International initiative on X-ray fundamental parameters

Roadmap document on atomic Fundamental Parameters for X-ray methodologies

Version 1.0

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Introduction

In a world were global challenges like the energy problem, environmental protection, hunger in overpopulated but economically less developed areas must be addressed, we need new solutions based on sound scientific foundations. A small but still very important contribution may be our ability to characterize new materials, and therein chemical and structural (in a wider sense) analysis by X-rays. Indeed, X-ray measurements already form the basis of an ever-increasing number of areas as varied as medical technology, renewable energy, semiconductor fabrication, law enforcement and planetary exploration. However, pushing the limits of X-ray technology requires a critical assessment and evaluation of available data related to the interactions of X-rays with matter (“fundamental parameters”).

The lack of recent reliable values with low associated uncertainties was pointed out during the European X-Ray Spectrometry conference (EXRS2008) held in June 2008 in Cavtat (Croatia). Here, within the framework of the European X-ray Spectrometry Association (EXSA), a common initiative was proposed by Physikalisch-Technische Bundesanstalt (PTB, Germany) LNE/Laboratoire National Henri Becquerel (France) and Technology University Wien (Austria) to overcome the uneven quality and incompleteness of current X-ray fundamental parameters which constitute a serious limitation for further progress of X-ray technologies.

The International Workshop on X-ray Fundamental Parameters started as an expression of common interest in the improvement of x-ray fundamental parameters by companies, university laboratories, and metrology institutions. It brings together industrial equipment developers as well as individuals directly involved in X-ray metrology experiments, theory, and computation. Its goal is to assess/evaluate the available data and, based on the evaluation results, to establish accurate critical data for common use in calibrating instruments and by all the workers in the field. It should also stimulate both new measurements and new calculations of the fundamental parameters with reduced relative uncertainties, taking advantage of modern technologies. As the most promising approach for this purpose, dedicated experimental determinations of selected fundamental parameters of interest combined with interpolations between these values by means of theoretical values derived by new calculations has been identified.

Under the auspices of EXSA, the new international initiative was immediately supported by the major manufacturers that were present as well as by three worldwide renowned metrology-institutions in Germany (PTB), France (LNE), and the US (NIST).

As a first step, a workshop was organized in Paris in October 2008, with the aim to have joint discussions involving theoretical experts, users, experimentalists, and industrial companies interested in such a subject. The workshop was attended by 29 participants from the 3 national metrology institutes, 8 industrial companies and 10 research institutions. Participants discussed the relevance of fundamental parameters in X-ray technology and applications, the status of FP compilations, and the present state of the art in related theory. Six working groups were created to cover topics from the reliability of computer codes to the accuracy of measured intensities and energies.

The second workshop was held in May 2009 in Berlin at PTB and attracted 43 participants from 3 national metrology institutes, 9 research institutes and 6 industrial companies. At this workshop, the established expert groups reported to the audience their initial findings under their specific domains and provided short assessment reports. Prioritization of FP requirements and other topics as reported by expert groups were discussed. The current status of data related to X-ray energies, relative intensities, fluorescence and Coster-Kronig probabilities was presented. Critical review of the available X-ray absorption data bases was given.

The third workshop was again held in Paris, on November 2010 with 30 attendees. Like in the previous meeting, the expert groups reported their work. Moreover, in spite of the difficult economic situation, and to avoid just talking instead of acting, it was proposed to start on a small scale with some more modest support from the manufacturers and existing experimental facilities, and a smaller list of high priorities. This initiative within the initiative lead to the meeting of a small but resolute group gathering LNE, PTB, Fribourg and Kyoto Universities and three industrial companies.

The fourth workshop was organized in Gaithersburg (USA) in July 2011, with about 30 participants, where the initiative entered a new dimension, as a step towards a very global project. The expert group reports were followed by a session devoted to statements of needs and competences from new attendees mainly from US and Japan. As a result of previous workshops, expert groups were revised to reflect completion of some tasks and realignment of others.

The expert group meetings during the FP workshops lead to the roadmap document compiled here, following mostly a pre-defined template where applicable. This document is supposed to be used as a reference document in financial applications aiming at FP determinations. It is expected to be updated by the FP initiative in its new expert group structure.

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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.

Relevance of topic:

Commercial users of XRF or EPMA or PIXE often have samples for which an FP approach is the only feasible one. Currently, almost the only critical applications of XRF/EPMA/PIXE use the relative method, where results are compared to known or certified standards. We very badly need to be able to do critical work on a much wider range of samples, and this entails use of FP.

This Expert Group has apparently come to the conclusion that the lack of knowledge of FP is particularly crucial in the low energy range, where the databases either have no data or have very unreliable data. However, critical work is hardly possible for many types of sample also at higher energies.

Needs and/or aim for improvements: (see "Relevance")

- see section on ‚Relevance‘ and supplemenatry information on industrial FP priorities
- perform dedicated experiments at points of interest where the theoretical data compilations differ significantly in order to decide on the reliability of calculations
- compensation for the growing lack of reference materials on the nanoscale

Methods and objectives for improvements: (see "Relevance")

Clearly, piecemeal projects will be started by interested users as funds become available. Every opportunity should be seized to extend other projects to allow sufficiently accurate measurements to be made in particular cases to allow contribution to FP knowledge.

Constraints for improvements

Allocation of experimental time or beamtime at large scale facilities; external funding to ensure skilled manpower; support to improve the necessary instrumentation and experimental methodology to reveal well-known uncertainty budgets.

Innovations, novel concepts and/or potential

- Calibrated and high-resolution instrumentation can contribute to reduced relative uncertainties of selected FPs
- Cross-checks by independent experiments probing the same FPs can contribute to the reliability of FPs
- New kind of very thin one-elemental or compound samples can provide access to FPs that could not be investigated so far in a reliable manner.

Perspectives

There are a variety of different communities served by these data, including benchtop XRF, Sy-XRF, EPMA, SEM-EDX, PIXE. Of these only PIXE has access to simultaneous complementary and quantitative data (particle scattering: Rutherford backscattering etc). This may allow useful cross-checking and benchmarking for critical work, since RBS measurements critically justified at 1% appears to be possible.

The variety of the community with respect to methods, samples, and analytical needs means that a systematic approach to development of the FP database is hardly feasible without massive investment, and every opportunity should be taken to push knowledge forward in particular cases of interest. If the big picture is borne in mind then the cases "of interest" will tend to favour regions of more FP interest, too.

International FP initiative - Expert Group 2 on 'Experimental facilities"

Updated report – Status on June 10th, 2012

Participants:
Jean-Claude Dousse (Univ. Fribourg)
Dan Horoaba (BAM) : no reply
Joanna Hoszowska (Univ. Fribourg)
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Matthias Müller (PTB)
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Contents:

1. Instrumentation for measuring fundamental parameters

Depending on the measured parameter, the instrumental equipment requires three main elements:

- An excitation source (photons or charged particles) to produce initial ionization
- A sample to be studied
- A detecting system to analyze resulting photon emission

Moreover, the measurement experimental conditions should be accurately characterized in terms of excitation and detection solid angle, sample characteristics (composition, thickness, etc) detection efficiency, energy and composition (harmonics) of the incident radiation

2. Excitation sources

2.1 X-ray sources

2.1.1 Radioactive sources

Radionuclides decay according to different modes; in particular, electron capture produces a vacancy in the inner shell that is followed by atomic rearrangement and consecutive X-ray emission. Moreover, most of the first decay steps lead to excited nuclear states, and ground state is reached through gamma transitions, that means either gamma or conversion electron emission; in the last case, as for electron capture, the atomic rearrangement produces characteristic X-rays of the daughter nuclide. Note that the latter can be used either as excitation photon beams or to directly measure transition energies and relative intensities or linewidths.

2.1.2 X-ray tubes

In traditional X-ray tubes, the initial step is electrons extraction from the heated cathode and acceleration towards an anode where they can produce ionization. Consequently, the resulting photon flux is the superposition of continuous component due to the electron scattering in the anode (Bremsstrahlung) and characteristic X-rays of the atomic rearrangement consecutive to the initial ionization.
These tubes are generally used as primary source of excitation, either with the whole energy range, or to produce secondary X-rays using a filter.
X-ray tubes can also be used with a monochromator (see section 2.5.1) to select a specific photon energy.

2.1.3 Synchrotron radiation

In the storage ring of a synchrotron facility, high energy electrons (or positrons) are moving on a circular orbit, thus consequently, emit continuous X-ray radiation tangentially to the electron path.
The intensity of the synchrotron beam is several orders of magnitude higher than the one of conventional X-ray tubes, thus it can be highly monochromatized and collimated.
Synchrotron radiation produced from bending magnets has a continuous energy spectrum, whereas insertions devices (wigglers or undulators) dramatically increase the emitted photon flux, however with a periodic energy structure.
For the last two types of sources, the initial photon flux is generally checked using a monitoring system (flux counter).

2.2 Electron sources

Electron excitation is provided through a setup rather similar to an X-ray tube, as the electrons are produced in a heated cathode, and accelerated by a high voltage.
A stable electron source requires stabilized filament current and high voltage supply and high vacuum.

2.3 Protons or charged particles sources

X-ray work based on particle ionization uses mostly proton beams in the MeV energy region, produced in electrostatic accelerators or in cyclotrons. Applications work focus mostly in the

1 to 3 MeV energy region. Apart from these application cores, both fundamental as well as applications can be found using alpha particles and proton beams below 1 MeV or up to 65 MeV. Although rare, fundamental work involving highly ionized heavy ions can also be found using high energy accelerators.

2.4 Summary

Source type	Energy range	Intensity	Advantages	Drawbacks
Radionuclide	Specific-depending on the nuclide	Depending on the nuclide activity	Compact	Half-life, radioprotection
X-ray tube	Soft and hard X-ray range	medium	compact, commercial available	Limited flux, high divergence
Synchrotron radiation	IR – hard X-rays	High	Intense Directional Polarized	Allocation of beam time
Electron sources	Min 0.1 keV Max 300 keV		Adjustment of the emissive thickness with the electron energy	Charge effects Bremsstrahlung
Charged particle sources	0.1 to 100 MeV	High	Very low background radiation and high ionization cross-sections	Experimental data regarding ionization cross-sections presents large scattering in some energy regions.

2.5 Optical systems

2.5.1 Monochromating optics

Crystals
Gratings
Multilayers

2.5.2 Collimating systems

Two-slit systems
Soller-slit collimators
(Poly)capillary optics
Parabolic X-ray mirrors
Parabolic (1- or 2- dimensional) X-ray multilayer optics

2.5.3 Focusing systems

(Poly)capillary optics

These can be used to focus the X-ray beam in order to increase the photon flux on a selected area of the sample to be analyzed. For a kind of capillary, this increase gain is generally restricted to the limited energy range for which it has been designed.

Fresnel-zone plates
Refractive lenses

Kirkpatrick-Baez system
Bent crystals
Spherical, cylindrical and toroidal X-ray mirrors
Elliptical (1- or 2- dimensional) X-ray multilayer optics

2.5.4 Spectral shapers
X-ray mirrors

3. Samples

As fundamental parameters are concerned, it is necessary to carefully select the target to be used.
It is necessary to determine:

- phase and state of material,
- purity,
- thickness
- roughness
- homogeneity
- radiation resistance

Reflectometers can be used to characterize some samples in terms of homogeneity, roughness. Standard reference or certified reference materials are available; however, complex structures or innovative materials with nanoscale structure can be hardly characterized at the metrological level.

4. Detecting system

4.1 Energy dispersive spectrometers

4.1.1 Semi-conductor detector
Si(Li) : typical detector – energy range - resolution
SDD : new type of detector with easy use – no necessity of N2 cooling – reduced energy range due to restricted thickness – ultimate resolution :
CdTe detectors.
Ge detectors.

4.1.2 Scintillation detectors.

4.1.3 Cryogenic detectors- bolometers
TES detectors

4.2 Wavelength dispersive spectrometers

4.2.1 Curved crystal spectrometers in reflection (Bragg case)
Johann-type
Johansson-type
Von Hamos-type

4.2.2 Curved crystal spectrometers in transmission (Laue case)
Cauchois-type
DuMond-type

4.2.3 Plane crystal spectrometers
    One crystal
    Two crystals (dispersive or non-dispersive setups)

4.2.4 Spherical grating spectrometers
    soft X-ray range

4.2.5 Associated detectors
    Photographic films
    Flow and sealed gas detectors (ionization chambers, proportional counters)
    Scintillation detectors
    Semiconductor detectors
    Position sensitive detectors
    Cryogenic radiometers

*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.

In the case of the flat-field spectrometers where the detector is fixed and the spectrum obtained in 1D or 2D without motion of the dispersive element, the detection system can be a CCD camera (2D) or a multi-channel plate (MCP, 1D).

5. Experimental arrangement for specific measurements

In the long run, priorization procedures to identify best practices are to be defined for measuring the different FPs

5.1 Binding and transition energies

Non-monochromatic excitation sources can be used. The detection system for the emitted fluorescence radiation should provide a high resolving power (~1000) and a well-known response behavior. State-of-the-art experimental arrangements are described in [15.

5.2 Transition probabilities

In the case of K shell transitions a non-monochromatic excitation source can be used. In the case of L shell and M shell transitions monochromatic sources are required for a selective excitation of the sub shells. The detection system for the emitted fluorescence radiation should provide at least a resolving power of 300. It has to be characterized in view of its response behavior and the energy dependence of the detection efficiency.
State-of-the-art experimental arrangements are described in [14, 16].

The high resolution high energy PIXE setup of ITN having a TES based cryogenic x-ray detector is a very good tool for line ratios studies since most of the x-ray lines can be separated in an easy way and there are no problems of differences in detection geometry or differences in detection yields due to polarization of the radiation.

5.3 Attenuation coefficients

A state-of-the art of the experimental conditions for measuring mass attenuation coefficients has been given by Creagh *et al.* [23]. This was produced in the frame of an IUCR X-ray attenuation project. They present several experimental configurations used for the measurement of attenuation coefficients. Recommended experimental procedures concern:

Sample thickness that should be such that 2 <=Ln(I0/I) <=4 for optimizing statistical counting
Geometrical requirements including collimation
Use of energy-dispersive detector

Thus the critical element is the target and the measurement of its composition and thickness.

5.3 Fluorescence yields

There are two recent approaches to measure fluorescence yields. Both approaches employing monochromatized X-rays for the excitation of the samples. The first approach is an extension of the conventional measurement setup where the target is installed at the entrance of the energy dispersive detector. The ionization, and consequent fluorescence, is produced by an X-ray beam imaging on the target with normal incidence. Both the transmitted primary beam and fluorescence radiation are recorded by the ED detector [24] and can be quantified according to the detector efficiency.

An alternative approach is the use of calibrated instrumentation to measure the intensity of the fluorescence radiation emitted by thin (10-90% transmittance) free-standing foils absolutely [10]. This approach was developed to measure the fluorescence yields of light elements where the approximation that the relative scattering contribution (known from calculations) is employed to the MACs. The attenuation of thin foils can be directly measured and used to substitute the photo-electric cross sections in Sherman's equation. The advantage of this methodology is the independence of reference measurements relying on tabulated fluorescence cross sections (e.g. commonly Fe K is used as a reference). In general, this approach could be also used for higher X-ray energies by using theoretical ratios of scattering and photo-electric cross sections.

To measure sub shell fluorescence yields one have to determine the Coster-Kronig factors first, because of the rearrangement of the initial L or M vacancy over the sub shells.

5.4 Coster-Kronig Factors

There are two different methods to determine Coster-Kronig (CK) factors. Both methods use monochromatized synchrotron radiation for a selective excitation of the sub shells involved. The first method is based on the measurement of the Auger electrons emitted during the CK transition, an example can be found in [24]. The second method is based on the measurement of the emitted fluorescence radiation and the transmission of the sample for the exciting X-ray energies. The transmission measurements can be used to derive the partial photo-electric cross sections relatively, which are needed for a normalization of the measured fluorescence intensities to the number of initially produced vacancies in each sub shell. More details on the method can be found in [Phd thesis M. Müller].

Standard reference measuring conditions are assumed to be required for this measurements.

5.5 Natural linewidth

The work [26] show a methodology to derive reliable values.

Standard reference measuring conditions are assumed to be required for this measurements.

This should not depend on the excitation source

The instrumental energy resolution should be comparable to the natural linewidth.

Precise determination of the instrumental response function is needed.

Nonlifetime linewidth broadenings should be considered.

6. Specific instruments

The list of specific instruments is to be completed based on external input that is very welcome.

PTB: three UHV chambers for reference-free XRF experiments in variable beam geometries supporting sample sizes from 10x10 mm^2 up to 300 mm wafers, calibrated detectors (photo diodes, SDDs, Si(Li)s and spherical grating spectrometer), monochromatized synchrotron radiation provided by three different beamlines: undulator beamline (78 to 1860 eV), dipole beamline (1.7 to 10.5 keV) and wavelength shifter beamline (8 – 50 keV). Details can be found in [1-14].

University Pierre et Marie Curie (Paris): IRIS : high spectral resolution x-ray spectrometer, working with bent crystal (Johann type) and electron excitation [15].

University of Fribourg (Laue-type Dumond bent crystal spectrometer, Bragg-type von Hamos bent crystal spectrometer) [16-17] http://physics.unifr.ch/

PANALYTICAL : X-ray tubes, detectors, optics

LNE-LNHB : SOLEX – Tunable monochromatic X-ray source [18]

ITN HRHE-PIXE setup – High resolution cryogenic x-ray detector EDS based spectrometer.
University of Guelph: accelerator providing protons up to 3 MeV energy. State-of-the-art Si(Li) and SDD detectors are available. The accel. is equipped with four beam lines: (1) a conventional broad-beam PIXE facility; (2) an older micro-PIXE facility with 5-10 micron spot size; (3) a state-of-the-art OMB nuclear microprobe; (4) an external beam milli-PIXE facility. it is item (2) that we shall use for the K fluorescence yield work. We have already used item (1) to improve the cross-section database for PIXE analysis.

University of Surrey Ion Beam Centre: We have 0.5 – 4 MeV protons (1H) or 0.5 – 6 MeV 4He excitation, with EDX (Si:Li, 140 eV resolution) but independent absolute quantitation with RBS (Rutherford backscattering spectrometry) and/or EBS (elastic backscattering spectrometry, that is, non-Rutherford). Scattering cross-sections for RBS are screened Coulomb, and known to < 0.3% typically; scattering cross-sections for EBS are evaluated in many important cases, and known to <5% typically.
The depth range of PIXE/RBS/EBS self-consistent analysis is not more than 20 microns, but layered samples in this thickness range can be unambiguously and accurately characterised with good depth resolution. PIXE has a lower energy cutoff around Na, but light element matrices can be characterised with RBS/EBS (and also nuclear techniques including PIGE – particle induced gamma emission). H can also be measured directly with He-ERD.

7. Tables of available facilities

These following tables are to be completed based on external input that is very welcome

	X-ray source			
Laboratory	**Type**	**Energy range**	**Flux**	**Energy resolution**
LNHB	Radionuclides			
LNHB	Monochromatic X-ray source SOLEX	Some 100 eV to 20 keV	10^2 to 10^4 photons /s	~1:1000
LNHB	SOLEIL Monochromatized radiation or white beam	Some 100 eV to 35 keV	10^9 to 10^{11} photons /s	~1:2000
University of Guelph	Accelerator (protons)	3 MeV		
PTB	Monochromatized synchrotron radiation (BESSY II)	78 eV to 50 keV	10^9 to 10^{11} photons /s	~1:2000

	Sample characterization			
Laboratory	**Type**	**Z range**	**Thickness**	**Methodologies**
PTB	Mass deposition, elemental composition, depth profiling, chemical speciation	B to U	Sub-monolayer to several µm	reference-free XRF, TXRF and GIXRF as well as NEXAFS

	Spectrometer			
Laboratory	**Type**	**Energy range**	**Energy resolution**	**Typical application**
University Pierre et Marie Curie	Johann-type bent crystal spectrometer	150-500 eV 500-3000eV	1 eV $\Delta E/E \approx 10^{-4}$	Valence band studies
University of Fribourg	Laue-type Dumond bent crystal spectrometer	> 11 keV	$\triangle E/E \sim 5 \cdot 10^{-5} \cdot \cot(\vartheta_{Bragg})$ (e.g. 7 eV @ 20 keV)	In-house x-ray metrology of x-ray transitions.
University of Fribourg	Bragg-type von Hamos bent crystal spectrometer	0.55-16.8 keV	$\triangle E/E \sim 5x10^{-4}$ (~0.8-8 eV)	Metrology of x-ray transitions, fundamental and applied atomic physics (in-house and at external facilities).
PTB	calibrated spherical grating spectrometer	0.1 to 1.7 keV	$\triangle E/E \sim 2x10^{-3}$	XES, FP determination

	ED Detector			
Laboratory	**Type**	**Energy range**	**Energy resolution**	
LNHB	Semi-conductor			
ITN	TES based cryogenic x-ray detector			
University of Guelph	`State-of-the-art Si(Li) and SDD detectors`			
PTB	Silicon drift detector	0.1 to 20 keV	125eV@Mn-Kα	windowless, calibrated efficiency and response behavior

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Expert group No.	*3.*	**Starting event:**	May 2009
Topic title	Theory & codes – challenges: competent use and update of existing software		
Expert group leader	Andreas Karydas		
Contributing co-authors	Stjepko Fazinić	Paul Indelicato	
	and others		

Detailed description of topic:

- To compile available codes (free/commercial/restrictions,etc.) and to identify which FP's can be computed (including element/energy ranges)
- To define inherent limitations to available codes in terms of the physical model incorporated (need to incorporate solid state phenomena)
- To define which FP's must be computed (difficult/impossible to measure)
- To define key FP's for certain element/energy ranges to be used to assess the reliability of codes by means of comparison with available or updated experimental data
- To assess uncertainty budgets for the complied theoretical data.To propose upgrades in existed software's (for example to extend the original energy/elemental range, improve FP's data bases).

Description of status:

- The widely used up to now theoretical data of FP's such as the photo-ionization cross sections [Scofield] have been based on the frozen core (FC) approximation with no explicit description of multiple ionization processes.
- Many FP's related with the x-ray emission process, particularly with intra-shell transitions, but also the photo-ionization cross sections in the neighbourhood of absorption edges are crucially affected by solid state phenomena not accounted for properly by existing codes.
- Theoretical FP's are inevitable in many energy/element range due to lacik of experimental dataSimulation codes fail to describe second order processes leading to fluorescence emission due to lack of reliable or incomplete data bases for certain FP's (electron ionization cross section close to absorption edges etc)

Relevance of topic:

Reliability of standard-free and/or reference-free quantification in XRF requires more accurate theoretical based or tabulated FP's to account for single or secondary processes that lead to the emission of characteristic x-rays by single atoms or materials.

Needs and/or aim for improvements:

- Accurate description of x-ray emission spectra, requires the incorporation of multiple ionization processes (shake off/up's), cascade x-ray emission etc, by means of more advanced models (etc the relaxed core (RC) approximation).
- Solid state phenomena have significant contribution in photo-ionization or de-excitation processes, especially in the soft x-ray energy region, but not incorporated up to now in the most of the codes, except of very elaborated one like the MCDF ones (multi-configuration irac-Fock). Systematic carefully selected comparisons among experimental and theoretical data are

required to assess direction for improvements.

Methods and objectives for improvements:

- Mapping of available advanced codes and systematic comparison among calculated FP's for certain "reference" elements and energy regions.
- Experiments of improved methodology and precision for the measurement and thus for the definition of "reference" experimental FP's to be used for codes validation. Cross checking among different set-ups is highly suggested.
- Different simulation codes need to be implemented to account for fluorescence emission from materials, in cases where secondary excitation phenomena play an important role. Customized simulation codes that allow incorporation of FP data defined or modified by the user need to be developed for an independent assessment.
- Well designed experiments are required in order to provide insight to secondary excitation phenomena and validate simulation codes.The final objective is to assess based on selected low uncertainty experimental data the reliability of existing or customized theoretical or simulation codes.

Constraints for improvements

- The generation of theoretical data requires a lot of human effort, whereas simulation data is a time consuming procedure. Careful selection of 'reference' cases is required.
- High precision and low uncertainty experimental data require advanced analytical methodology
- Even in large scale facilities the allocated beam time for basic study of FP's is rather restricted and it is only performed in conjunction to support advanced characterization of materials.

Innovations, novel concepts and/or potential

The detailed description of x-ray emission spectra including multi-ionization processes and solid state phenomena appear to have high importance in the quantitative soft x-ray analysis.

Advanced theoretical MCDF based codes need to be extensively validated

Customized simulation codes may overcome inherent restrictions imposed by widely used packages optimizing thus their predictions.Reference or standards free FP oriented advanced experiments need to be prioritized at large scale facilities.

Networking and mobility among theorists or theorists and experimentalists will better address current needs.

Perspectives

- To produce 'reference' set of theoretical/experimental FP'sTo improve and optimise networking among theorists/experimentalists

Expert group No.	4	**Starting event:**	Jan. 2011
Topic title	Compilations		
Expert group leader	J.L. Campbell		
Contributing co-authors	P. Caussin		

Detailed description of topic:

The fundamental parameters (FP) approach to X-ray fluorescence analysis demands an extensive database from the field of atomic physics. The oft-heard and facile observation that such databases are well-established is incorrect. Such databases are founded largely upon compilations of measured data. Compilers need to probe into observed inconsistencies and to assess the impact of methodological differences, and to take a critical and selective approach. They should recognize that different approaches may actually measure different quantities. In situations where the values to be recommended by such compilations require interpolations, the latter should be guided but not dominated by theory. An example of an XRF database is that of Elam et al (2002), which has been the starting point for this document.

Description of status:

Expert Group 4 has presented two detailed reports on the status and usefulness of existing compilations; these reports have been published by the International Radiation Physics Society. Out of that detailed work grow recommendations to (i) extend and improve existing compilations: (ii) create new ones, (iii) undertake new experimental and theoretical projects to improve unsatisfactory situations revealed in our reports. This document will not reproduce the detail of the earlier reports. References will be found in our first report.

References:

J.L. Campbell, IRPS Bulletin 24 (1), 17-30 (2010)

P. Caussin, IRPS Bulletin 24 (2), 12-16 (2010)

Relevance of topic

The Fundamental Parameters approach to XRF analysis is of growing importance in an era when new materials are appearing faster than analytical standards can be devised, prepared and certified. Even in the absence of such rapid change, the value of the FP approach in terms of turnaround time of analysis is manifest, given the absence of need for standards. Moreover, the same FPs that are basic to XRF analysis are important in other areas such as radiation transport, radiation protection, medical physics, and many other radiation applications in industry, security, etc.

Needs and/or aim for improvements:

Four sub-areas are addressed here

1. Binding (edge) energies and X-ray energies

Earlier compilations, some of which were subsets of others, were superseded by the NIST compilation of Deslattes (2003). That work chose a small set of high-precision ($\Delta E/E=10^{-6}$–10^{-7}) measurements of absolute X-ray energies at limited Z-values as the starting point. Weighted averages of earlier tabulated values which had good precision but lacked absolute calibration were incorporated, with care taken to translate them to the new scale. Sophisticated DF theory was employed as a means of interpolation in Z. There remain gaps in K and L experimental data in the $50<Z<80$ region and in L data at low energies; these need to be addressed. Moreover, this work covers only K and L X-rays (and edges), whereas XRF now demands use of M X-rays. The NIST compilation should be extended in this regard, using internally derived M, N, binding energies and published outer shell binding energies. Second order processes merit attention. To take one example, the shake-up process in copper (closed 3d shell) creates 3d holes whose interaction with the core 2p or 3p hole results in a plethora of Kα and Kβ satellites; in lighter elements, the open 3d shell complicates matters further. Such satellites could in principle be represented by a small set of equivalent lines of defined energy.

The above work is somewhat academic if X-ray energy shifts due to chemical bonding are neglected. NIST's extensive X-ray photo-electron spectroscopy database, based on critical evaluation of published literature, has 22000 entries, including chemical shifts of binding energies. However, it is a significant step from there to a manageable tool that can be applied to an extended Deslattes X-ray energy database in order to correct it according to the particular chemical compounds that may exist within an XRF sample.

2. Relative Intensities (RIs) of X-rays within the K, L and M series:

2.1 K X-rays: The Elam database relied upon one compilation of data done at the very outset of the Si(Li) and Ge spectrometry era. Experimental work in that era supports the RI predictions of Scofield's DF theory. The necessary interpolations in Scofield were done years ago. However, questions must be addressed before a tabulation is prepared. Should the following be added: (i) shake satellites, (ii) radiative Auger satellites? If the answer is "yes", then quick compilations are needed to indicate and focus the necessary experimental work which needs to follow. Such work is addressed also in section 1 above.

2.2 L X-rays: As with the K shell, the predictions of Scofield's DF approach appear to be good in the medium- and high-Z regions, although measured data are far fewer. A simple compilation comparing Elam's 2002 numbers with Scofield DF predictions plus newer measured data would be helpful in assessing potential improvement. The low-Z region is largely unexplored experimentally and therefore demands attention.

2.3 M X-rays: The growing need to utilize M X-rays in XRF calls for an improvement in their RIs over the empirical database of Elam et al. But there are no Scofield-type DF predictions, only limited earlier DHS ones. ED X-ray spectroscopy at these low energies (< 4 keV) has been insufficiently sophisticated to provide these data. Further, it is not clear that there is merit in experimental and theoretical attempts to do, because their use in XRF would be confounded by our lack of knowledge of the M subshell fluorescence and Coster-Kronig probabilities – see 3.3 below.

Finally, at very low atomic numbers, fluorescence yields are modified by chemical bonding. Therefore RIs must also be affected. Little is known here.

3. Fluorescence and Coster-Kronig probabilities

3.1 K shell (ω_K): Recent compilations largely reflect the earlier Krause and Bambynek compilations. A divergence between these for $20<Z<30$ was resolved in 2010 at LHB. Accordingly the tabulation used in the Elam database, which is based upon an erroneous paper that was subsequently withdrawn, should be replaced by that of Bambynek. Bambynek's recommended values agree closely with the DHS theoretical predictions of Chen et al.

Neverthless, there remain issues at Z< 20 where data are sparse and mostly rather old. Does the Walters&Bhalla HS theory provide a description? – more accurate experimental data are needed for low-Z atoms. Significant chemical bonding effects on ω_K are predicted and some have been measured, but clarity does not exist.

3.2 L subshells (ω_i and f_{ij}). Recent compilations reveal major problems. Many data are old, and there is wide scatter, especially for the L1 subshell. Regions around discontinuities lack sufficient data to define them. Trends appear that may suggest method-dependency. The older KX-LX coincidence method does not address the L1 subshell. The newer synchrotron method can do so, but it requires assumptions about near-edge (L1, L2, L3) behaviour of photo-electric cross-sections, and the corresponding theory has not matured sufficiently that it can reliably describe these; indeed using simple DHS PE cross-sections from Scofield induces a model-dependence which may not be justified.

3.3 M subshells (15 parameters!). Although predictions and measurements do exist, we are very far from a clear picture. The measurements are in an X-ray energy region where it only now that we are understanding Si detector response and efficiency; and all such measurements have neglected the significant contribution of the Lorentzian profile to lineshapes.

4. Attenuation coefficients and Interaction Cross-Sections

4.1 Attenuation coefficients

Several experimental compilations and theoretical tabulations exist. Some are several decades old. Some provide parameterizations. Our published graphical comparison (Caussin), now extended, shows their differences, mostly in the 100eV to 1000eV (all Z) and Z < 6 or Z > 90 (all energies) regions. There are also differences in the vicinity of edges, some caused by interpolation errors, other caused by disagreement over jump ratios or simply overlooked edges. All of these works neglect near-edge structures. Two major theoretical works (Scofield, Chantler) are widely cited and their predictions can be accessed on NIST's website. These (independent-particle model) predictions do not differ greatly but they do differ. All of these works neglect near-edge structures arising from collective effects in photo-ionization.

4.2 Photo-electric cross-sections

These dominate the attenuation coefficients. They are also pertinent to synchrotron determination of L fluorescence and CK yields, where it is clear that they need refinement to handle collective electron effects.

4.3 Compton and Rayleigh cross-sections:

These are useful in XRF for determining sample thickness and for quantifying content of invisible elements having Z < 10. Hubbell's NIST tables from 1975 and also within EPDL97 give theoretical values based on computational wavefunctions.

Modern S-matrix calculations underlie the RTAB database at Lawrence Livermore Lab., but there is no analogous tabulation for the Compton cross-sections. Necessary small corrections to both were recently indicated by Prof. Pratt and colleagues.

5. Level widths and X-ray natural widths

The 2001 compilation of Campbell and Papp was forced to use very old data in several regions.

Experimental work at Fribourg suggests that the compilation requires updating.

Methods and objectives for improvements:

1.1 Edge energies and X-ray energies:

1.1A Deslattes' own values for outer subshell binding energies can be deduced from the existing database. Photo-electron spectroscopy values of binding energies can be obtained from a literature survey and used to refine the values used, and hence obtain the desired M X-ray energies.

1.1B: New high-precision experimental determinations of X-ray energies are needed in the areas of atomic number where gaps exist.

1.1 C: The second objective may be aided by use of the very extensive tables of Cauchois and Sénémaud (Pergamon,1978), which would require a lot of work to convert to digital format.

1.1D: New high-precision experiments are needed to delineate configuration interaction and shake satellites (especially in atoms with open 3d shell) and to find simple representations that describe them by a small number of equivalent lines.

1.2 Chemical effects on binding energies: Following Papp's proposal, five areas of work are proposed: (i) Experimental electron spectrometry measurements on chemical compounds; (ii) comparison of results with the NIST XPS database; (iii) data analysis and interpretation using Mulliken's fractional charge concept from Chemistry;(iv) parameterization of binding energies versus fractional charge; (v) construction of an easily used database that will be a modifier of the extended Deslattes database. Before that work commences, it would be useful to derive from the NIST PES database and other sources a limited tabulation that shows the magnitude of the effects involved, and thus limits the necessary workload.

2.1 K X-ray relative intensities: Experimental work appears necessary to improve our knowledge of CI and shake satellites; this is the essentially the same work as proposed in 1.1D above. Similar work is needed to improve our knowledge of radiative Auger satellites, especially the KMM case, and to find appropriate representations within the database. Von Hamos spectrometry appears to be a promising approach. Emerging high-resolution detector technologies can contribute.

2.2 L1, L2 and L3 X-ray RIs: New systematic experiments are needed at low Z. Recent observation at PTB of 30% discrepancies from Scofield's Ll/Lα ratio for nickel shows one approach. Emerging high-resolution detector technologies can contribute here.

2.3 M1,M2, M3, M4 and M5 X-ray RIs: See 3.3 below.

3.1 K fluorescence yield: Highly accurate experiments are needed at Z< 20; in their data analysis, these must not assume values for other FPs, a weakness of many published works. Both experimental and theoretical work is needed to determine the systematics of the influence of chemical bonding. (Some of the published experimental work appears to be of dubious value)

3.2 L subshell fluorescence and CK yields: While the addition of WD spectroscopy has significantly improved the synchrotron photo-ionization method of Jitschin, careful thought is needed regarding how the data are processed to extract Coster-Kronig probabilities. Supportive theoretical work on collective electron effects when the absorbed photon energy is near an absorption edge is urgently necessary to support existing synchrotron work.

Papp suggests electron-electron coincidence experiments, conceding that this new generation of work would take time and effort. A revival of Campbell's 1975 method of L conversion electron – L X-ray coincidences, with the conversion electrons well-resolved in a $\pi\sqrt{2}$ magnetic spectrometer may merit serious thought as a means of exploring the L1 shell. The ability to compare two different approaches would be valuable.

But even if one of these avenues provides improved FPs, their use in XRF will be problematic until the photo-electric cross-sections are also improved. Advances in both directions are needed. Therefore, Papp proposes an interim practical solution, pertinent to industrial XRF as follows. Conduct experiments in the style of the synchrotron experiments of Jitschin, Dousse and others, but with different excitation sources than a synchrotron; use, for example, filtered Mo and Rh X-ray tubes; process the data assuming Scofield's PE cross-sections; extract values for ω_i and f_{ij}. The combined set of PE cross-sections and extracted parameters will constitute a practical, empirical database for that analysis approach. The parameters will not be regarded as FPs and will not be compared with theory; they will not even be compound parameters; instead they will be practical parameters (PPs).

3.3 M subshell fluorescence and CK yields

Experiments to separate 5 subshells are just too difficult to contemplate, since they involve not only 15 ω_i and f_{ij} values, but also the RIs for each of the 5 subshells. And if PE cross-sections are to be invoked in these experiments, then we have a repeat of the issues that are problematic in the L-shell situation. Therefore we have a proposal similar but not identical to that of Papp's in the L-shell case. One would simply measure M X-ray production spectra from thin foils, excited by either (i) several monoenergetic lines; or (ii) widely used excitation setups such as filtered Rh and Mo tubes; then fit the spectra and extract several ("effective") line energies and intensities; deduce line production cross-sections. Because of the low energies, excellent QA would be needed regarding detection efficiency and lineshape. There is no attempt here to determine FPs. The approach produces PPs.

4. Attenuation coefficients and Photo-electric cross-sections

4.1 Attenuation coefficient measurements

There seems little point in making any new tabulations of old attenuation coefficient data. Given improved technology, it would be valuable to undertake multi-laboratory determinations of attenuation coefficients, including detailed attention to near-edge structures, for selected elements of importance. However, if old history is not to be repeated, it will be essential that the advice of previous experts such as Gerward and Creagh be followed in such work, and that similar previous exercises such as that of the International Union of Crystallography are examined first..

4.2 Theoretical work on near-edge structure

On the theoretical front, new attempts are needed to understand how collective effects introduce near-edge structure in PE cross-sections. Such new and improved PE cross-sections could be added to theoretical Rayleigh and Compton cross-sections to produce a new theoretical attenuation coefficient tabulation.

Comparison of the outcomes of 4.1 and 4.2 would help to refine progress on both fronts.

4.3 Compton and Rayleigh cross-sections

A major effort should be undertaken to create an extensive tabulation of modern theoretical Compton differential cross-sections, analogous to the existing Rayleigh database RTAB.

5. Level widths and X-ray natural widths

The Campbell and Papp compilation of 2001 needs to be updated in light of new experimental data. Further measurements are needed to replace 60-year old data.

Constraints for improvements

Recognition by funding agencies that there is a need to make significant improvements in the database for XRF analysis.

Recognition by industry that there is value in making significant improvements in the database for XRF analysis.

Efficient coordination of international collaborative projects, including arrangements of PhD projects.

Access to major facilities.

Funding for equipment, supplies, personnel and travel.

Rigorous characterization of X-ray detectors as regards lineshape and efficiency (consequently continued progress in the study of detector response by measurement and simulation).

Acceptance of the need for rigorous quality assurance of experimental work.

Innovations, novel concepts and/or potential

These are present at various points in the material above.

Perspectives

- The existing large XRF-related database is the product of very many small research groups, often somewhat isolated, with their own biases – often without sufficient QA - hence the distressing spread in compiled data. This was the 20th century approach.
- A **small** amount of further compilation will be useful but we must shift attention away from poring over old data.
- We are now in a new century.
- We have new excitation and detection technologies.
- We have vastly greater computation capacity.
- Future thrust must be one of coordinated research groups with strong QA, and coordinated comparisons among results of these groups.

Expert group No.	*5.*	**Starting event:**	May 2009
Topic title	Technical Terms		
Expert group leader	Burkhard Beckhoff		
Contributing co-authors	Terrence Jach	Marie-Christine Lépy	

Detailed description of topic:

- Definition and clarification of the usage of technical terms.
- To destinguish between instrumental and fundamental parameters
- To destinguish between atomic, derived and compound fundamental parameters
- To indicate the basic definition of uncertainties
- To quote related committees and documents
- To provide the translation of relevant FP terms to major languages

Description of status:

- Conventional XRF quantification does not always destinguish correctly between instrumental and fundamental parameters (reason: use of 'normalized intensities')
- Literature indications do often not clearly distinguish between atomic, derived and compound fundamental parameters (reason: experimental separation of access)
- Each atomic fundamental parameter should be characterized by its value and its associated standard uncertainty [GUM]. References: GUM: Guide to the expression of Uncertainty in Measurement ISO, 1993

Relevance of topic:

- Reliability of standard-free and/or reference-free quantification in XRF requires to distinguish instrumental / experimental parameters from fundamental parameters
- Usage of derived or compound fundamental parameters may lead to restrictions

Needs and/or aim for improvements:

- Identification of derived or compound fundamental parameters
- Representation of all parameters by means of atomic fundamental parameters
- Translation of terms into major languages

Methods and objectives for improvements:

- Identification of derived or compound fundamental parameters by relevant experts in the field and internal committee works aiming on agreement on definitions
- Representation of all parameters by means of atomic fundamental parameters involving relevant experts and internal committee works
- Translation of terms into major languages by native speaking experts

Constraints for improvements

- Potentially different expertise in adjacent fields of methodology and/or application, e.g. photon versus particle induced x-ray emission spectroscopy
- Potentially different expertise in existing committes of various organisations such as IUPAC, ICRC, ISO, IAEA, and VAMAS
- Lack of appropriate communication channels into adjacent communities and committees

Innovations, novel concepts and/or potential

- Survey on definitions of atomic, derived and compound fundamental parameters• Classification of literature values as atomic, derived and compound values
- Road-map generation on relevant achievements and intententions
- Posting of road-map on NMI or EXSA website as a reference for FP publications and external communication channels

Perspectives

- Input generation to adjacent scientific comunities
- Input generation to external committees of different organizations
- Updates of FP road-map part on technical terms

Expert group No.	*6.*	**Starting event:**	May 2009
Topic title	Establishment of common data base accessible to the public		
Expert group leader	Michael Mantler		
Contributing co-authors			

Objectives:

– All data obtained under the terms of this initiative should be published (copyright issues tbc)
– The recommendations of Group 4 for the characterization of new experimental as well as theoretical data and assignment of proper uncertainty budgets should be taken into account.
– The data may be published:
- in journals
- the EXSA-web page
- the individual web-pages of the participants of the projects.

Input request to contributors of the FP initiative:

This input request addresses all members of the Fundamental Parameter Initiative who have measured and/or collected values of fundamental parameters and are willing to share these data with other members.

At this point “sharing the data” should be understood as making them accessible via the password-protected web pages of EXSA under the copyright-restrictions imposed by the authors/owners.
Such data can be anything within the scope of the FP initiative and include individual new values obtained by experimental and/or theoretical methods, any type of collections of original published of unpublished data, “best values” obtained by evaluation of existing data or fitting methods (including fit coefficients or software routines). Also any hints to literature are welcome, personal experience about their application, digitized literature data, software that extracts data from collections, comparative presentations of data from different sources, etc.
However, in order to avoid any legal conflicts, the colleagues providing such data should be in the possession of eventually existing copy rights and make clear under which conditions the data can be used by members of the initiative (classified as “internal use within the initiative”) or distributed the outside world (unclassified, with proper references,).
Please send me just a short message describing the data and providing all key information (as far as applicable) such as:

- A short title (e.g., “Mass attenuation coefficients for Si, 1-3 keV”).
- Author(s), related publication(s), short description of data range, date and method of determination, etc.
- Copyright owner and restrictions; conditions for distribution.
- Size of data file(s); in case of printed material please indicate number of pages and print quality (fit for OCR?).
- URL as far as download links exists.

Supplementary information of expert group 1

LNE Sharing a passion for progress TU VIENNA PTB EXSA

International initiative on X-ray fundamental parameters

‘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.
    - preferred element range : Zn to U
    - high priority elements: Sn, Sb, Ba, Hf, Ta, W, Pt, Au, Pb
2. Photoelectric cross sections (or photon mass attenuation coefficients) in the energy range between 0.5keV and 3keV :
    - preferred absorbers: Mg, Al, Si, Ca, 3d elements, Sn, Sb, Hf , Bi

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 SiO2)
3	Transition probabilities (radiative, C.K., Auger)	All, L,M,N	down to 0.1keV transition	< 1% for high energy < several percent for low energy including for minor lines	
4	Photon energies of characteristic emission	All, L,M,N	especially low energy		*Energy variation by chemical state such as S-Ka and Kb in S compounds. * Energy table of minor M lines and N lines are desired, such as Ba-MiiNiv(?) interference to Na-Ka.
5	Differential cross section of coherent /incoherent scattering of photon	All, especially light elements down to H	5 - 40	< 1%	* Differential cross section of coherent and incoherent scattering are used for estimating non-measuring elements (H,C,O..) for quant analysis of composition and thickness.
6	Electron ionization cross section for each sub shell			< several percent	* Both of elastic and inelastic scattering cross sections are desired. * These are utilized for the calculations of tube spectra and the secondary excitations by photoelectrons and Auger electrons.

Expert group No.		**Starting event:**	
Topic title	*X-ray energies in chemical states for FP*		
Expert group leader	*Tibor Papp*		
Contributing co-authors	*John A. Maxwell*		

Detailed description of topic:

The x-ray energies can vary with varying chemical states in the energy range of 10 eV. The general x-ray detectors and evaluation methods are sensitive to a 1eV. Therefore overcrowded peaks in a spectrum limit the sensitivity of the Fundamental Parameter method and x-ray analysis. Even in a simple spectrum, having the majority elements x-ray peaks shifted will skew the energy calibration and will make the lower energy peaks being misrepresented. On the other hand there are a large number of possible chemical compound and a database need to be manageable.

In the world of chemists there are several approaches to establish the fractional state. One approach what we have studied and found useful is to categorize the binding energies via the Mulliken charge.

Although there is a binding energy database managed by NIST, in this context it has very limited use. The data is not evaluated, it is a collection. It is limited to a few eV range.

Therefore a large set of measurements is necessary. There are several electron spectrometers operating in the range on 10eV to 10keV. Therefore from the same measurements binding energies of the atomic shells can be measured. It can be related to a few characteristic x-ray line excitation, for example Cu Ka1 and Ag Ka1 lines, covering the range of 10 eV to 20 keV.

The emphasis is on the FP point of view here, to establish a manageable approach. Our vision is that an approach where the chemical state parameter is also fitted and add a correction to the x-ray energies would make the FP a robust method. For example if the model assumption is that the fractional charge is x on one of the component of a binary compound, then the fractional charge on the other component would be (1-x).

Description of status:

We have tested the concept of using the Mulliken charge on two elements, and obtained satisfactory results.

We have access to such electron spectrometers, and upon financing an other spectrometer can be put in operation. Such spectrometers exist at several synchrotron beam lines.

References:

Relevance of topic:

The x-ray energies are relevant in x-ray analysis and in energy transfer calculations, in medical and radiation shielding and in energy generation fields.

Needs and/or aim for improvements:

The x-ray energies are not well established for chemical states. There is virtually no database to handle such issues. In an analysis if the main elements, or bulk elements are in a chemical state, they energy shift will be significant, as they will anchor the energy calibration. The minority elements especially far from the high intensity peaks are difficult to analyse. In the low x-ray energy range, below 3 keV, the typically used detectors are Si or Ge material based. For these detectors the energy and width calibration are not expected to be a monotonic function, and in the monotonic range is not expected to be a linear function. Therefore, adding the x-ray energy unreliability and variability by the chemical shift adds a further level of insecurity on the quality of the obtained data.

Methods and objectives for improvements:

Using broad energy range photoelectron spectrometers, theoretical methods and software packages, like GAUSS, to establish a database. Develop a simple few parameter approach to organise the database.

Constraints for improvements

Funding.

Innovations, novel concepts and/or potential

The novel concept is that the binding energies would be characterised as the reference element and the chemical shift based on the Mulliken charge. Therefore the analysis would be based on the identification of the element and its fractional charge. Since the fractional charge is correlated it would offer a constrain as well, making the analysis manageable.

Perspectives

X-ray energies are very basic in many basic research and applications. Accurate energies are available only for a limited number of atomic shells. An internally consistent data set would improve the reliability of derived data and large number of fields. This is ranging from medical fields to nuclear physics. Several application of x-ray analysis would benefit, including RoHS verification, demanded by legislations.

Expert group No.		**Starting event:**	
Topic title	Collective excitations in electron transport in nano-materials		
Expert group leader	*Tibor Papp*		
Contributing co-authors			

Detailed description of topic:

Typical physical systems which are frequently studied are the atom, dominated by the central potential, and the infinite periodic potential, e.g. solid state. These are the two extrema of the scale. The nano-materials differ from both, as the size determines how much of the quantum effects manifested. It is expected that varieties of collective excitations will be present. In low energy electron impact in the range of 5 keV and below, their presence has a significant strength, in many cases they are the dominating ones. Below we will present a few examples of collective excitations, such as plasmons, core to collective state and giant resonances. The energy and strength of the excitation depends on the chemical state as well as the size and shape of the nano-materials. We propose a study of material classes to establish the type and strength of collective excitations.

Description of status:

We have measured a large number of scintillation crystals, semiconductive detector materials, nanostrings, and nanospheres. We have concluded that the REELS (Recoil Electron Energy Loss Spectroscopy) very well suited for such studies. A new REELS spectrometer design with new proprietary lenses is underway.

Relevance of topic:

Between the dimensions of the atomic scale and the bulk scale, there are the dimensions of the nanomatter scale, where the quantum mechanical properties can manifest themselves in an unknown and unusual manner. For many nanosctructures there are size ranges where the matter exhibits some specific properties that may be remarkably different than the physical and chemical properties of bulk materials. In context of nanotechnology, these are referred to as "Emergent Properties". Some of these peculiar properties are known but many may yet be discovered.

Nano-materials are a new dimension of matter, with unexpected and unknown properties. Rather easy to make them and are abundant in nature, as well. Therefore future analytical techniques will be developed to quantify their properties. Electron microscopes are used for imaging. Therefore the electron transfer properties are a need to know in interpretation. Since the collective excitation has large cross sections, therefore it will probably be used for energy transfer design.

Needs and/or aim for improvements:

The knowledge on this subject is novel. Hardly considered previously. The contribution to electron scattering can be dominating. Having a giant resonance present changes the interaction.

Methods and objectives for improvements:

A broad scattering angle REELS spectrometer allows efficient analysis of the electron energy loss processes. Understanding the ranges of electrons in a nanomaterial or nanomaterial embedded in a matrix will be improved.

Constraints for improvements

Finances, man power, and development time.

Innovations, novel concepts and/or potential

Innovation part is to develop a complex analytical technique for collective excitation. One element is a REELS spectrometer development, combined with an XPS (x-ray photoelectron spectroscopy) what allow simultaneous measurement in a broad scattering angle.

Perspectives

Developing a broad scattering angle REELS spectrometer will allow efficient analysis of the electron energy loss processes.

Collective excitation can channel the energy transfer for a desired fashion. Therefore it is important in batteries, solar cells, x-ray and gamma ray detectors as well as radiation interaction in biological matter.

In perspective electron microscopes can have an attachment for collective excitation mapping.

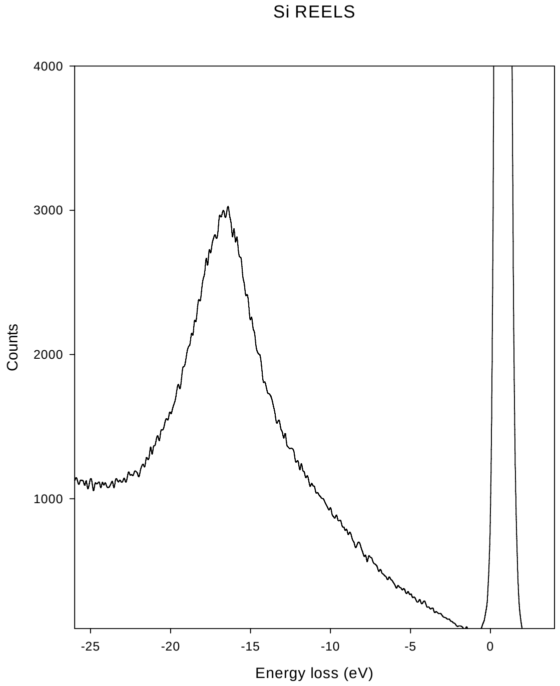
A few examples for the collective excitations present in electron transport, for demonstration of the significance.

(excerpt from the periodic report *Collective excitation in the ionization of atoms, in semiconductors and biological tissues* , Researcher: Dr. Tibor Papp, FP7-MC-IRG 224938)

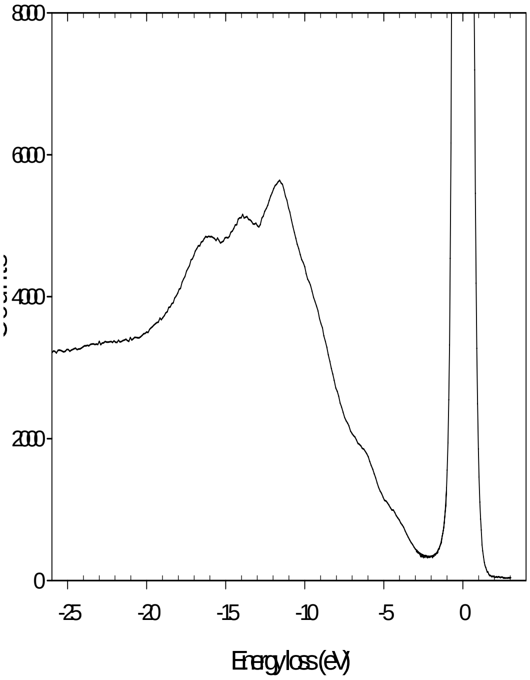
It is well known that that the dominant energy loss process for energetic electrons in solids, among them semiconductors, is plasmon creation [D. Pines, Rev. Mod. Phys. 28(1956)184]. These plasmons then decay by emitting an electron-hole pair. Since the details of this decay is not well known, models for e-h pair creation in semiconductors (and scintillators) usually overlook this two-step process.

To make an insight into these details, we have measured the electron energy loss process in CdTe and CZT detectors. CZT is a Cd(Zn)Te crystal with a few per cent zinc content.

In the figure below the CZT and Si detector energy loss processes are compared. The peak at zero energy loss is the elastic scattered peak. For Si material the broad peak at 16.8 eV energy loss is the plasmon loss peak. In the spectrum of CdTe there are two additional peaks beside the plasmon peak in this region. Their origins are collective excitations.

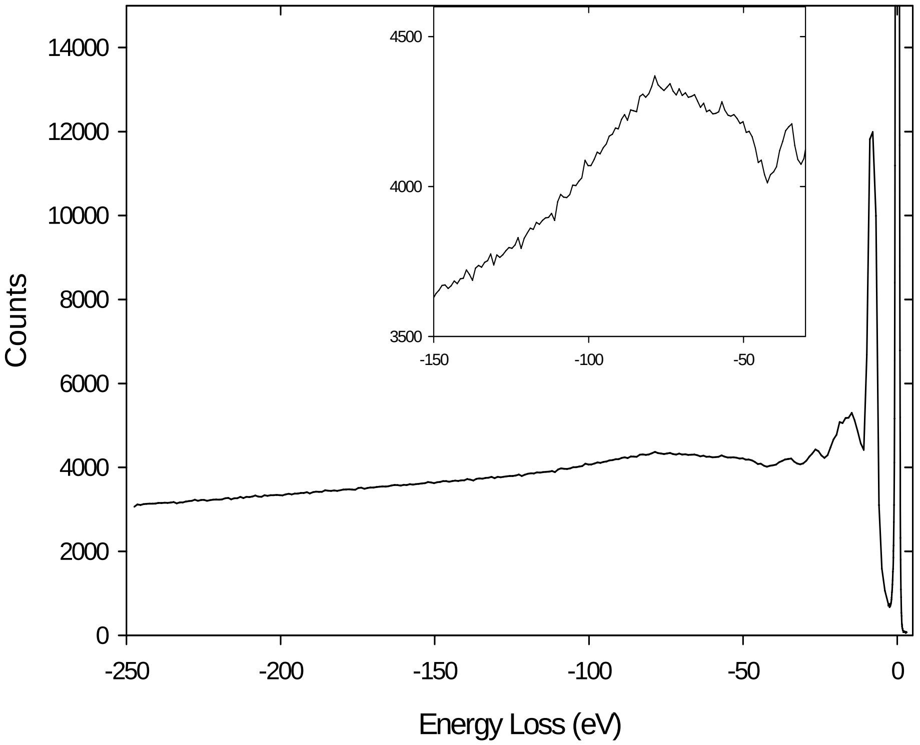


REELS spectrum of Si



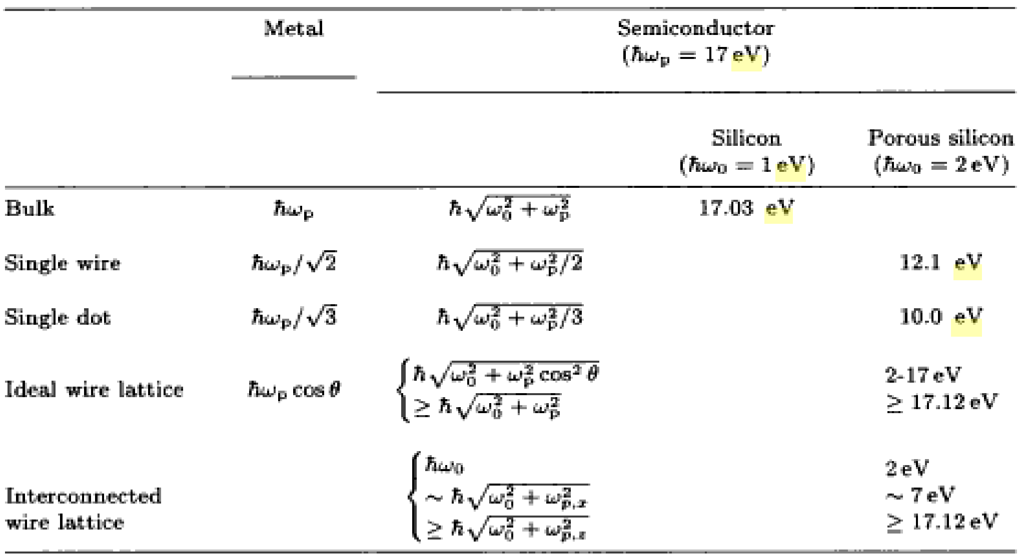
REELS spectrum of CdTe semiconductor detector material. It is very different than for Si or Ge.

Another example for collective excitation is a giant resonance. In the figure below we present the energy loss spectrum of Cd metal. At the zero energy loss we see the inelastic scattered peak. Left from it is the plasmon loss peak. We expected to see the giant resonance about 60 eV loss, with a breath of 60 eV. Indeed it is present. In the inset it is magnified. As the total intensity considered, this giant resonance is the dominating loss process. Its intensity is larger than for the Plasmon peak.



Here we have presented three examples for three different types of collective excitations in frequently used and studied materials. It may worth mentioning here, that for example the plasmon energies for different forms of silicon vary.

TABLE I. – *Plasmon energies.*



	Metal	Semiconductor ($\hbar\omega_p = 17$ eV)		
			Silicon ($\hbar\omega_0 = 1$ eV)	Porous silicon ($\hbar\omega_0 = 2$ eV)
Bulk	$\hbar\omega_p$	$\hbar\sqrt{\omega_0^2 + \omega_p^2}$	17.03 eV	
Single wire	$\hbar\omega_p/\sqrt{2}$	$\hbar\sqrt{\omega_0^2 + \omega_p^2/2}$		12.1 eV
Single dot	$\hbar\omega_p/\sqrt{3}$	$\hbar\sqrt{\omega_0^2 + \omega_p^2/3}$		10.0 eV
Ideal wire lattice	$\hbar\omega_p \cos\theta$	$\begin{cases} \hbar\sqrt{\omega_0^2 + \omega_p^2 \cos^2\theta} \\ \geq \hbar\sqrt{\omega_0^2 + \omega_p^2} \end{cases}$		2-17 eV ≥ 17.12 eV
Interconnected wire lattice		$\begin{cases} \hbar\omega_0 \\ \sim \hbar\sqrt{\omega_0^2 + \omega_{p,x}^2} \\ \geq \hbar\sqrt{\omega_0^2 + \omega_{p,z}^2} \end{cases}$		2 eV ~ 7 eV ≥ 17.12 eV

Expert group No.		**Starting event:**	
Topic title	*Developing a methodology to measure Coster-Kronig and fluorescence yields*		
Expert group leader	*Tibor Papp*		
Contributing co-authors	*John A. Maxwell*		

Detailed description of topic:

Developing a methodology to measure Coster-Kronig and fluorescence yields for L-shells. Previously, the Coster-Kronig and fluorescence yield determination was based on assumptions on the functional form of the energy dependence of the photo-ionization cross-section and a long-range extrapolation using this functional form. Experimental findings demonstrate that this assumption is not valid therefore the long-range extrapolation cannot be justified. Although a previous paper has called attention to this by indicating that this could have a range of factor of 2 effects on some of the values, recent understanding indicates that there are additional complications due to a collective excitation contribution. Therefore this estimation of model dependence was probably too optimistic.

The full details of the photo-ionization cross sections will not be available in the foreseeable future, and large surprises are expected, however the determination of the parameters for specific excitations, like Mo and Rh excitation would be feasible. These examples were chosen as they are frequently used in XRF analysers.

Description of status:

Currently the Coster-Kronig and fluorescence yield determination is mainly based on the synchrotron photo-ionization method, pioneered by Dr. Jitschin at PTB [1-3]. This method has severe limitations, both experimentally and conceptually. It assumes essentially the previous knowledge of the photo-ionization cross-sections, or at least its functional form. In the measurements they have observed that the experimental data deviate from the assumed simple exponential form. Since a far point extrapolation of data is used in this method, this assumption is a cornerstone of the method. To handle the new observation they have included the so-called linear response approximation (LRA) in the theoretical calculation. The collective response of all atomic electrons to the external field basically causes a screening of the field, which can be treated in a linear response approximation (LRA). This model is still somewhat an independent particle approach, as the ionization and description of the atom are made in the framework of the independent particle model. However this factor alone makes the result very model dependent.

An example demonstrates well the impact of the model of the photoionization energy dependence on the final results. In [4] the C-K parameters were derived for Xe with and without the inclusion of the LRA yielding almost a factor of 2 difference.

In proton impact ionization evidence was found that the independent particle model is inherently incapable of describing the ionization [5]. This study dealt with the strong and energy dependent alignment of proton impact ionisation suggesting a strong indication for the significance of collective excitation. Except for closed-shell ^1S states these states are superpositions of product states, and therefore the collective excitation is expected. However, this is typically ignored in the x-ray analytical techniques fields.

Recent measurements [6] with a different technique using crystal diffraction spectrometers clearly demonstrate that there is very different energy dependence, with a large number of structures in the absorption coefficient; see figure 4 of ref. [6]. Figure 6 of ref. [6] also calls attention to the strong deviation from theory, and raises the issue of whether facing an unknown problem such a degree of extrapolation can be justified. Comparing figure 6 and figure 4 the astonishing contradiction is that the x-ray yield curve does not match the ionization curve shape. Therefore the question remains whether there is an underlying physics explanation, other than that the decay parameters are not parameters at all, e.g. they are not constants. This is not an unusual experimental finding as other authors have made similar observations using proton-induced ionization. Our view is that there could be several ordinary simple data treatment issues that could explain these findings.

As a conclusion the experimental data show that the energy dependence of the photo-ionization cross section does not have the simple exponential form, and it deviates from the theory. Extrapolation of an unknown form is not justified in our view.

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[5] T. Papp, J. L. Campbell and J. A. Maxwell, Phys. Rev. A **1993;** 48, 3062

[6] W. Cao, J. Hoszowska, J.-Cl. Dousse, and Y. Kayser, M. Kavčič, M. Žitnik, K. Bučar, A. Mihelič, J. Szlachetko and K. Sabkowska, Phys. Rev. A **2009;** 80, 012512

Relevance of topic:

The Coster-Kronig and fluorescence yield data are basic ingredients of the FP method particularly for L & M shell x-rays. It is also used in several basic physics fields.

Needs and/or aim for improvements:

For the determination of C-K parameters we have concluded that the necessary extrapolation at the synchrotron photoionization is a limiting factor in accuracy, therefore other approaches should be investigated. The aim for improvement is to obtain a data set that would be internally consistent with the applied ptotoabsorption coefficient at that given energy. This would allow a better representation in model spectra. The FP method uses model spectra to “fit” the measured spectra and reducing the errors in the model spectra will result in more accurate analyses.

It would be desirable to consider coincidence measurements between the photoelectron and the C-K and Auger electrons. Using synchrotron radiation for excitation, the photoelectron energy can be tuned close to the C-K electrons energy. In this way the spectra of the electrons emerging from the solid would be identical for the photo and the C-K electrons. Therefore, systematic errors originating from the interpretation of the electron energy loss would cancel out. This could give directly the C-K parameters.

This approach would give the true parameters, which is useful only if the full detail of the photoelectric cross section is known and implemented in the XRF program. However, this condition probably will not be met in the near future.

To measure the photoionization cross section in a broad energy range, with sufficiently dense measuring points, for each element is a large job. This raises the question, whether an interim scheme can be employed. We have investigated such a possibility on industrial XRF equipment. The typical approach is to use a few energy ranges, selected by a prefilter, as the primary exciting radiation. An example is Mo or Rh Kα radiations. For this one energy range, assuming the Scofield photoelectric cross sections, the fluorescence yield and C-K parameters can be obtained. Although this will not yield the true physical values, the values they do yield are consistent with the photoionization cross sections used, giving an internally consistent method.

This parameter may not be the optimum for calculating the secondary fluorescence. At that energy range the photoabsorption coefficient might be different than the one from the applied model used at the higher energy value. However this would be a secondary effect.

Methods and objectives for improvements:

Using the energy for the ionisation, which typically used in XRF equipment, the x-ray production cross sections of the subshells can be determined via measuring the photoelectrons emitted from each individual subshell in coincidence with the x-rays. This is the primary and needed information. In terms of application, a photoionisation model can be selected and the cross sections given by the model can be used to separate out the C-K and fluorescent yield parameters. This approach will work for the low energy x-rays as well. However it has to be verified at the higher energies where the excitation procedures and the x-ray spectra are tremendously simpler.

It is necessary to understand that well developed and well understodd spectroscopy should be used. The present situation of the C-K parameters unreliability goes to the choice of improper equipment and methods and not using the necessary sophisticated characterisation and data processing.

Constraints for improvements

Finances, manpower, access to synchrotron laboratory, and equipments.

Innovations, novel concepts and/or potential

The potential of the method is that it can deliver the fundamental parameters. The x-ray production cross sections will be true measured data. Then any future set of photoabsorption coefficients can be used to derive the C-K and fluorescence yield data directly. In each case it would be an internally consistent data set.

Perspectives

A full FP can be used. The data is also necessary in any energy transfer calculation program, from biomedical sciences, to energy production, shielding and security issues.

To demonstrate the difficulty: The photoabsorbtion cross section does not have a simple energy dependence. While the absorption coefficient is a concave shape, the fluorescence intensities are having a convex shape. It does not seem to be proportional. The issue of extrapolation is also demonstrated.

W. Cao, J. Hoszowska, J.-Cl. Dousse, and Y. Kayser, M. Kavčič, M. Žitnik, K.Bučar, and A. Mihelič, J. Szlachetko andK. Słabkowska, Phys. Rev. A 80 (2009) 012512
L-subshell Coster-Kronig yields of palladium determined via synchrotron-radiation-based high-resolution x-ray spectroscopy

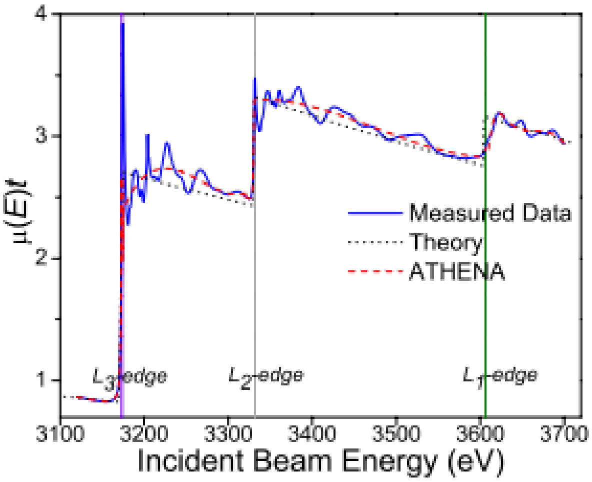

FIG. 4. (Color online) Experimental and theoretical [18] photoabsorptions for a 1.66-μm-thick palladium sample. For comparison, the smoothed background calculated by means of the ATHENA program is also plotted.

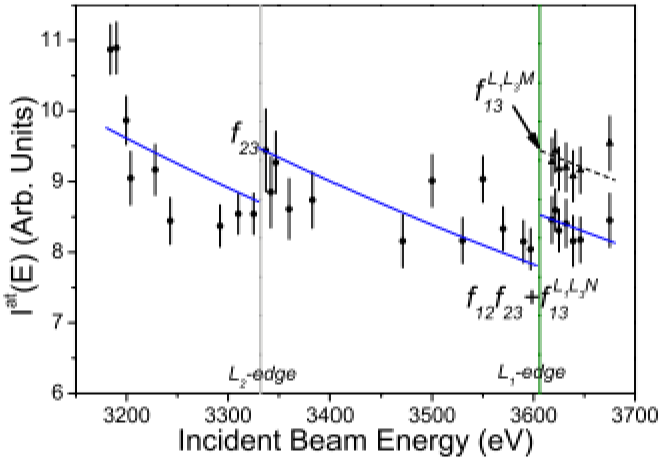

FIG. 6. (Color online) Atomlike fluorescence intensities $I^{at}(E)$ plotted against the incident-beam energy. Experimental points are depicted with solid circles, while solid lines represent the fitted curves. The data set used to derive the partial Coster-Kronig yield $f_{13}^{L_1L_3M}$ is plotted separately (solid triangles), while dashed line stands for the fitted values. Vertical lines indicate the L edges.

Supplementary information of expert group 5

International FP initiative - Expert Group on 'Technical Terms'

Intermediate report of group 5 - March 2009

Burkhard Beckhoff (PTB), Marie-Christine Lépy (LNE) and Terrence Jach (NIST)

1. Introduction

X-Ray Spectrometry (XRS) is based on the excitation of an inner-shell electron by an incident photon or by a charged particle followed by the emission of a photon. The energy of the emitted photon is characteristic for the transition of an outer-shell electron filling the inner-shell vacancy. As simultaneous excitations of more than one electron are possible, the emission spectra can become complex depending, on both the specific excitation conditions and the state of the atom in a solid specimen. In the general case, the set of fluorescence lines potentially emitted after an inner-shell ionization is characteristic for the element so that the fluorescence radiation can serve to identify an element. The intensity of the element-specific fluorescence radiation allows for the determination of the concentration or mass deposition of the respective element. Hence X-Ray Fluorescence (XRF) analysis has become a well-established multi-elemental and non-destructive analytical technique in all kinds of archaeometric, biomedical, environmental, forensic, geological and industrial applications. In different configurations, matrix and trace constituents of a sample or layer thicknesses can be determined, providing lateral or depth-profiling elemental information.

The quantitation of XRF spectra is, in general, based on the use of appropriate reference materials that are as similar as possible to the sample to be analyzed, as the interplay of often unknown instrumental and fundamental atomic parameters determines the measured element-specific fluorescence count-rates in a complex manner. For the relative uncertainties of analytical results to decrease, the knowledge of both instrumental and fundamental parameters must improve. This becomes even more critical in view of the analytical challenges regarding novel nanoscale materials, for which insufficient or no appropriate reference materials are available.

In the FP expert group on 'Technical Terms' representatives of the French, German and US national metrology institutes, LNE, PTB and NIST respectively, aim to clarify relevant FP-related terms and provide referencs to works of technical committees addressing these issues.

2. Instrumental and fundamental parameters

The fluorescence intensity of an element *i* in a sample depends, apart from the sample composition and special structure, on the various *instrumental and atomic fundamental parameters* involved. The following *example* will serve to clarify the corresponding basic terms:

The concentration C_i of the element *i* in a homogeneous multi-elemental sample *s* of thickness *T* can be calculated without additional references using the following formula:

$$C_i = \frac{N_i}{N_0 \tau_{i,E_0} Q \frac{\Omega_{det}}{4\pi} \frac{1}{\sin\theta} \frac{1-\exp(-\mu_{tot,i}T)}{\mu_{tot,i}}}$$

(changed theta)

where

E_0 is the photon energy of the incident (excitation) radiation

N_0 is the intensity of the incident (excitation) radiation at the photon energy E_0 that can be derived e.g. from

$P_0 = S_0 / \sigma_{diode,E_0}$ which is the radiant power of the incident radiation to be converted into the incident radiation intensity N_0 employing

S_0 as the signal of a calibrated photodiode measuring the incident radiant power with

σ_{diode,E_0} as the spectral responsitivity of the calibrated photodiode at the photon energy E_0

θ is the angle of incidence with respect to the sample surface

ψ is the angle of observation with respect to the sample surface

E_i is the photon energy of the fluorescence line *l* of the element *i*

$N_i = R_i / \varepsilon_{det,Ei}$ is the intensity of the fluorescence line *l* of the element *i* with

R_i as the detected count rate of the fluorescence line *l* of the element *I* and

ε_{det,E_i} is the detection efficiency of the Si(Li) detector at the photon energy E_i

Ω_{det} is the effective solid angle of detection defined by both the fluorescence detection area and its distance from the sample as well as the foot print of the excitation radiation on the sample surface (the latter being relevant for grazing incidence)

τ_{i,E_0} is the photo electric cross section of the element *i* at the photon energy E_0

$\mu_{tot,i} = \mu_{S,E_0} / \sin\theta + \mu_{S,E_i} / \sin\psi$

where

$\mu_{S,E}$ is the absorption cross section of the sample *s* at the photon energy *E*

$Q = \omega_{Xi}\, g_{l,Xi}\, (j_{Xi} - 1) / j_{Xi}$ (This doesn't include contributions to the yield from other edges or cascades)

ω_{Xi} is the fluorescence yield of the absorption edge *Xi* (of the element *i*)

$g_{l,Xi}$ is the transition probability of the fluorescence line *l* belonging to the absorption edge *Xi*

j_{Xi} is the jump ratio at the absorption edge *Xi*

In the above example one may associate the given quantities with the two groups of parameters as follows:

Instrumental or *experimental* parameters:

1. sample thickness *T*
2. angle of incidence θ
3. angle of observation ψ
4. energy of the incident (excitation) radiation E_0
5. intensity of the incident (excitation) radiation N_0, derived e.g. from $P_0 = S_0 / \sigma_{diode,E_0}$, i.e. the measurement of the incident radiant power by a photodiode of known spectral reponsivity
6. intensity of the fluorescence radiation $N_i = R_i / \varepsilon_{det,E_i}$, derived e.g. from the detected count rate R_i and the corresponding detection efficiency ε_{det,E_i}
7. effective solid angle of detection Ω_{det}

Fundamental parameters:

1. photo electric cross section τ_{i,E_0}
2. jump ratio j_{Xi} at the absorption edge *Xi*
3. fluorescence yield ω_{Xi}
4. absorption cross section $\mu_{S,E}$
5. photon energy of the fluorescence radiation E_i
6. transition probability $g_{l,Xi}$ of the fluorescence line *l* belonging to the (sub)shell *Xi*

In the case of flat samples excited at shallow incident angles or near a Bragg condition, the modulation of the incident radiant power by the X-ray Standing Wave (XSW) intensity [1,2] has to be included as an additional factor. Secondary and tertiary excitation channels within a homogeneous layer or bulk sample as well as intra-layer excitation and absorption effects can be likewise included as indicated in detail in the literature [3]. When part of the experimental parameters such as the spectral distribution of the excitation radiation, e.g. in case of an X-ray tube, or the efficiency of the detectors employed are not known well enough, one may try to compensate this lack of a-priori knowledge by using appropriate reference materials. The reliability of this reference-based quantitation approach strongly depends on the use of reference materials that should be as similar as possible to the specific samples to be analysed, in particular with respect to the specimen matrix. This includes, of course, sufficient a-priori knowledge of the spatial distribution of the main matrix constituents as is the case for homogeneous and layered samples. Depth gradient variations in the matrix concentrations may also be dealt with when known a-priori.

3. Atomic fundamental parameters

Besides the instruments' contributions, the relative uncertainties of the XRF analytical results are also affected by the tabulated *atomic fundamental* parameters of the elements, some of which only have estimated uncertainties. There are several XRF-related databases containing atomic fundamental parameters [4-13] such as transition and Coster-Kronig probabilities, fluorescence yields, photo-ionization cross sections, and scattering cross sections. Many compilations are based on the selection of values considered to be the most reliable ones according to certain criteria. These values may be selected from both theoretical and experimental data. A crucial point is that there have only been few experiments aiming to improve atomic fundamental data with respect to its relative uncertainty. Furthermore, some databases contain extrapolations that do not take into account the drastic changes in the electron configuration at certain adjacent atomic numbers, such as when one (sub)shell becomes completely filled and a new (sub)shell starts to fill up, or transition probabilities involve a (sub)shell that no longer has any electrons. In the latter case only considerably smaller values of the respective transition probabilities can be expected due to potential thermal broadening, chemical binding, or solid state effects. Another drawback of the compilations currently available is that there have been too few experiments in the last decades focusing on the determination of relevant atomic data with improved relative uncertainties, so that many of these uncertainty values are still based on estimates made in the 1970’s [5, 13]. Apart from experiments in the gas phase involving coincidence techniques, solid state experiments involve detection systems providing moderate to high energy resolution and often employ a reference sample whose relevant fundamental parameters or macroscopic properties are assumed to be well known. The advent of tunable synchrotron radiation and calibrated instrumentation has allowed for experiments aiming at the determination of sets of fundamental parameters belonging to a predominant or interesting inner-shell ionization of one-elemental specimens [14-23].

The atomic fundamental parameters most relevant for XRS are the following:

1. Photo electric (ionization) cross section τ_{i,E_0} indicating the probability that an incident photon of energy E_0 creates a vacancy in the (sub)shell Xi of an atom.

2. Elastic scattering cross section σ_{coh,E_0} where an incident photon of energy E_0 is scattered at an atom without any energy loss.
3. Inelastic scattering cross section σ_{incoh,E_0} where an incident photon of energy E_0 is scattered at an atom suffering an energy loss.
4. Fluorescence yield ω_{Xi} indicating the probability that the filling of an inner-shell vacancy is characterised by the emission of a fluorescence photon (as opposed to of an Auger electron).
5. Photon energy E_i of a fluorescence line *l* belonging to the (sub)shell *Xi* of an atom.
6. Energetic width Γ_l of a fluorescence line *l* (relevant for high-resolution XRS).
7. Transition probability $g_{l,Xi}$ of the fluorescence line *l* indicating the probability that a photon belonging to the line *l* is emitted instead of a photon associated with all other lines belonging to the same (sub)shell *Xi* of an atom.
8. Coster-Kronig transition probability $f_{j,k}$ indicating the probability that a vacancy created in the subshell X_k is transferred to the subshell *Xj.*
9. Total cross section $\sigma_{\mathrm{tot,E}}$ indicating the probability that an incident photon of energy E_0 interacts with an atom, (generally expressed in barns per atom, b=10^{-24} cm^2).
10. Binding energy B_{Xi}: energy required to ionise Xi subshell

4. Derived fundamental parameters

In the course of employing the respective atomic fundamental parameters and appropriate conversion factors, many derived terms exist,. The following *derived fundamental parameters* come about for practical reasons, such as the normalization of unknown quantities in experimental results:

1. mass absorption coefficient : μ/ρ ($\mathrm{m}^2.\mathrm{kg}^{-1}$ or $\mathrm{cm}^2.\mathrm{g}^{-1}$) is a macroscopic parameter directly linked to $\sigma_{tot,E}$:

$$\mu / \rho = \sigma_{tot} / uA$$

where *u* is the atomic mass unit (u=1,660 540 2 x 10^{24} g) and *A* is the relative atomic mass of the target element.

2. linear absorption coefficient : μ is the linear attenuation coefficient

3. absorption jump ratio (used to calculate the photoelectric cross section associated with a specific subshell *Xi* from the corresponding total photoelectric cross section, hereby assuming that the subshell cross section has the same energy dependence as the total one)

4.

5. Basic definition of uncertainties

Each atomic parameter should be characterized by its value and its associated standard uncertainty [24].

6. Compound fundamental parameters

As it may be difficult under certain experimental conditions to separate a fundamental parameter from another, compound fundamental parameters were sometimes introduced. Examples for *compound fundamental parameters* are the fluorescence production cross section being the product of the subshell photoelectric cross section and the corresponding fluorescence yield.

7. Related committees and documents

IUPAC International Union of Pure and Applied Chemistry Compendium of Chemical Terminology 2nd Edition (1997);

ICRU International Committee on Radiation Units and Measurements
ICRU Report 10b Physical Aspects of Irradiation
ICRU Report 17 Radiation Dosimetry: X-rays Generated at Potentials 5 to 150 kV Radiation Quantities and Units
ICRU Report 60 [ICRU, 1998] : ICRU report 60. Fundamental quantities and units for ionizing radiation. International Commission on Radiation Units and Measurements, Bethesda, Maryland (1998)
ICRU Report 19 Fundamental Quantities and Units for Ionizing Radiation (mainly dosimetry)
ICRU Report 33 (1980) Radiation Quantities and Units (1980)

ISO committee TC201 on surface analysis, subcommittees:
TC201/WG2 TXRF
TC201/WG3 X-ray reflectivity
TC201/SC1 *Terminology [See ISO 18115 (15.7.2001), Surface Chemical Analysis--Vocabulary; ISO 181115 Amendment 2 (20.2.2006)]*
TC201/SC7 XPS

VAMAS (Versailles Project on Advanced Materials and Standards) committee TWA2 surface chemical analysis (NIST contact, Ced Powell)

IAEA

ANSI

8. Conclusion and perspectives

The reliability of atomic fundamental parameters in X-ray spectrometry can be improved by either careful compilations of existing data bases, theoretical calculations based on appropriate many-body approximations or by dedicated experiments to determine selected atomic fundamental parameters. The main advantage of improved fundamental parameter values is their straightforward applicability to probing new materials for which no appropriate reference materials exist.

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10. Translation of FP terms to major languages

Translations of parameters:

English	German	French	Russian
Photo electric (ionization) cross section	Photoelektrischer Wechselwirkungsquerschnitt	Section efficace photoélectrique (d'ionisation)	Сечение фотоионизации (фото-электрическое ?)
Fluorescence yield	Fluoreszenzausbeute	Rendement de fluorescence	Выход флюоресценции
Photon energy	Photonenenergie	Energie du photon	Энергия фотона
Transition probability	Übergangswahrscheinlichkeit	Probabilité de transition	Вероятность перехода
Transition probability for absorption	Übergangswahrscheinlichkeit für Absorption	Probabilité de transition d'absorption	Вероятность перехода поглощения
Transition probability for spontaneous emission	Übergangswahrscheinlichkeit für spontane Emission	Probabilité de transition d'émission spontanée	Вероятность перехода спонтанной эмиссии
Transition probability for stimulated emission	Übergangswahrscheinlichkeit für induzierte Emission	Probabilité de transition d'émission stimulée	Вероятность перехода стимулированной эмиссии
Scattering	Streuung	Diffusion	Рассеяние
Scattering cross-section	Streuquerschnitt	Section efficace de diffusion	Сечение рассеяния
Elastic scattering	Elastische Streuung	Diffusion élastique (cohérente)	Упругое рассеяние
Elastic scattering cross section	Elastischer Streuquerschnitt	Section efficace de diffusion élastique	Сечение упругого рассеяния, упругое сечение
Inelastic scattering	Inelastische Streuung	Diffusion inélastique	Неупругое рассеяние
Inelastic scattering cross section	Inelastischer Streuquerschnitt	Section efficace de diffusion inélastique	Сечение неупругого рассеяния
Sample thickness	Probendicke	Epaisseur de l'échantillon	Толщина образца
Angle of incidence	Einfallswinkel	Angle d'incidence	Угол падения
Angle of observation	Beobachtungswinkel	Angle de détection	Угол наблюдения
Energy of the incident (excitation) radiation	Energie der einfallenden (anregenden) Strahlung	Energie du rayonnement incident	Энергия падающего пучка (излучения)
Intensity of the incident (excitation) radiation	Intensität der einfallenden (anregenden) Strahlung	Intensité du rayonnement incident	Интенсивность падающего пучка (излучения)
Incident radiant power	Einfallende Strahlungsleistung	Flux incident	Мощность падающего излучения

Spectral responsivity	Spektrales Ansprechvermögen	Réponse spectrale	Спектральная чувствительность
Intensity of the fluorescence radiation	Intensität der Fluoreszenzstrahlung	Intensité du rayonnement de fluorescence	Интенсивность флуоресцентного излучения
Detected countrate	Detektierte Zählrate	Taux de comptage détecté	Скорость счета (детектируемая)
Detection efficiency	Nachweisempfindlichkeit	Rendement de détection	Эффективность детектирования
Effective solid angle of detection	Effektiver Raumwinkel der Detektion	Angle solide effectif de détection	Эффективный пространственный угол детектирования
Jump ratio jX_i at the absorption edge X_i	Sprungverhältnis jX_i an der Absorptionskante X_i	Saut jXi au seuil d'absorption Xi	Скачок в отношении jX_i на пороге поглощения X_i
Absorption	Absorption	Absorption	Поглощение
Absorption cross section	Absorptionsquerschnitt	Section efficace d'absorption	Сечение поглощения
Absorbance	Absorptionsvermögen	Absorbance	Спектральная поглощательная способность
Absorption coefficient	Absorptionskoeffizient	Coefficient d'absorption	Коэффициент поглощения
Attenuance	Abschwächung	Atténuance	
Attenuation coefficient	Abschwächungskoeffizient	Coefficient d'atténuation	Коэффициент затухания, ослабления
Auger yield	Augerausbeute	Rendement Auger	Выход оже-электронов
Electron ionization	Ionization durch Elektronen	Ionisation à l'aide des électrons	Ионизация электронами
Line width	Linienbreite	Largeur de raie	Ширина линии
Natural line width	Natürliche Linienbreite	Largeur naturelle de raie	Ширина радиационной линии
Photoionization	Photoionisation	Photoionisation	Фотоионизация, ионизация светом
Radiant power, flux	Strahlungsleistung, Fluß	Flux	Поток излучения, лучистый поток
Coster-Kronig transition probability	Coster-Kronig Übergangswahrscheinlichkeit	Probabilité de transition de Coster - Kronig	Вероятность перехода Костера - Кронига
Energetic width	Energetische Breite	Largeur énergétique	Энергетическая ширина

NB.: For other major languages volunteers have to be identified during the FP workshops.