Determination of Chlorides in Ionic Liquids by Wavelength Dispersive X-ray Fluorescence Spectrometry

Willem Vereycken, Sofía Riaño, Tom Van Gerven, and Koen Binnemans*

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ABSTRACT: The synthesis of ionic liquids (ILs) usually involves two steps: (i) quaternization of a precursor followed by (ii) a salt metathesis reaction to introduce the desired anion. A consequence of the second step is that most ILs still contain some amount of the initial anion, often chloride. In this work, wavelength dispersive X-ray fluorescence (WDXRF) spectrometry is presented for the direct measurement of chlorides in ILs. The WDXRF settings were optimized, and the system was calibrated for the detection of chloride in several analogues of the commercially available IL Aliquat 336, $[A336][X]$ (with $X = I^-$, Br^-, NO_3^-, or SCN^-). The Cl $K\alpha$ intensity showed excellent linearity for samples with a conversion >0.80 (approximately Cl < 8000 ppm). Synthetic quality control samples showed that the instrumental error and deviations induced by the calibration procedure were small with maximum values of 1 and 5%, respectively. Detection and quantification limits depended strongly on the matrix (i.e., anion system and dilution) but were relatively low: 42−191 and 127−578 ppm Cl, respectively. Compared with other analytical techniques used for this purpose, the strengths of WDXRF include its ease of use, rapid measurements, the near absence of sample preparation steps, and versatility in terms of anion systems and chloride concentration range.

WDXRF for Cl Detection in Ionic Liquids
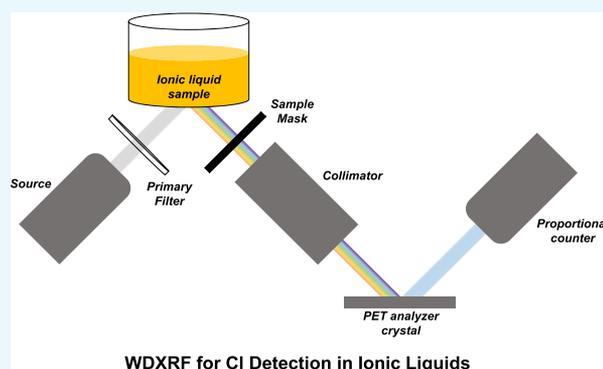
INTRODUCTION

Ionic liquids (ILs) are a special type of solvent consisting solely of ions. Their remarkable properties such as a wide liquidus range, intrinsic conductivity, non-volatility, and non-flammability have made them a promising class of materials. Numerous studies have shown great potential in various applications ranging from synthesis to solvent extraction.[1−3] Many different synthetic routes have been developed for the preparation of ionic liquids. These can be divided into two groups depending on whether they involve halides (often chloride) or not. The halide-free synthesis route is not widely applied because it limits the variety of ILs that can be produced.[4,5] In the other route, the synthesis of ionic liquids is usually composed of two major steps.[2,6] The first step constitutes cation formation through the quaternization of a suitable precursor (e.g., an imidazole, amine, phosphine, or pyridine). This is often performed using a chloroalkane resulting in the formation of the corresponding chloride salt. In the second step, the desired anion is introduced through an anion metathesis or anion exchange reaction

$$Q^+Cl^- + MA \rightleftharpoons Q^+A^- + MCl \tag{1}$$

with Q^+ as the cation, A^- as the desired anion, and M^+ as an alkali metal, Ag^+, or NH_4^+. Ionic liquids that are synthesized via

this two-step procedure will consequently always contain some amount of residual chloride impurities.[7]

These chloride impurities can strongly influence the physical and chemical properties of the synthesized ionic liquids. Residual chlorides are, for example, known to influence the viscosity, density, melting point, and electrochemical window of ionic liquids.[8−10] In addition, chlorides can also adversely affect transition metal-catalyzed and enzyme-catalyzed reactions carried out in ionic liquids.[11−15] The detection and quantification of such impurities are thus important for various applications. A variety of analytical techniques have been reported in the literature to monitor the chloride content of ionic liquids.[16] A simple $AgNO_3$ test, where the chlorides are precipitated as silver chloride, is often used to quickly confirm their absence.[17,18] This method is, however, not very reliable, and a quantification of the precipitate is also not straightforward. Alternatively, Volhard titration can be performed for quantification purposes. However, this approach is not

compatible with thiocyanate ILs. Chloride-selective electrodes have also been suggested but cannot be used for hydrophobic ILs and suffer from sensitivity and calibration difficulties.[8] One of the more popular and successful techniques for the quantification of chloride impurities is ion chromatography (IC).[19,20] It allows the simultaneous detection of all anions present in the IL. However, the method is most applicable to only hydrophilic ILs, the optimization can become time-consuming, and some anions, such as bis-(trifluoromethylsulfonyl)imide, can show long retention times on the column resulting in long measurement times. Total reflection X-ray fluorescence (TXRF) has also been presented for this purpose.[21,22] Low detection limits (e.g., 20 ppm Cl in the undiluted IL) and excellent recoveries have been obtained. However, the technique is sensitive to various sample preparation parameters such as the sample amount and drying time and is therefore more prone to human errors.[23] Other reported techniques include capillary electrophoresis (CE),[24] (laser ablation) inductively coupled plasma mass spectrometry ((LA-)ICP-MS),[25,26] and electrochemical methods.[27] Most of these are characterized by either long analysis times or time-consuming sample preparations, calibrations, and method developments.

Here, to the best of our knowledge, for the first time, wavelength dispersive X-ray fluorescence (WDXRF) spectrometry is presented for the determination of residual chlorides in an IL. WDXRF is generally only applied to solid samples, and the measurement of liquid samples is rather rare as these samples are usually dried, absorbed into a carrier/membrane, or solidified prior to measurement to avoid leakage inside the device.[28,29] Examples where WDXRF has been applied to liquid samples include, e.g., the measurement of trace elements and sulfur in petrochemical compounds.[30] The main advantage of a direct WDXRF measurement of liquid samples is its ease of use: measurements can be performed without the need for extensive sample preparation steps, which are usually required for solid samples (e.g., grinding or pelletizing). WDXRF can thus provide a rapid, non-destructive assessment of the chloride content of both undiluted and diluted IL samples for a wide variety of concentrations, i.e., ranging from a full chloride IL to a nearly entirely metathesized IL. It should be noted that WDXRF is an element-specific technique and that it cannot differentiate between different chloride containing ILs, e.g., a perchlorate IL.

The WDXRF measurement of chlorides in ILs was studied for the commercially available hydrophobic ionic liquid Aliquat 336 (a mixture of different quaternary ammonium chlorides, with trioctylmethylammonium chloride as the main component, [A336][Cl]) and its bromide, iodide, nitrate, and thiocyanate analogues. These particular anions were chosen based on their relevance for solvent extraction research and metal separations and purifications.[31,32] The main goal of this work was to develop a quick and easy tool for the assessment and monitoring of the degree of conversion of an IL metathesis process (cf. eq 1).

■ RESULTS AND DISCUSSION

Several WDXRF system settings were optimized for the detection of chlorides in IL samples. These measurements were performed on undiluted [A336][I] samples as this IL results in the heaviest matrix and low Cl Kα intensities can be expected (*vide infra*). The optimization process involved a balancing of the Cl Kα intensity, separation of the lines (for

current systems, the Rh Lα line is the main interference), and minimizing the background. Figure 1 shows the obtained
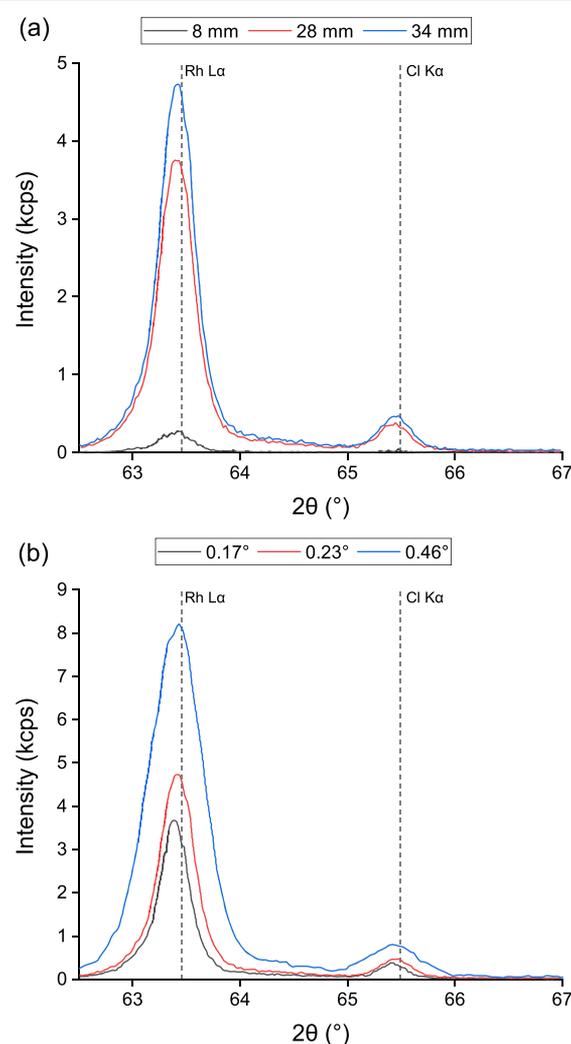
Figure 1. WDXRF spectra of an undiluted [A336][I] sample containing approximately 1000 ppm chlorides. (a) Different sample mask sizes for a 0.23° collimator and (b) different collimators (angular spread) for a 34 mm mask.

spectra of a [A336][I] sample containing approximately 1000 ppm chlorides for different sample masks and collimators (i.e., variation in the X-ray angular spread). Spectra for a sample with a higher chloride concentration (approximately 12,000 ppm) are provided in the Supporting Information, Figure S1. Figure 1a shows that a reduction in the size of the mask significantly reduces the obtained intensities by removal of the radiation from the edge of the cup. Lowered intensities can negatively affect the limit of detection and quantification (LOD and LOQ, respectively). In terms of intensity, the use of a large mask is thus preferred. However, this does also result in sample volume restrictions. The 34 mm mask requires the use of large 10 mL sample cups. The use of the 8 mm mask would allow the use of smaller cups, which only require 2 mL of the sample. Despite significantly reduced intensities, a good linear response can still be achieved with a 2 mL sample for the lower Cl concentration range (Supporting Information, Figure S2). Nevertheless, it was chosen to favor higher intensities over a smaller sample volume and to continue only with 10 mL

samples. Figure 1b shows that a collimator with an intermediate angular spread of 0.23° gives a good balance between Cl Kα intensity and separation with the Rh Lα line. An increased angular spread is beneficial for the intensities, but the resolution with the Rh line becomes worse due to the widening of the peaks. The following measurements were all performed with the optimized settings described in the Experimental Section.

Calibration lines were constructed by plotting the measured intensity of the Cl Kα line as a function of the chloride content. The chloride content was defined as "IL conversion" and not as an exact concentration such as mol L^{-1} or ppm. The reason for this is that the quaternary compound concentration is prone to change throughout a metathesis process due to a change in the water content of the IL. Moreover, the exact composition and concentration of the quaternary compound in Aliquat 336 are not entirely known (the literature reports values around 1.8 mol L^{-1}).[33−35] The ionic liquid conversion was defined as

$$\text{conversion} = \frac{V([A336][X])}{V([A336][Cl]) + V([A336][X])} \quad (2)$$

with $V([A336][Cl])$ and $V([A336][X])$ as the volumes of water-saturated pure [A336][Cl] and [A336][X] that can be mixed to obtain an IL of a certain chloride content. A conversion of 0 corresponds to pure [A336][Cl], and a conversion of 1 corresponds to pure [A336][X] (a residual chloride content of a maximum of 20 ppm, *vide supra*). Some measurements were performed on undiluted ionic liquids, i.e., no added diluent, just saturated with water. However, for most of the current work, the IL samples were diluted to 70 wt % with diisobutyl ketone (DIBK). Dilution of ILs is often applied to increase their usability by reducing the viscosity.

The calibration lines for the determination of the chlorides in [A336][I], [A336][Br], [A336][NO$_3$], and [A336][SCN] 70 wt % in DIBK are shown in Figure 2a. The calibration for undiluted water-saturated [A336][I] is provided in the Supporting Information (Figure S3). The horizontal axis is defined as (1 − conversion) to obtain an upward trend. The lines show an excellent linear behavior for the first section up to a (1 − conversion) of 0.2 ($R^2 > 0.999$) (Figure 2b). Due to the large chloride concentration range and significant matrix changes, the calibration lines show a deviation from this linearity for higher chloride concentrations ((1 − conversion) > 0.2). Deviations from linearity are not desirable for calibrations; however, the non-linearity can be fitted with a quadratic correction allowing quantifications to still be performed. For this, the fitting should be based on sufficient data points.[36] The data points ranging between (1 − conversion) 0.2 and 1.0 were fitted with a quadratic equation, while the remaining data points ranging from 0.0 to 0.2 were fitted with a linear equation. Fitting parameters are provided in the Supporting Information, Table S1. The use of two separate fittings results in a better fitting of the data points overall. Moreover, much of the interest for this technique lies with ILs with higher conversions where good linearity is observed.

The [A336][I] and [A336][Br] lines show a convex shape; the [A336][NO$_3$] line has a concave shape, while the [A336][SCN] line is nearly linear. The shapes of the calibration lines can be understood by considering the X-ray mass attenuation coefficients of the different anion systems. As the cation and diluent concentrations remain unchanged
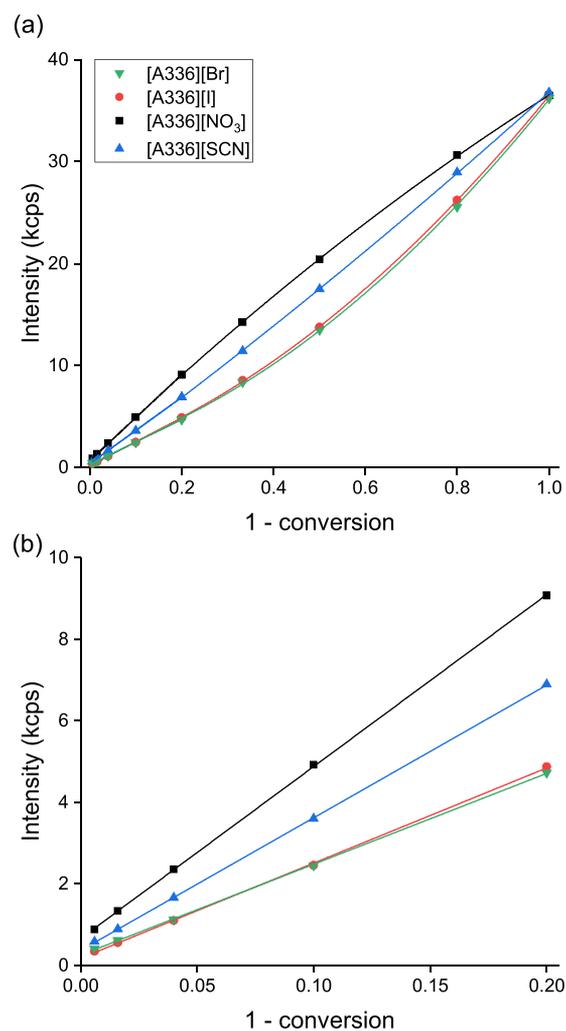
Figure 2. Calibration lines for the determination of chloride in [A336][I], [A336][Br], [A336][NO$_3$], and [A336][SCN] 70 wt % in DIBK: (a) full concentration range; (b) linear section of calibration lines.

throughout the calibration series, it suffices to look at the contribution of the anions, which can be inferred from the X-ray mass attenuation coefficients of elemental media.[37] In general, heavier elements such as bromine and iodine are characterized by higher X-ray mass attenuation coefficients than lighter elements such as nitrogen, oxygen, chlorine, or sulfur. Increased iodide or bromide concentrations thus result in a matrix with a higher mass attenuation coefficient compared with a pure chloride system. Going through the calibration series from a high to a low chloride concentration, the X-ray mass attenuation coefficient of the matrix increases, which in turn results in decreased X-ray intensities at the detector. The measured intensities are lower than what would be expected from a linear behavior, and the lines show a convex shape. Nitrates, consisting only of oxygen and nitrogen atoms, are characterized by reduced X-ray mass attenuation coefficients compared with chlorides. This decrease therefore causes intensities, which are higher than what would be expected from a linear calibration line, and a concave shape is observed. Thiocyanates contain a sulfur atom, the element adjacent to chlorine; hence, similar mass attenuation coefficients can be expected resulting in a nearly linear line shape.

Using the linear section of the calibration curves, an estimation of both LOD and LOQ can be made. The LOD can be calculated using eq 3, and the LOQ can be calculated using eq 4 with σ as the standard deviation on the y axis intercept and S as the slope of the linear portion of the calibration line.[38]

$$LOD = \frac{3.3\sigma}{S} \tag{3}$$

$$LOQ = \frac{10\sigma}{S} \tag{4}$$

The obtained LOD and LOQ expressed in terms of the conversion and ppm Cl are given in Table 1 for all shown

Table 1. Limits of Detection (LOD) and Quantification (LOQ) for the Detection of Cl in Various Ionic Liquids Using WDXRF

system	conversion		ppm Cl	
	LOD	LOQ	LOD	LOQ
[A336][I] undiluted	0.996	0.989	191	578
[A336][I] 70 wt % in DIBK	0.996	0.989	126	384
[A336][Br] 70 wt % in DIBK	0.998	0.993	86	262
[A336][NO$_3$] 70 wt % in DIBK	0.998	0.995	62	187
[A336][SCN] 70 wt % in DIBK	0.998	0.996	42	127

calibration lines. The chloride concentrations are calculated based on the assumption that Aliquat 336 contains 1.8 mol L^{-1} quaternary compounds.[33−35] Comparing the obtained values, the best results are obtained for the least heavy matrices, which is to be expected based on the higher signal intensities. Less deviation from linearity, e.g., [A336][SCN], also results in lower values for LOD and LOQ. It is also interesting to note that, for [A336][I], the same LOD and LOQ (expressed in terms of conversion) are obtained whether or not the system is diluted. This means that dilution with a hydrocarbon such as DIBK reduces the matrix density such that lower chloride concentrations can be detected but that this lowering is compensated by the dilution itself.

In the final set of experiments, the variation or error on the measurement of the Cl Kα intensity was calculated based on triplicate measurements of several samples of different conversions. These samples were prepared according to the same procedure as the calibration solutions; however, a different batch of [A336][X] was used and different chloride contents (conversions of 0.40, 0.85, and 0.97) were chosen

compared to those reported in Table 3. By doing so, these measurements also allowed for the validation of the constructed calibration lines and an estimation of the sensitivity of the calibration standards and lines toward experimental variations (e.g., pipetting errors, different batches of [A336][X], different sample cups, etc.). The results are summarized in Table 2. The standard deviation on the measured intensities is below 1%, which indicates that the measurement is precise and that the inherent instrumental error on the measurement is small. What is important, however, is the error induced by the sample preparation. That is, the deviation of the measured conversion with respect to the intended theoretical conversion can be up to 5%, while most values remain below 2%. This can also been seen from the obtained recoveries, i.e., the relation of the measured to theoretical conversion. Despite some variation on the recoveries, values of around 100% indicate that the method and the reported calibration lines are accurate within 5%.

The results indicate that WDXRF is a suitable technique for the assessment of the chloride content of IL samples within a wide range of conversions. Such samples can be obtained when the IL metathesis process itself is studied or monitored, and WDXRF can thus indicate the progression of the process and whether or not additional metathesis steps are necessary. The obtained LOD and LOQ are relatively low; however, other techniques such as TXRF or IC are generally characterized by lower values. Hence, if a final purity assessment of a metathesized IL product with low chloride concentrations (<150 ppm Cl) is required, then other techniques should be considered in combination with WDXRF.

■ CONCLUSIONS

WDXRF was presented for the detection of chlorides in ionic liquids. Reliable measurements can be performed on 2 mL samples, but larger 10 mL samples are preferred. The constructed calibration lines showed excellent linearity for low chloride contents or high conversions, i.e., >0.80. The achieved LOD and LOQ were sufficiently low, e.g., 42 and 127 ppm Cl for [A336][SCN] 70 wt % in DIBK, respectively. However, a final assessment of IL purity (Cl <150 ppm) would preferably be performed with a different technique such as IC or TXRF. The influences of the instrumental error and deviations induced by the calibration standard preparation procedure were assessed and shown to be a maximum of 5%. Compared with other techniques reported for chloride detection in ILs, WDXRF offers rapid measurement, a

Table 2. Triplicate Measurement of Validation Samples

system	theoretical conversion	measured intensity (kcps)	measured conversion	recovery (%)
[A336][I] 70 wt % in DIBK	0.400	17.324 ± 0.122	0.406	101.44 ± 0.77
	0.850	3.122 ± 0.025	0.874	102.81 ± 0.13
	0.970	0.676 ± 0.001	0.979	100.89 ± 0.01
[A336][Br] 70 wt % in DIBK	0.400	17.240 ± 0.047	0.397	99.22 ± 0.30
	0.850	3.244 ± 0.010	0.866	101.87 ± 0.05
	0.970	0.798 ± 0.008	0.976	100.58 ± 0.04
[A336][NO$_3$] 70 wt % in DIBK	0.400	23.342 ± 0.083	0.418	104.51 ± 0.60
	0.850	6.338 ± 0.021	0.865	101.81 ± 0.06
	0.970	1.690 ± 0.028	0.976	100.58 ± 0.07
[A336][SCN] 70 wt % in DIBK	0.400	21.313 ± 0.090	0.398	99.40 ± 0.60
	0.850	4.691 ± 0.024	0.867	102.02 ± 0.09
	0.970	1.181 ± 0.007	0.975	100.52 ± 0.02

straightforward calibration procedure, minimal sample preparation steps (samples can be measured directly, pure, or diluted with a diluent), and is applicable to nearly the entire range of chloride concentrations, i.e., ranging from a chloride IL to a product with a high conversion (≤0.998).

EXPERIMENTAL SECTION

Materials. Aliquat 336 was purchased from Thermo Fisher Scientific (Merelbeke, Belgium). NaBr (≥99.5%) and

Table 3. Mixtures of [A336][Cl] and [A336][X] (with X = Br⁻, I⁻, SCN⁻, or NO₃⁻) That Were Used for the Calibration of the WDXRF Spectrometer

conversion	volume [A336][Cl] (mL)	volume [A336][X] (mL)
0.000	12.000	0.000
0.200	9.600	2.400
0.500	6.000	6.000
0.667	4.000	8.000
0.800	2.400	9.600
0.900	1.200	10.800
0.960	0.480	11.520
0.984	0.192	11.808
0.994	0.072	11.928

diisobutyl ketone (DIBK, >96%) were acquired from Acros Organics (Geel, Belgium). KI (≥99.5%) was bought from Honeywell Riedel de Haën (Seelze, Germany). KSCN (>99%) and NaNO₃ (>99.5%) were purchased from Chem-Lab (Zedelgem, Belgium). Water was of ultrapure quality and deionized with a Merck Millipore Milli-Q Reference A+ system. All chemicals were used as received without any further purification.

Ionic Liquid Synthesis. The bromide, iodide, nitrate, and thiocyanate analogues of [A336][Cl] were prepared through a salt metathesis reaction (cf. eq 1). A sample of 200 mL of [A336][Cl] was contacted four times with an equal volume of a 2 mol L⁻¹ salt solution of the respective anion in a separatory funnel for 30 min using an RS-1 reciprocal shaker (JeioTech) operated at 250 rpm. NaBr, KI, NaNO₃, and KSCN were used for the preparation of the bromide, iodide, nitrate, and thiocyanate ILs, respectively. The ionic liquids were subsequently washed for a minimum of two times using an equal volume of ultrapure water to remove any dissolved salts. The absence of chloride ions was qualitatively checked using total reflection X-ray fluorescence (TXRF; Bruker S2 Picofox) (limit of detection, 20 ppm Cl).[22] If found to be impure, then the ionic liquids were subjected to additional contacts with the salt solution and additional washing steps.

WDXRF Measurements. Measurements were performed on a Bruker S8 Tiger 4 kW WDXRF system equipped with a Rh anode, a PET (pentaerythritol) diffraction crystal, and a gas-flow proportional counter detector. A 50 μm Be filter was used to protect the X-ray tube from an accidental sample leak. The system was operated at 30 kV with a 13 mA tube current. All measurements were performed on the Cl Kα line (2.622 keV) under atmospheric helium with the IL samples in polyethylene cups (XRF Scientific) with a 4 μm polypropylene film (Chemplex) bottom, which were rotated at 0.5 rev/s. Optimal measurement parameters were a 10 mL sample volume, a 34 mm collimator mask, and a 0.23° collimator. Samples were measured until the counting statistical error

(CSE) was below 1%, and the measurement times generally varied between 30 and 300 s.

Preparation of Calibration Solutions. The WDXRF system was calibrated with solutions prepared by mixing varying amounts of [A336][Cl] and [A336][X] (with X = Br⁻, I⁻, NO₃⁻, or SCN⁻). Table 3 displays the mixtures that were prepared for the calibration of the system. In the case where DIBK was used as a diluent, it was applied after mixing the pure ILs.

ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00586.

The Supporting Information includes the study of measurement parameters (sample mask and collimator) for a [A336][I] sample containing 12,000 ppm Cl, calibration lines for the determination of chlorides in undiluted [A336][I] for 2 and 10 mL samples, and fitting parameters used for the calibrations (PDF)

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Notes

The authors declare no competing financial interest.

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