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Determination of Halide Impurities in Ionic Liquids by Total Reflection X-ray Fluorescence Spectrometry

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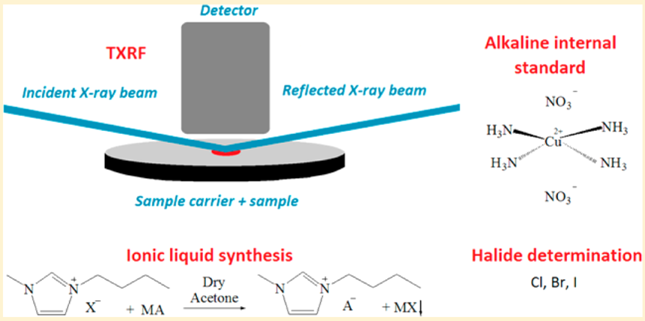
ABSTRACT: The determination and quantification of halide impurities in ionic liquids is highly important because halide ions can significantly influence the chemical and physical properties of ionic liquids. The use of impure ionic liquids in fundamental studies on solvent extraction or catalytic reactions can lead to incorrect experimental data. The detection of halide ions in solution by total reflection X-ray fluorescence (TXRF) has been problematic because volatile hydrogen halide (HX) compounds are formed when the sample is mixed with the acidic metal standard solution. The loss of HX during the drying step of the sample preparation procedure gives imprecise and inaccurate results. A new method based on an alkaline copper standard $Cu(NH_3)_4(NO_3)_2$ is presented for the determination of chloride, bromide, and iodide impurities in ionic liquids. The 1-butyl-3-methylimidazolium ($[C_4mim]$) ionic liquids with the anions acetate ($[C_4mim][OAc]$), nitrate ($[C_4mim][NO_3]$), trifluoromethanesulfonate ($[C_4mim][OTf]$), and bis(trifluoromethylsulfonyl)imide ($[C_4mim][Tf_2N]$) were synthesized via a halide-free route and contaminated on purpose with known amounts of $[C_4mim]Cl$, $[C_4mim]Br$, $[C_4mim]I$, or potassium halide salts in order to validate the new method and standard.



Ionic liquids (ILs) are solvents that consist entirely of ions.[1−5] Typical cations are 1-alkyl-3-methylimidazolium, *N*-alkylpyridinium, tetraalkyl ammonium, tetraalkyl phosphonium, and *N*-alkyl-*N*-methylpyrrolidinium ions. Typical anions of ionic liquids are chloride, bromide, thiocyanate, acetate, tetrafluoroborate, hexafluorophosphate, triflate, and bis(trifluoromethylsulfonyl)imide ions. Ionic liquids can have unique properties such as an extremely low vapor pressure, an intrinsic ionic conductivity, a low flammability, and a wide electrochemical window and can act as good solvents for many classes of organic and inorganic compounds. Depending on their chemical structure, ionic liquids can be either miscible or immiscible with water. Ionic liquids are used as solvents for catalytic reactions,[6,7] as solvent for processing of biopolymers,[8,9] as electrolytes for electrodeposition of metals,[10−12] as the organic phase in solvent extraction,[13−15] and as engineering fluids,[16,17] and they find many applications in analytical chemistry.[18−21] Although halide-free routes have been developed for the synthesis of ionic liquids,[22−24] most ionic liquids are still prepared from chloride or bromide ionic liquids via a metathesis reaction (Figure 1).[25−29]

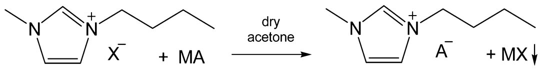


Figure 1. General metathesis reaction for the synthesis of imidazolium-based ionic liquids. A = desired anion, M = alkali metal or silver, and X = Cl, Br, or I.

Depending on the experimental procedure and the nature of the anion, newly synthesized ionic liquids prepared from halide ionic liquids via a metathesis reaction will always contain smaller or larger quantities of halide impurities. It is known that the halide impurities strongly influence the physicochemical properties of ionic liquids.[30] For instance, chloride impurities increase the viscosity of tetrafluoroborate ionic liquids.[30] Halide impurities also have a negative effect on the reactivity of reactions with organometallic catalysts in ionic liquids and on enzymatic reactions.[31−33] For these reasons, it is important to quantify the halide impurities in ionic liquids. Synthetic chemists often rely on the "$AgNO_3$ test" to check the purity of their new ionic liquids: a few drops of a silver(I) nitrate solution are added to an aqueous solution of the ionic liquid (for hydrophilic ionic liquids) or to the washing water that has been used to rinse a hydrophobic ionic liquid.[29,34,35] The absence of a silver halide precipitate is then accepted as a proof of purity. However, this method is unreliable and cannot be used to quantify the concentration of halide impurities. At best, an upper limit of halide concentrations can be estimated. More quantitative results can be obtained by argentometric titrations (Volhard method) or by turbidometric measurements using Nessler cylinders.[36] Chloride- and bromide-selective electrodes have been tested for the determination of halide impurities in ionic liquids, but they are not sensitive enough and the calibration procedure is difficult.[30] For each ionic liquid cation,

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a different calibration curve needs to be constructed. Moreover, this technique cannot be used for ionic liquids that are not miscible with water. By far, the most often used method for determination of halide impurities in ionic liquids is ion chromatography (IC).[37−41] This analytical technique is generally applicable to the determination of many different anions and is not restricted to halide ions. However, some ions such as bis(trifluoromethylsulfonyl)imide show very long retention times on the IC columns with strong tailing as a result. Moreover, the development of analysis methods can be time-consuming, especially when different nonaqueous solvents need to be used for dissolution of the ionic liquid samples. Other methods that have been described in the literature for the determination of halide impurities in ionic liquids include capillary electrophoresis (CE),[42] inductively coupled plasma mass spectrometry (ICPMS),[43] UV−vis absorption spectroscopy,[44] and electroanalytical methods.[45,46] Each of these methods has its specific advantages and disadvantages.

In this paper, we describe for the first time the use of total reflection X-ray fluorescence (TXRF) spectrometry for the determination of halide impurities in ionic liquids. TXRF is related to energy-dispersive X-ray fluorescence (EDX), but the X-ray beam is directed at a very small angle to a smooth substrate (less than 0.5°) and is under these circumstances totally reflected on the surface.[47−54] The total reflection leads to the formation of standing waves above the surface and down to a few nanometers just below the surface, so that all X-ray fluorescence is generated by atoms close to the surface. Samples are prepared on optically flat carriers, typically polished quartz glass disks. Solutions are pipetted onto these sample carriers and, after evaporation, the dry residues are analyzed. A major advantage of TXRF is that an easy calibration can be carried out by addition of a single internal standard element. Other advantages include the simple sample preparation, the fast analysis, the small amounts of sample needed, the very wide dynamic range (from ppb to 100%), and the low maintenance costs. TXRF is a trace analysis technique, and in the cases of homogeneous samples without organic materials such as water samples, detection limits of close to 1 ppb can be reached for the most X-ray sensitive elements. It is also a multielement technique, and many different elements can be determined simultaneously. A typical TXRF spectrum containing copper and halides is given as an illustration in Figure 2.

Applications of TXRF include the determination of impurities on silicon wafers in the microelectronic industry[55,56] and the analysis of surface water samples,[57] wastewater samples,[58,59] biological fluids (blood, blood serum, urine),[60−62] pharmaceutics,[63] geological material,[64] and aerosols,[65] as well as the identification of artist pigments on paintings[66] and for forensic investigations.[67] TXRF has already successfully been used for the determination of bromate,[68] perchlorate,[69] and bromide present in solid material.[70] The determination of dissolved halide salts is more challenging. Different authors have reported the possibility of hydrogen halide (HX) evaporation during the drying step when an acidic internal standard is used for the TXRF measurements.[71−75] Almost all metal standards are diluted in 2−5 wt % of acid to obtain a stable standard without the risk of metal hydrolysis and precipitation. The acid can react with the halide and form HX compounds, which are volatile and then evaporate during the drying step.[75] One way to bypass this problem is to perform the measurement indirectly by precipitation of silver halides with $AgNO_3$ and measuring the excess of silver or by adding $AgNO_3$ to the sample on the sample holder.[71,73] Another option is to work in alkaline conditions, but not all standards are stable under these conditions and metal hydroxides could precipitate at higher pH values.[72] A better approach is probably to use a neutral standard such as NH_4VO_3 which has been used for the determination of fluorine.[74] Recently, we introduced $Cu(NH_3)_4(NO_3)_2$ as a new internal standard which can be used for the determination of halides in aqueous solutions. This standard is stable under alkaline conditions, leaves no absorbing matrix behind on the carrier, and is soluble in organic solvents. Given the great potential of TXRF for determination of trace amounts of halogens and the absence of reliable analysis methods for halogens by TXRF, we explored the applicability of TXRF for the determination of halide ion impurities in ionic liquids. In this paper, we describe analytical protocols for the determination of chloride, bromide, and iodide impurities in ionic liquids by total-reflection X-ray fluorescence (TXRF). It should be mentioned that TXRF is an element-specific analytical method, so that chlorine, bromine, and iodine concentrations are measured, rather than chloride, bromide, and iodide concentrations.

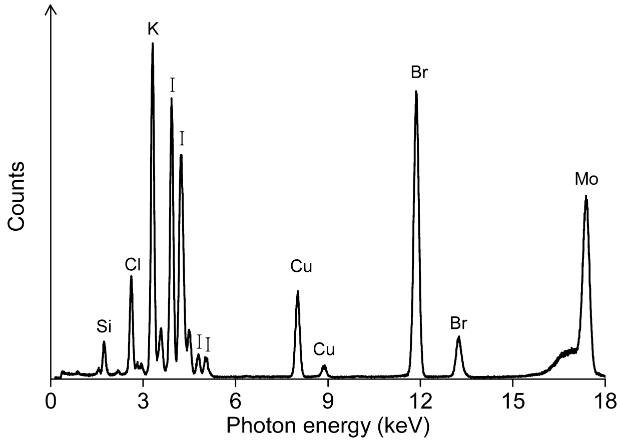

Figure 2. Typical TXRF spectrum, showing the peaks of chlorine, bromine, iodine, and copper. The molybdenum peaks are due to Rayleigh and Compton scattering of photons of the molybdenum X-ray source; potassium was the counterion of the halides, and the silicon peaks come from the quartz sample carrier and its pretreatment.

■ EXPERIMENTAL SECTION

Chemicals. 1-Butyl-3-methylimidazolium chloride ($[C_4mim]Cl$, 99%), 1-butyl-3-methylimidazolium bromide ($[C_4mim]Br$, 99%), 1-butyl-3-methylimidazolium iodide ($[C_4mim]I$, 99%), a 30 wt % 1-butyl-3-methylimidazolium methyl carbonate solution in methanol ($[C_4mim][MeCO_3]$), trifluoromethanesulfonic acid (HOTf, 98%), and an 80 wt % aqueous solution of hydrogen bis(trifluoromethylsulfonyl)imide (HTf_2N) (80 wt %) were purchased from IoLiTec (Heilbronn, Germany). Nitric acid (65 wt %) and the ammonia solution (25 wt %) were purchased from Chem-Lab NV (Zedelgem, Belgium). Acetic acid (99%) and ethanol were obtained from VWR (Leuven, Belgium). Potassium chloride (KCl, 99.9%), potassium iodide (KI, 99.9%) and potassium bromide (KBr, 99.9%) were obtained from Applichem (Darmstadt, Germany). The detergent RBS 50 pF was obtained from Chemical Products R. Borghgraef (Brussels, Belgium). The copper(II) nitrate standard (1000 ppm) was purchased from SCP Science (Courtaboeuf, France), and the silicone solution in isopropanol was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany). The halide purity of all chemicals were first checked by a standardless TXRF method and approved to be useable without further purification.

Synthesis of 1-Butyl-3-methylimidazolium Acetate, [C$_4$mim][OAc]. Acetic acid (10 mL, 180 mmol) was added slowly to a 30 wt % methanol solution of [C$_4$mim][MeCO$_3$] (140 mL, 175 mmol) and stirred for 1 h under a dynamic vacuum (Schlenk line) to obtain [C$_4$mim][OAc] (33.072 g; 167 mmol; 95% yield) which was further dried on a Schlenk line for 48 h at 60 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6, d/ppm): 10.18 (s, 1H), 7.91 (s, 1H), 7.84 (s, 1H), 4.21 (t, 2H, J = 7.2 Hz), 3.89 (s, 3H), 1.77 (m, 2H, J = 7.4 Hz), 1.59 (s, 3H), 1.23 (m, 2H, J = 7.5 Hz), 0.87 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75.48 MHz, DMSO-d_6, d/ppm): 173.2, 136.9, 123.6, 122.2, 48.4, 35.6, 31.3, 23.3, 18.7, 13.2.

Synthesis of 1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide, [C$_4$mim][Tf$_2$N]. A 80 wt % HTf2N solution (40 mL, 147 mmol) was added slowly to a 30 wt % methanol solution of [C$_4$mim][MeCO$_3$] (100 mL, 125 mmol) and stirred for 1 h under a dynamic vacuum (Schlenk line) to obtain [C$_4$mim][Tf$_2$N] (50.012 g; 119 mmol; 96% yield) which was washed three times with Milli-Q water and further dried on a Schlenk line for 48 h at 60 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6, d/ppm): 9.10 (s,1H), 7.75 (s, 1H), 7.68 (s, 1H), 4.16 (t, 2H, J = 6.9 Hz), 3.86 (s, 3H), 1.78 (m, 2H, J = 6.9 Hz), 1.26 (m, 2H, J = 7.4 Hz), 0.91 (t, 3H, J = 7.4); ^{13}C NMR (75.48 MHz, DMSO-d_6, d/ppm): 136.4, 123.6, 122.2, 119.5 (q, J = 322 Hz), 48.5, 35.7, 31.3, 30.6, 18.7, 13.2.

Synthesis of 1-Butyl-3-methylimidazolium Trifluoromethanesulfonate, [C$_4$mim][OTf]. A HOTf solution (6.8 mL, 76 mmol) was added slowly to a 30 wt % methanol solution of [C$_4$mim][MeCO$_3$] (18.2 mL, 76 mmol) and stirred for 1 h under a dynamic vacuum (Schlenk line) to obtain [C$_4$mim][OTf] (16.555 g; 58 mmol; 76% yield) and further dried on a Schlenk line for 48 h at 60 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6, δ/ppm): 9.06 (s, 1H), 7.74 (s, 1H), 7.67 (s, 1H), 4.15 (t, 2H, J = 7.3 Hz), 3.86 (s, 3H), 1.78 (m, 2H, J = 7.7 Hz), 1.27 (m, 2H, J = 7.7 Hz), 0.91 (m, 3H, J = 7.3 Hz); ^{13}C NMR (75.48 MHz, DMSO-d_6, δ/ppm): 136.3, 122.7, 122.1, 116.4 (q, J = 375 Hz), 48.5, 35.5, 31.2, 18.6, 13.0.

Synthesis of 1-Butyl-3-imidazolium Nitrate, [C$_4$mim][NO$_3$]. A 65 wt % HNO$_3$ solution (12.0 mL, 173 mmol) was added slowly to a 30 wt % methanol solution of [C$_4$mim][MeCO$_3$] (140.0 mL, 175 mmol) and stirred for 1 h under vacuum to obtain [C$_4$mim][NO$_3$] (34.248 g; 170 mmol; 98% yield) and further dried on a Schlenk line for 48 h at 60 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6, δ/ppm): 9.13 (s, 1H), 7.77 (s, 1H), 7.70 (s, 1H), 4.16 (t, 2H, J = 7.2 Hz), 3.84 (s, 3H), 1.76 (m, 2H, J = 7.4 Hz), 1,27 (m, 2H), 0.90 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75.48 MHz, DMSO-d_6, δ/ppm): 136.6, 123.6, 122.2, 48.5, 35.6, 31.3, 18.7, 13.2.

Preparation of the Alkaline Cu(NH$_3$)$_4$(NO$_3$)$_2$ Standard. 2.5 mL of a 25 wt % NH$_4$OH aqueous solution was added to 5 mL of a 1000 ppm copper standard containing 5 wt % of nitric acid. The solution was further diluted to 50 mL in order to obtain a copper standard with a concentration of 100 ppm.

Preparation of the Halide Contaminated Ionic Liquids. The contaminants [C$_4$mim]X or KX were dissolved in water or ethanol, and small amounts of the solutions were added to the halide-free ionic liquid. This makes the addition quantitatively more correct and easier than adding a weighed amount of ionic liquid to the pure ionic liquid. The reported concentrations are not the halide concentrations present after dilution with water or ethanol, but the halide concentrations in the ionic liquid when no solvent would be present. Weighing of the ionic liquid samples was performed in a glovebag under nitrogen atmosphere.

Preparation of Chloride Contaminated Ionic Liquid Solutions. [C$_4$mim]Cl was dried for 48 h in a vacuum oven at 50 °C. 0.986 g (27.8 mmol) and 0.138 g (7.0 mmol) of the salt were dissolved in 50 and 500 mL of Milli-Q water, respectively, to obtain solutions of 4000 and 100 ppm chloride. 2.5, 1, 0.5, and 0.25 mL of the 4000 ppm chloride solution of [C$_4$mim]Cl were added to 1 g of [C$_4$mim][OAc] or [C$_4$mim][NO$_3$] to obtain concentrations of 10 000, 4000, 2000, and 1000 ppm chloride in the contaminated [C$_4$mim][OAc]. 4, 2, and 1 mL of a 100 ppm chloride of [C$_4$mim]Cl were added to 1 g of [C$_4$mim][OAc] or [C$_4$mim][NO$_3$] to obtain solutions of 400, 200, and 100 ppm chloride in the contaminated ionic liquids. The solutions were further diluted with Milli-Q water to a final volume of 50 mL.

Preparation of Bromide Contaminated [C$_4$mim][Tf$_2$N] Solutions. [C$_4$mim]Br was dried for 48 h in a vacuum oven at 50 °C. 0.548 g (2.5 mmol) and 0.138 g (0.6 mmol) of the salt were dissolved in 50 and 500 mL of ethanol, respectively, to obtain solutions of 5000 and 125 ppm bromide. 2.5, 1, 0.5, and 0.25 mL of the 5000 ppm bromide solution of [C$_4$mim]Br were added to 1 g of [C$_4$mim][Tf$_2$N] to obtain concentrations of 10 000, 4000, 2000, and 1000 ppm bromide in [C$_4$mim][Tf$_2$N]. One mL of a 125 ppm bromide of [C$_4$mim]Br was added to 1 g of [C$_4$mim][Tf$_2$N] to obtain a solution of 100 ppm bromide in the ionic liquid. The solutions were further diluted with ethanol to a final volume of 50 mL.

Preparation of Bromide Contaminated [C$_4$mim][OTf] Solutions. [C$_4$mim]Br was dried for 48 h in a vacuum oven at 50 °C. 0.689 g (3.1 mmol) and 0.170 g (0.8 mmol) of the salt were dissolved in 50 and 500 mL of Milli-Q water, respectively, to obtain solutions of 5000 and 125 ppm bromide. 2, 1, 0.4, and 0.2 mL of the 5000 ppm bromide solution of [C$_4$mim]Br was added to 1 g of [C$_4$mim][OTf] to obtain concentrations of 10 000, 5000, 2000, and 1000 ppm bromide in the contaminated ionic liquid [C$_4$mim][OTf]. 5, 2, and 1 mL of a 125 ppm bromide solution of [C$_4$mim]Br was added to 1 g of [C$_4$mim][OTf] to obtain a 500, 200, and 100 ppm bromide contaminated [C$_4$mim][OTf] ionic liquid. All solutions were further diluted with Milli-Q water to a final volume of 50 mL.

Preparation of Iodide Contaminated Ionic Liquid Solutions. [C$_4$mim]I was dried for 48 h in a vacuum oven at 50 °C. 0.528 g (2.0 mmol) of the salt was dissolved in 50 mL of Milli-Q water to obtain solutions of 5000 ppm iodide. 2, 1, 0.4, and 0.2 mL of the 5000 ppm iodide solution of [C$_4$mim]I were added to 1 g of [C$_4$mim][OTf], [C$_4$mim][NO$_3$] or [C$_4$mim][OAc] to obtain concentrations of 10 000, 5000, 2000, and 1000 ppm iodide in the ionic liquids. The solutions were further diluted with Milli-Q water to a final volume of 50 mL.

Preparation of Ionic Liquids Contaminated with KBr Salts. The halide salt KBr was first dried in a vacuum oven at 50 °C for 48 h. Afterward, 0.074 g (0.6 mmol) of KBr was dissolved in 500 mL of Milli-Q water to obtain a solution of 100 ppm Br. The contaminated ionic liquid [C$_4$mim][OTf] was prepared in the same way as described above for the ionic liquid contaminants.

Instrumentation and Analysis Methods. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance 300 spectrometer, operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C. 18.2 MΩ·cm Milli-Q water was prepared with a Synergy UV water purification system. The halide anion concentrations were determined with a benchtop total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker). Calibration curves and calculated concentrations of chlorine, bromine, and iodine were made with the elemental sensitivities supplied by Bruker. Glasswork and sample carriers were washed for 30 min with hot RBS 50 pF and for 2 h with hot nitric acid to remove all impurities. Afterward, they have been rinsed with Milli-Q water and acetone and dried in an oven at 60 °C for 2 h. All dilutions were prepared with Milli-Q water to avoid chloride or bromide contamination during the sample or standard preparation. 0.5 mL of each contaminated sample was added to 0.5 mL of the alkaline copper standard and mixed to obtain a homogeneous solution. If necessary, dilution of the internal standard was made in order to obtain equal halide and copper concentrations during measurements. The sample carriers were first pretreated by adding 20 μL of silicone solution. After 2 min, 10 μL of the mixture containing the sample and internal standard solution was added onto the sample carrier and dried for 60 min in an oven at 40 °C. The halide concentrations in the contaminated ionic liquids were measured 6 to 10 times. The effect of the matrix on the recovery rates was studied by mixing 0.5 mL of a 10 000 ppm chloride or bromide contaminated ionic liquid with 0.5 mL of a 10 and a 100 ppm alkaline copper standard, respectively. Samples which gave an ionic liquid droplet with a diameter smaller than 3 mm on the carrier after the drying process were not measured and were prepared again.

■ RESULTS AND DISCUSSION

Choice of Sample Preparation. Measuring elemental concentrations and in particular of elements emitting low energy X-rays, such as chlorine, in nonvolatile samples like ionic liquids is a challenge. In general, sample masses lower than 10 μg after drying of the aqueous samples are advised. However, solid samples with higher sample masses can be measured with TXRF as well.[76] The sample amount is kept low in order to avoid matrix effects. In the case of ionic liquids, a small, viscous droplet will be present on the sample carrier in which all the elements are dissolved. Therefore, some precautions were taken to reduce the matrix effects as much as possible. The ionic liquids were diluted at least 100 times in water or ethanol. In this way, 10 μL of the solution gives a maximum of 100 μg of a sample on the sample carrier. This 100-fold dilution also has a significant influence on the detection limits which increase by the same factor. Twenty μL of silicone solution was used in the case of aqueous samples, and sampling was performed 2 min after the addition of the silicone solution. This fast sampling procedure was used because it ensures flat and thin distributed ionic liquid droplets on the carrier. Isopropanol from the silicone solution which is not yet evaporated after 2 min distributes the aqueous sample over the carrier whereas silicones ensure that the droplet remains fixed in the center of the carrier. A sample was not measured in the rare case that a droplet smaller than 3 mm was obtained after drying. Ideal samples are flat, homogeneously distributed over the carrier, and between 0.3 and 0.8 mm in diameter. The samples were dried slowly at 40 °C for 1 h. Higher temperatures decrease the viscosity of the ionic liquid and could lead to shrinkage of the ionic liquid droplet on the carrier and thus to a thicker droplet.

Chloride Impurities in Ionic Liquids. The most common method for the synthesis of [C$_4$mim][OAc] or [C$_4$mim][NO$_3$] is by the addition of KOAc or KNO$_3$ to [C$_4$mim]Cl in dry acetone. In this reaction, the formed KCl is insoluble and it precipitates and can be removed by filtration. The main impurity in the ionic liquids obtained from this synthesis method is [C$_4$mim]Cl. Therefore, to reproduce these conditions, different amounts of [C$_4$mim]Cl were added to [C$_4$mim][OAc] or [C$_4$mim][NO$_3$] and measured with an alkaline copper standard. Although we observed in our recent study on the determination of halides in aqueous solution by TXRF that concentrated matrices are harmful for the quantification of chloride,[75] this issue was not observed in the case of chloride determination in ionic liquids.[75] Recovery rates (RR) between 85% and 110% were obtained in the case of [C$_4$mim][NO$_3$] for chlorine concentrations above 400 ppm and between 90% and 98% in the case of [C$_4$mim][OAc] over the whole concentration range (Table 1). The difference between chlorine determination in aqueous solutions and ionic liquids could be due to the difference in distribution of chlorine and copper in both samples after the drying process. Copper and chlorine are dissolved homogeneously in the ionic liquid droplet which remains on the sample carrier after the drying procedure. This is not always the case when a solvent evaporates and crystallization processes of the remaining salts start to occur. The formation of crystals is dependent on the solubility product of the corresponding salts. This means that some salts crystallize faster than others and form aggregates, giving a less homogeneous distribution of all elements on the sample carrier. The relative standard deviations (RSDs) were smaller than 15% in all cases (Table 1, Figure 3). We also observed that concentrations of 200 ppm were difficult to measure. This is because of the 100-fold dilutions in which only 2 ppm of chloride is actually measured. Overlapping peak tails of, for example, argon, and small chloride contaminations on the carrier, in the starting products or on the glassware can therefore have a large influence on the recalculated end results. The same observation was also made for determination of chloride in water samples.[75]

Table 1. Recovery Rates (RR) and Relative Standard Deviations (RSD) of the Chloride Concentrations (Added as [C$_4$mim]Cl) in the Ionic Liquids [C$_4$mim][OAc] and [C$_4$mim][NO$_3$]

	[C$_4$mim][OAc]		[C$_4$mim][NO$_3$]	
[Cl] (ppm)	RR (%)	RR (%)	RSD (%)	RSD (%)
10 000	92	7	85	10
5000			89	6
4000	90	8		
2000	94	14	100	9
1000	97	5	98	12
400	91	10	110	6
200	96	10	137	5
100	98	13	191	10

Bromide Impurities in Ionic Liquids. The hydrophobic ionic liquid [C$_4$mim][Tf$_2$N] was selected to demonstrate that the method can also be applied to water insoluble ionic liquids. In general, [C$_4$mim][Tf$_2$N] can be easily synthesized by a metathesis reaction between an alkali salt such as LiTf$_2$N and a halide precursor such as [C$_4$mim]Br or [C$_4$mim]Cl. [C$_4$mim]Cl was not chosen as an impurity because there is an overlap

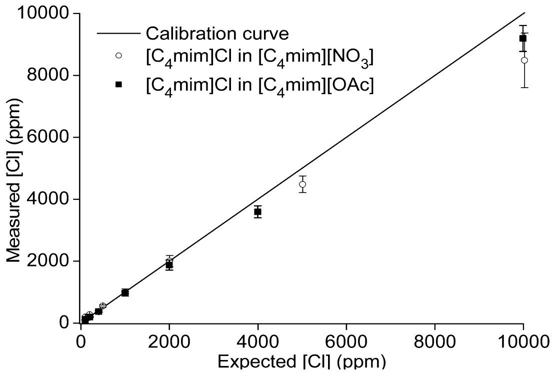

Figure 3. Plot of the recovered chloride concentrations (added as $[C_4mim]Cl$) in $[C_4mim][OAc]$ and $[C_4mim][NO_3]$.

Table 2. Recovery Rates (RR) and Relative Standard Deviations (RSD) of the Bromide Concentrations (Added as $[C_4mim]Br$) in $[C_4mim][Tf_2N]$ and $[C_4mim][OTf]$

	$[C_4mim][Tf_2N]$		$[C_4mim][OTf]$	
[Br] (ppm)	RR (%)	RSD (%)	RR (%)	RSD (%)
10 000	105	6	100	5
5000			103	3
4000	105	9		
2000	113	4	96	8
1000	100	6	105	6
500			101	6
200			102	9
100	100	6	97	4

between the chlorine and sulfur peak, present in the Tf_2N anion, in the TXRF spectrum. After synthesis and several washing steps with water, almost all LiBr is removed from the hydrophobic ionic liquid phase and the main impurity remaining in the ionic liquid is $[C_4mim]Br$. This impurity was imitated by adding a known amount of $[C_4mim]Br$ to the $[C_4mim][Tf_2N]$ ionic liquid, which was synthesized via a halide-free method. The reliability of the copper standard $Cu(NH_3)_4(NO_3)_2$ was also tested for the presence of $[C_4mim]Br$ impurities in the hydrophilic ionic liquid $[C_4mim][OTf]$. The recovery rates of $[C_4mim]Br$ in both ionic liquids were found to be in between 96% and 113%, and the relative standard deviations (RSDs) were smaller than 10% (Figure 4, Table 2). In general, the recovery rates and RSD values for bromine are better than those for chlorine. This is due to the lower absorption of the secondary, higher energy X-rays of bromine by the ionic liquid matrix.

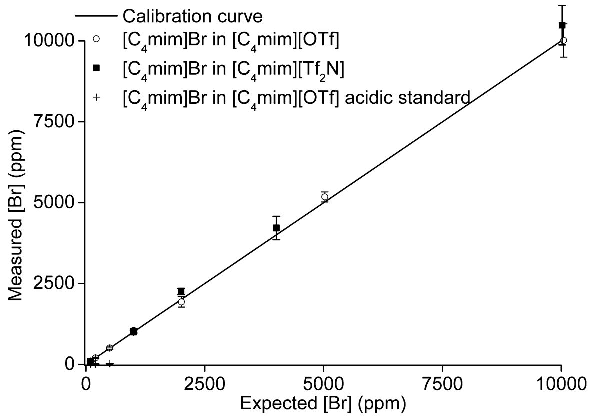

Figure 4. Plot of the recovered bromide concentrations (added as $[C_4mim]Br$) in $[C_4mim][Tf_2N]$ and $[C_4mim][OTf]$.

Furthermore, an acidic copper standard was tested in the lower bromine concentration range with $[C_4mim][OTf]$ as contaminated ionic liquid. The recovery rates of 100, 200, and 500 ppm bromine in the ionic liquid were 15%, 8%, and 6%, respectively, with RSD values between 10% and 20%.

Iodide Impurities in Ionic Liquids. The ionic liquids $[C_4mim][NO_3]$, $[C_4mim][OAc]$, and $[C_4mim][OTf]$ were all contaminated on purpose with various amounts of $[C_4mim]I$. The measured iodide concentrations for the ionic liquids $[C_4mim][OAc]$ and $[C_4mim][NO_3]$ were about 70% higher than the expected values although the RSD values were all smaller than 5% (Table 4). By correcting the sensitivity factor for iodine, a new and good fitting calibration curve was obtained. However, it has to be mentioned that this sensitivity factor was very different from the one used for a pure water phase. Depending on the matrix, different sensitivity factors for one element are possible in TXRF, but deviations of about 70% are strange. The values found for $[C_4mim]I$ in $[C_4mim][OTf]$ were quite scattered and did not lie on one straight calibration line. For a concentration of 10 000 ppm, a recovery rate of 131% was found and the recovery rates decreased to 37% with decreasing concentrations of iodide in the ionic liquids. Also, the RSD values are much higher than in $[C_4mim][NO_3]$ or $[C_4mim][OAc]$ (15−26%) (Table 3). At high iodide concentrations, small crystals were observed in the ionic liquid on the sample carrier. It is possible that the solubility of the iodide salt in the ionic liquid is not high enough after drying and that the distribution of iodide and copper in the sample is no longer homogeneous, resulting in wrong results. Moreover, the sensitivity of iodine is lower than that of chlorine when a TXRF apparatus with a molybdenum source is used. For concentrations below 500 ppm and a 100-fold dilution, no iodine peaks could clearly be detected. A TXRF apparatus with a tungsten source could be a solution for this problem because the iodine sensitivity of the peak is much higher.

KX Impurities. Although less KX impurities are present in synthesized ionic liquids, they are also investigated as possible contamination. Due to the lower solubility of KX salts in ionic liquids,[77] a lower concentration range was selected. KBr concentrations of 100, 200, and 500 ppm were added to $[C_4mim][OTf]$. Also KI and KCl salts were tested but at higher concentration in order to obtain a higher signal-to-noise ratio of the characteristic peaks after dilution. Formation of crystals was observed in the ionic liquid, and the recovery rates were far lower than 100%. Again, a homogeneous distribution of the halide salt and copper standard is necessary to obtain equal matrix effects for both elements and in order to find correct concentration values. Due to the much higher sensitivity of bromine for primary X-rays (iodine is measured on the low energetic L-line), significantly lower concentrations could be tested. Recovery rates of 88%, 89%, and 94% were obtained for 100, 200, and 500 ppm bromide, respectively. The RSD values were below 10% (Table 4).

Matrix Effects. One of the main advantages of using TXRF in comparison with EDX is the lower matrix effect. This advantage is valid if the sample is embedded in small amounts of matrix and if heavier, less matrix sensitive elements are measured. There were significant matrix effects when larger sample amounts were used or when light elements were

Table 3. Recovery Rates (RR) and Relative Standard Deviations (RSD) of the Iodide Concentrations (Added as $[C_4mim]I$) in $[C_4mim][NO_3]$, $[C_4mim][OTf]$, and $[C_4mim][OAc]$

	$[C_4mim][NO_3]$		$[C_4mim][OTf]$		$[C_4mim][OAc]$	
[I] (ppm)	RR (%)	RSD (%)	RR (%)	RSD (%)	RR (%)	RSD (%)
10 000	163	4	131	12	169	1
5000	165	4	94	15	171	3
2000	152	3	39	26	178	4
1000	139	4	37	15	175	3

Table 4. Recovery Rates (RR) and Relative Standard Deviations (RSD) of the Bromide Concentrations (KBr) in $[C_4mim][OTf]$

	$[C_4mim][OTf]$	
[Br] (ppm)	RR (%)	RSD (%)
500	94	5
200	89	5
100	88	6

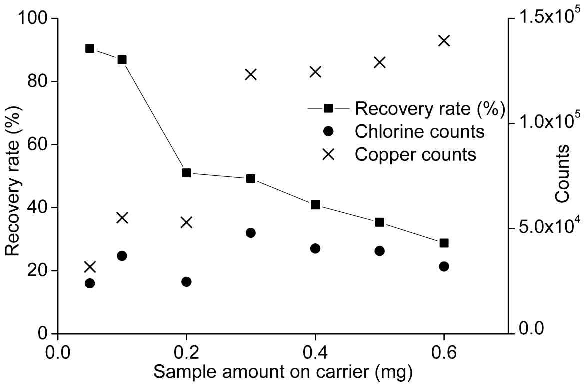

Figure 5. Influence of the sample amount on the chlorine recovery rate (■) and number of counts for copper (×) and chlorine (●). Sample: 0.5 mL of a 10 ppm alkaline copper standard and 0.5 mL of a 10 000 ppm chloride impurity (added as $[C_4mim]Cl$) in 1 g $[C_4mim][OAc]$ diluted in 50 mL H_2O. Measured concentrations after dilution were 5 ppm Cu and 100 ppm Cl.

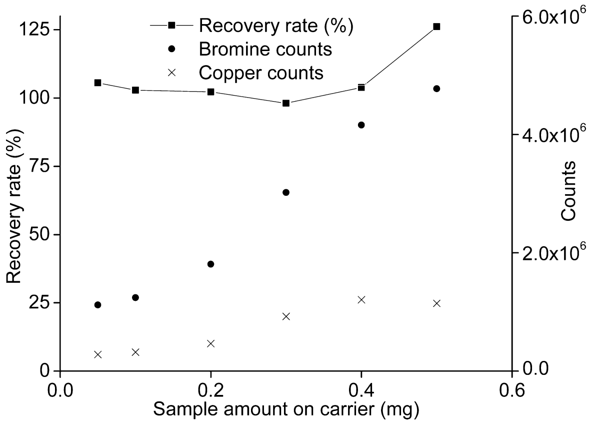

Figure 6. Influence of the sample amount on the bromine recovery rate and number of counts. Sample: 0.5 mL of 100 ppm alkaline copper standard and 0.5 mL of a 10 000 ppm bromide impurity (added as $[C_4mim]Br$) in $[C_4mim][Tf_2N]$ diluted in 50 mL of ethanol. Measured concentrations after dilution were 50 ppm Cu and 100 ppm Br.

measured. For conventional TXRF measurements, it is advised to add a maximum of 10 μg onto the sample carrier. For ionic liquids, this is a problem because they form a nonvolatile matrix on the carrier, which cannot be removed during the drying process. In our measurements, a maximum sample weight of 100 μg was used. Working with lower amounts is possible by further diluting the ionic liquid. The drawback of dilution is that the number of counts and thus the detection limit of halides in ionic liquids will decrease. Working with high sample amounts can give larger errors on the recovery rates (Figures 5 and 6). The main scattering process for low energy secondary X-rays is a photoelectric effect. Here, a secondary X-ray, produced by a lighter element in the matrix, totally loses its energy by ejecting again an electron from a specific matrix element. The element-specific *mass attenuation coefficient*, defined as the absorption of radiation of a specific wavelength per unit mass, is significantly higher for the energy X-rays of the lighter elements.[78] Large amounts of organic matrices, such as ionic liquids, will significantly absorb secondary X-rays and decrease the number of counts for the lighter elements. The absorption is less pronounced for X-rays coming from heavier elements and is thus not equal to all elements present in the sample. The count ratio between chlorine or bromine and the copper standard is changing and has an influence on the calculated concentration. The effect is very clear when chlorine is determined with the copper standard. The recovery rates for chlorine in 50 or 100 μg of ionic liquid on the sample carrier are still above 85%. The chlorine recovery rates drastically decrease when the sample amount is further increased. The number of counts for copper is increasing with increasing sample amount. In addition, the counts originating from chlorine are even decreasing due to absorption of the matrix when more sample is loaded on the sample carrier (Figure 5).

For the same reason, the shape of the droplet is of crucial importance when measuring chlorine concentrations. Multiple thicker droplets on the sample carrier give lower recovery rates than a flatter homogeneous droplet with a large diameter because the chlorine X-rays have to travel longer distances through the matrix. Shorter drying times for instance give larger solvent matrices, while higher drying temperatures or the absence of a silicone coating on the sample carrier give often multiple thick droplets. Furthermore, thick droplets can contaminate the detector, which is positioned very close to the sample. Therefore, it is recommended to follow the sample preparation instructions very carefully in case of chlorine measurements. For an ionic liquid contaminated with bromide, the effect is reversed but much less pronounced (Figure 6). Copper is a lighter element than bromine, which means that the secondary X-rays of copper are more strongly absorbed by the matrix than those of bromine.

Due to the very small angle of the incident primary X-ray beam, TXRF is only analyzing the surface of the ionic liquid droplet. Therefore, the penetration depth, which is defined as the depth at which the X-ray intensity is reduced to 1/e, is very low. The penetration depth depends on the energy of the X-rays, the type of matrix, the shape of the remaining ionic liquid droplet, and the incident angle of the primary X-rays. Klockenkämper reported penetration depths in TXRF measurements ranging between 5 and 320 nm.[54] An inhomogeneous accumulation of copper or the halides at the ionic liquid surface could lead to wrong results. Recent articles reported the enrichment of the larger anions and cations on the ionic liquid−air interface.[79−81] Moreover, Maier et al. found that the first few nanometers of the water-free ionic liquid [EMIM]-[$EtOSO_3$] (where [$EtOSO_3$] is ethyl sulfate) were enriched with the larger cation $[Pt(NH_3)_4]^{2+}$ and depleted with the smaller chlorine anion of the complex $[Pt(NH_3)_4]Cl_2$.[82] A platinum enrichment factor of 3 was found in comparison with the bulk patina concentration. The enrichment of metal complexes on the ionic liquid−air surface could lead to determination of halide concentrations which are too low. In our measurements, it was expected that copper would segregate more to the surface than the halides ions. However, the effect was not observed which could be due to four different reasons. First, the penetration depth of the X-rays is deeper than the surface which was studied in the cited references. Second, our studies were performed with ionic liquids which were not extremely dry. Surface effects in wet ionic liquids can be different from surface effects in dry ionic liquids, but such comparative studies have not been described in the literature yet. Third, the error which is due to absorption is much larger than the error which is due to enrichment of copper and depletion of the halide at the surface. Anyhow, it is advisable to use sample amounts which are similar to those used for construction of the calibration curves.

Detection limits. The detection limits of TXRF depend on different parameters such as the concentration, matrix, measuring time, etc. Detection limits between 0.100 and 0.200 ppm were found for measured chlorine concentrations below 100 ppm after ionic liquid dilution. The detection limits in the same concentration range were between 0.005 and 0.020 ppm for bromine and 0.100 and 0.150 ppm for iodine. Unfortunately, it was necessary to dilute the ionic liquid 100 times to avoid matrix effects and contamination of the detector. This also means that the actual detection limits for halides in ionic liquid increase 100-fold to a maximum of 2 ppm bromine, 20 ppm chlorine, and 15 ppm iodine. Another problem is measuring chlorine in ionic liquids containing sulfur because there is a significant overlap between the characteristic X-ray peaks of these elements. Future research will focus on the removal of the matrix from the impurities to reach the very low detection limits of the equipment.

■ CONCLUSIONS

It has been proven that chloride and bromide contaminations in ionic liquids could be detected and quantified accurately and precisely by measuring the chlorine or bromine content with TXRF as long as the total amount and the shape of ionic liquid droplet on the sample carrier were carefully controlled. The results were not as good for iodide impurities. Two calibration curves could be drawn through the different data points, but the sensitivity factor was lying about 70% above what was expected. Moreover, a precipitate and an inhomogeneous distribution were observed on the sample carrier which was giving incorrect results and was probably due to a lower solubility. A similar observation was made for high concentrations of halide salts in the ionic liquid. The detection limits of halides are in the ppb range but increase 100-fold due to the required dilution to 2, 20, and 15 ppm for bromine, chlorine, and iodine, respectively.

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Notes

The authors declare no competing financial interest.

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