fluorescence yields, transition and CK probabilities

3. fluorescence production cross sections

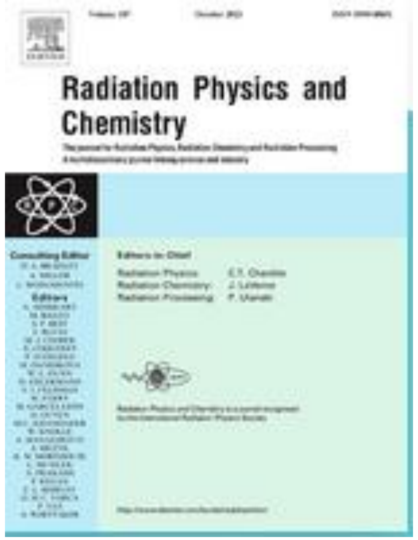
Collaboration partners interested: **Univ. NOVA Lisbon, LNHB, NIST, Universities Fribourg & Surrey, others**

5.8 Special FP Issue in Radiation Physics and Chemistry (M. Guerra)

Goal of the special issue on FP:

1. Reflections of the multiple interactions and synergy between research groups, metrology institutes and companies on a global level; in particular among members of the FP initiative
2. Enhanced visibility of the FP initiative for gathering new members that can expand or improve our outreach with respect to economic, environmental, scientific and societal challenges

- commitment of several key persons in the field to submit high quality works to this special issue
- further FP partners are more than welcome to submit manuscripts



Guest editors:
Mauro Guerra, Burkhard Beckhoff, Marie-Christine Lépy and José Paulo Santos

6. Recent and upcoming activities

- Collaborative works (proposal 3 ; some overlap with proposals 1 and 5) involving several XRF instrument manufacturers and institutes in 2022 – experiment on well-known sample with well-known instrumental parameters
- LNHB and PTB consider to host a FP follow-up workshop in 2023
- FP determinations within EURAMET metrology partnership program project on 'Operando battery metrology' 21GRD01 - Sept. 22 stakeholder meeting

Meet us for a coffee at EXRS 2022 for further discussions.

www.EXSA.hu/fpi.php