# Ionic Liquids as a Reference Material Candidate for the Quick Performance Check of Energy Dispersive X-ray Spectrometers for the Low Energy Range below 1 keV

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ABSTRACT: Ionic liquids (ILs) are proposed as simple and efficient test materials to evaluate the performance of energy dispersive X-ray spectrometers (EDS) in the low energy range below 1 keV. By only one measurement, C Kα, N Kα, O Kα, and F Kα X-ray lines can be excited. Additionally, the S Kα line at 2.3 keV and, particularly, the S L series at 149 eV complete the picture with X-ray lines offered by the selected ILs. The well-known (certifiable) elemental composition of the ILs selected in the present study can be used to check the accuracy of results produced with the available EDS quantification routines in the low energy range, simultaneously, for several low atomic number elements. A comparison with other reference materials in use for testing the performance of EDS in the low energy range is included.
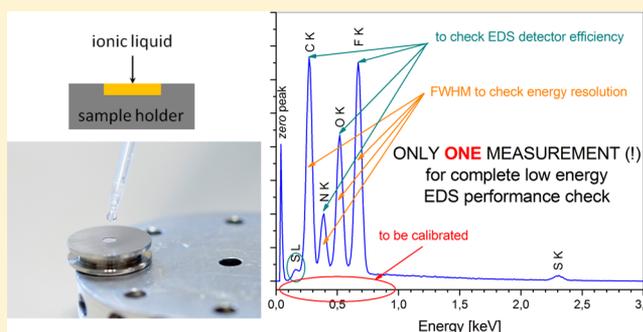
Energy dispersive X-ray spectrometers (EDS) constitute one of the analytical tools mostly employed for quick analysis of the elemental composition of solid samples. The excitation of the characteristic X-rays can be induced by electrons, as is the case in a scanning electron microscope (SEM), or by X-rays coming from an X-ray tube. Both respective techniques, electron probe microanalysis (EPMA) and X-ray fluorescence analysis (XRF), in their version with EDS detection, i.e., ED-EPMA and ED-XRF, are able to provide accurate qualitative and quantitative results. Unlike conventional XRF,[1] in the soft X-ray energy range below 1 keV, state-of-the-art ED-EPMA is able to identify elements of low atomic number down to Beryllium (Be Kα: 108.8 eV) with high sensitivity.[2] The reason for this lies in the use of high-transmission, thin polymer windows protecting the EDS detector. The newest implementation of silicon nitride windows to EDS detectors further improves the light element sensitivity.[3] Hence, even the detection of X-ray lines below 100 eV, including Li K line at 54 eV, becomes possible without necessity to renounce to the detector window. Current developments of detector windows based on graphenic carbon enable detection below 100 eV as well.[4]

The progress leading to higher EDS efficiency, particularly in the low-energy range, is being accompanied by technological developments in the detector manufacturing process as well as in the counting electronics. The energy resolution of a state-of-the-art EDS already approaches the theoretical limits.

Beyond all these recent, impressive developments with the hardware of EDS systems, one has to steadily evaluate the accuracy of the analytical result produced with the new EDS instruments, particularly when using X-ray lines in the low energy range. Recently, a systematic study on "light" compounds such as borides, carbides, nitrides, oxides, and fluorides has proven that the application of a traditional quantification model to X-ray lines below 1 keV measured with the new silicon drift detector (SDD) EDS systems works satisfactory; i.e., an accuracy below 5%-rel. can be attained.[5] However, when "standardless" ED-EPMA quantification is applied, such accuracies are too optimistic. Successful standardless quantitative analysis needs accurate knowledge of the performance parameters of the EDS system, such as EDS efficiency, its behavior with respect to pile-up effects or artifacts like incomplete charge collection (ICC) for the very low energy range. A minimum of control of the performance parameters of an EDS spectrometer can be ensured by applying the recommendations given in the international standard ISO 15632 "*Microbeam analysis - selected instrumental performance parameters for the specification and checking of energy dispersive X-ray spectrometers for use in electron probe microanalysis*".[6] In this document, it is specified how the calibration state of the energy scale, the energy resolution, and the L/K intensity ratio of copper or nickel as a measure for the spectrometer efficiency shall be evaluated. A case study on checking various EDS systems according to a procedure and a dedicated test material in line with the ISO 15632 standard is described in ref 7. An overview with the main instrumental EDS parameters to be checked, including test materials mostly used for calibration purposes, was given recently in ref 8. Therein, regarding the EDS performance

check at energies below 1 keV, a new test material (EDS-TM003) in form of a B−C−N−O thick layer, constituted from individual alternating B−C and C−N−O ultrathin sublayers, deposited on Si(100) wafer as substrate is highlighted. The considerable manufacturing effort and related high costs associated with this material motivated us to look for further alternative options. Otherwise, the availability of reference materials containing mainly (or exclusively) light elements with certified composition is very scarce. Ref 5 gives a good overview on potential reference materials containing light elements such as stoichiometric or mineral compounds. In the past, our lab has spent considerable effort in preparing candidates reference materials containing light elements tailored for various analytical methods.[9,10]

The present paper proposes a class of material that is able to offer a set of several Kα X-ray lines below 1 keV in one measurement, as a suitable certified reference material (CRM) candidate to be applied for the quick and accurate evaluation of EDS performance in the low energy range. The promising reference material with properties like excellent spatial homogeneity, stability, well-known and also variable elemental composition, easy accessibility, low costs, etc., is the class of ionic liquids (ILs).[11] They are in principle molten salts with a melting point below 100 °C and a very low vapor pressure (<0.01 Pa at around 440 K for the ILs in this contribution).[12] The cation is organic, whereas the anion can be organic or inorganic. While ionic liquids have attracted the interests of chemists and physicists in various field of research and development, their use as a reference material has been proposed[13,14] and the only activity so far was to successfully test them as a reference material for quantitative X-ray photoelectron spectroscopy (XPS).[15]

EXPERIMENTAL SECTION

Ionic Liquids. Ionic liquids either were purchased from IoLiTec Ionic Liquids Technologies GmbH (Heilbronn, Germany) in the highest available grade or were a donation from AC^{2}T research GmbH (Wiener Neustadt, Austria). Small amounts of the ionic liquid were bottled into small vials and dried and stored for degassing in vacuum at 10^{-6} to 10^{-7} mbar. Samples were prepared to exhibit a flat surface by filling up a 0.2 mm deep cavity of 2 mm diameter in a customized SEM sample holder of 1.2210/115CrV3 steel and immediately transferred into the SEM chamber; see graphical abstract figure.

Safety Considerations. According to EC regulation,[16] the used ILs are classified as follows: acute oral and dermal toxicity, skin corrosion, and chronic aquatic toxicity and dangerous to the environment. Considering the very low sample amount (approximately 2 μL) and careful handling, no harm or health risks are expected.

SEM/EDS. Three EDS spectrometers have been tested with the newly proposed material: (i) an SDD EDS of type XFlash (Bruker Nano GmbH, Berlin, Germany), (ii) an SDD EDS of type UltraDry (Thermo Scientific, U.S.A.), and (iii) a Si(Li) EDS (EDAX, U.S.A.). All X-ray spectra have been taken at 3 kV beam voltage and at a takeoff angle of 35°.

RESULTS AND DISCUSSION

For the testing of EDS performance in the low energy range, the 1,3-alkylimidazolium ionic liquid class with the bis-(trifluoromethylsulfonyl)imide counterion (Figure 1) was chosen, since it offers several, well separated and well balanced intensities of Kα X-ray lines below 1 keV: C Kα, N Kα, O Kα, and F Kα. Additionally, the S Kα line at 2.3 keV and particularly the S

$[C_nC_1im]^+$ $[NTf_2]^-$

C$_1$C$_1$im NTf2: R$_1$ = Methyl = CH$_3$
C$_2$C$_1$im NTf2: R$_2$ = Ethyl = CH$_2$CH$_3$
C$_3$C$_1$im NTf2: R$_3$ = Propyl = CH$_2$CH$_2$CH$_3$
C$_4$C$_1$im NTf2: R$_4$ = Butyl = CH$_2$CH$_2$CH$_2$CH$_3$
C$_6$C$_1$im NTf2: R$_5$ = Hexyl = CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$
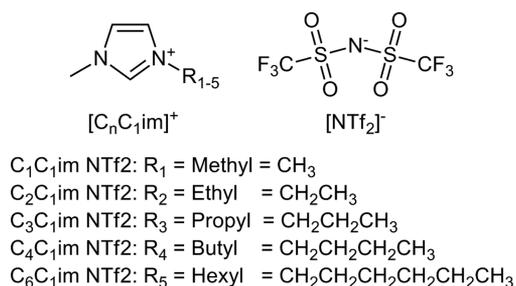
Figure 1. Structures of the ionic liquids used in the present study.

L series at 149 eV can also be taken into account for testing the EDS performance. The ionic liquid sample can be easily prepared to exhibit a flat surface by filling a small cavity in a conventional SEM stainless steel sample holder. This preparation ensures the application as a neat, homogeneous bulk sample thick enough to avoid any excitation of elements from the sample holder. The ionic liquids used in this study are sufficiently conductive so that no additional efforts are necessary to make the surface conductive. A high chemical stability at elevated temperatures without detectable decomposition for the proposed ILs is reported[17] and is ensured by the chosen storing conditions (room temperature, in vacuum, absence of light; also see the corresponding material safety data sheets). A slight enrichment of the [NTf$_2$] anion and longer alkyl side chains might be possible in the very near surface (a few nanometers).[18,19] However, this surface effect has no significant consequences on the purpose of the low-energy EDS test material as proposed here.

X-ray spectra of ionic liquids excited at 3 kV together with a representative SEM micrograph are shown in Figure 2a. The spectra were normalized to the integral Bremsstrahlung intensity within the energy range from 0.9 to 1.1 keV. It can be clearly seen that the X-ray peaks (all Kα lines) are separated from each other and well balanced in intensities. Furthermore, the relative elemental peak intensities vary as expected upon changing the stoichiometry of the ionic liquid, i.e., increasing the relative amount of carbon by variation of the side chain length of the ionic liquid. The SEM micrograph shows a nontextured surface demonstrating excellent lateral homogeneity. In-depth homogeneity at a depth of >1 nm was reported for the proposed IL class.[15,19−21]

If we compare the X-ray spectrum of an ionic liquid candidate test material with that of the recently proposed EDS-TM003,[8] see Figure 2b, it can be concluded that the selected ILs are competitive for the evaluation of the EDS performance by means of the interference-free lines available below 1 keV. Additionally, the proposed ILs offer a well-separated F K line at 677 eV as well as the S L series at 149 eV for a regular performance check. The X-ray line of lowest energy at which EDS-TM003 emits is the B K line at 184 eV. Boron is an element not present in the ILs selected in the present study, but the element can be easily incorporated either by introducing a boron containing functional group on the cation or by changing the anion to a boron containing anion (e.g., tetraphenylborate, tetrafluoroborate). As already pointed out in the introduction, the idea behind the consideration of ILs as an EDS test material for the low energy range is to find a suitable material as effective as the EDS-TM003 sample, however, having associated considerably less manufacturing effort and production costs.

In order to demonstrate the capabilities of the new test material(s), a set of three EDS systems have been tested with
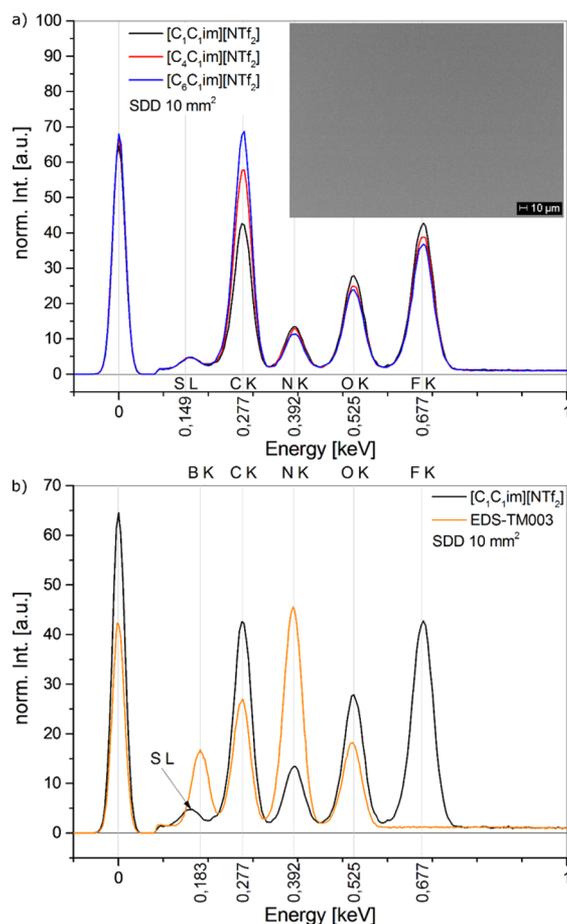
Figure 2. (a) 3 kV X-ray spectra below 1 keV of three selected ionic liquid test materials, together with an exemplary SEM micrograph of the IL surface of one sample showing the excellent lateral homogeneity. (b) Overlap of X-ray spectra of two candidate test materials for the energy range below 1 keV: the ionic liquid $[C_1C_1im][NTf_2]$ and EDS-TM003,[8] measured under identical conditions (3 kV excitation, same geometry and detector).

Figure 3. Comparison of X-ray spectra of the IL candidate test material $[C_1C_1im][NTf_2]$ recorded with three different EDS systems under otherwise equal conditions. Without it being necessary to quantitatively evaluate the spectra, note the following results: (i) similar intensity ratios of the C K, N K, and O K to the F K line, (ii) best energy resolution for the SDD EDS system with 10 mm² detector area, and (iii) best capability to detect the S L series at 149 eV in favor of the 10 mm² SDD EDS system.

regard to their low-energy performance. Two of the EDS systems tested are of the SDD type with a detector area of 10 and 100 mm², respectively. The third EDS has a 10 mm² Si(Li) detector. The corresponding X-ray spectra of one ionic liquid test material measured with the three EDS systems under comparable conditions are presented in Figure 3. The spectra have been normalized to the maximum intensity of the F K line. Several EDS instrumental parameters and performance results determined for the energy range below 1 keV can be easily recognized from this comparison: (i) The calibration state of the energy scale of the two SDD systems in the range below 1 keV is acceptable; i.e., the energy shifts are below 10 eV, as proposed in ref 7 for other energies. The energy scale for the Si(Li) EDS was not properly calibrated. Significant peak (negative) shifts of about 10 eV are visible for the position of the N K and C K lines. (ii) The energy resolution, expressed as the full-width-at-half-maximum, of the SDD EDS system with 10 mm² detector area is superior to that of the other two EDS systems. With lower energies, the energy resolution of the Si(Li) EDS worsens in comparison to that of the SDD 100 mm² system. Such a broadened C K peak measured by this EDS is typical for ICC.[22] (iii) The heights of the C K, N K, O K, and F K peaks obtained with the three EDS systems are quite similar, pointing to rather
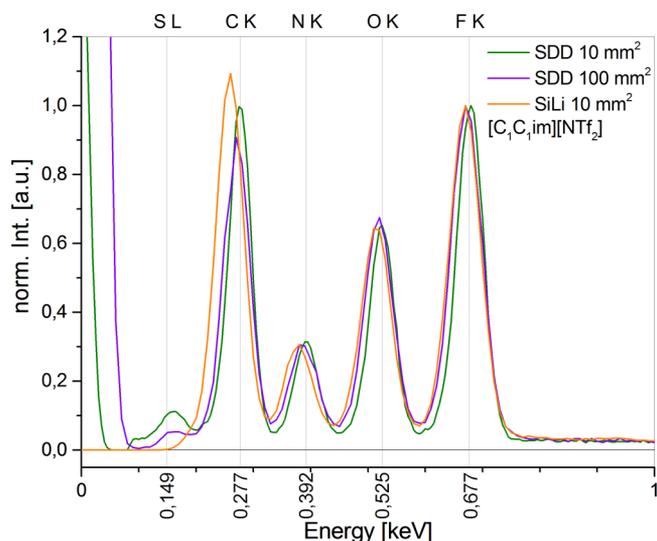
similar spectrometer efficiencies. This was expected since the detector windows of all three EDS detectors employed were of the same type (Moxtek AP3.3). Care must be taken when the EDS efficiency is quantitatively evaluated: the peak height is affected by the spectrometer efficiency but also by the energy resolution. Moreover, the ICC effect may occur for C K, so that an additional, asymmetric broadening of the C K peak accompanies the significant shift of the peak to smaller energies. A physical background subtraction for an accurate evaluation of the net peak areas is challenging and at this stage unnecessary when the task is to qualitatively asses the low-energy EDS performance, i.e., either by comparing spectra of two different systems (as in Figure 3) or by comparing spectra taken with the same EDS system at regular intervals. (iv) The ability to detect the S-L series at about 149 eV is featured only by the 10 mm² SDD EDS, whereas in the case of the 100 mm² SDD, the S-L series is barely visible and not detectable at all by the Si(Li) detector. For those EDS systems able to detect S L series, the evaluation of the intensity ratio of the lines S L at 149 eV and S Kα at 2.307 keV can be considered as a quantitative measure for the spectrometer efficiency at low energies. It can be expected that future EDS systems will be able to detect X-rays below 200 eV with increased sensitivity. (v) It is interesting to note that the normalized spectrum in the case of the Si(Li) detector shows a higher intensity in the C K line than it would be expected from the trend seen in the case of the SDDs with the same type of detector window (Figure 3). As noticed already in (ii), the significantly increased width of the C K peak shifted to a lower energy indicates ICC effect rather than contamination of the Si(Li) detector.

It has been shown that the present selection of ILs is suitable as candidate materials for testing the EDS performance. To formally develop them as a certified reference material, additional tests, such as stability and homogeneity,[23] will be carried out according to ISO Guide 35:2006 *Reference materials - General and statistical principles for certification.*[24] Beam-induced specimen

damage could not be observed in the present proof-of-principle study, performed at moderate conditions (3 kV accelerating voltage, probe currents below 1 nA, and acquisition times of a few minutes). However, beam-induced sample damage cannot be excluded at harder conditions. Stability tests to be carried out for certification purposes according to ISO Guide 35[24] will define thresholds for electron probe doses at which the ILs might suffer damage and X-ray spectra may change. They will be specified in the certification report.

CONCLUSIONS AND OUTLOOK

The possibility of using ionic liquids as reference material for testing the EDS performance in the energy range below 1 keV was investigated, and the proof-of-concept was successful. Several instrumental parameters, such as the energy scale, energy resolution, and spectrometer efficiency can be checked with only one measurement of the proposed ionic liquid test material. Either the periodical check of the EDS spectrometer in the low energy range can be efficiently performed by simply comparing the spectra taken over a large time scale or the low-energy performance of different EDS systems can be quickly evaluated qualitatively by comparing spectra of the same ionic liquid test material measured under the same experimental conditions.

The big advantage of the IL based test materials is the possibility for a quick check of several instrumental parameters of the EDS system in the delicate low energy range. Additionally, having such samples characterized by constant lateral and in-depth stoichiometry of light elements in the sampling volume, a quite plane surface, it is possible to validate matrix correction models for quantification in the energy range below 1 keV. This can be carried out as part of a quick test procedure to be applied in any service laboratory or as a more systematic study on various sets of classes of ILs with certified elemental composition. For the latter approach, a well-known EDS system is necessary, at best a calibrated system as those reported in refs 8 and 25. This would also enable re-evaluation of fundamental parameters of low atomic number elements as provided by older atomic databases (e.g., mass attenuation coefficient, fluorescence yield, ω, etc.). It is planned to certify the elemental composition of selected ionic liquid test materials by, e.g., combustion analysis.

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Author Contributions
M.H. planned all experiments and did the spectra analysis. M.H. and V.-D.H. wrote the manuscript. V.-D.H. and W.E.S.U. participated in the discussion of the results and gave valuable input during the preparation of this paper.

Notes
The authors declare no competing financial interest.

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