

IC-MS Determination of Anionic Ionic Liquids, Counterions, and Impurities

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ABSTRACT

The term “ionic liquid” commonly refers to organic salts with relatively low melting points (below 100 °C)¹ which usually consist of an organic cation or anion and a counterion, in either organic or inorganic form. Ionic liquids have unique characteristics, including extremely low vapor pressure, excellent thermal stability, electrical conductivity, and high polarity. The miscibility of ionic liquids with water or organic solvents varies with side-chain lengths on the cation and with choice of anion. A wide range of applications using ionic liquids has been reported in many areas such as catalysis, organic chemistry, electrochemistry, and separation science.²⁻⁸

Little information has been reported for ensuring the quality of ionic liquids, especially for catalysis and pharmaceutical or electrochemical applications.⁹ Impurities in an ionic liquid can change its physical properties, reduce catalytic efficiency, or cause other adverse effects due to the toxicity of some ionic liquids, such as imidazoliums.¹⁰ Therefore, an analytical method is desired for quality assurance, the assessment of residues, and the effectiveness of any removal process.

This study describes a comprehensive ion chromatography mass spectrometric (IC-MS) method for the determination of anionic ionic liquids, anionic counterions, and anionic impurities. Chromatographic separation was achieved on an IonPac[®] AS20 hydroxide selective anion-exchange column. A 30 minute gradient was applied to separate 17 anionic analytes and a single quadrupole mass spectrometer was used for selective, sensitive detection.

After a simple dilution, samples were injected directly onto the IC-MS system and quantified against standard calibration curves with $R^2 > 0.99$. Method detection limits (MDLs) were analyte dependant; however, quantification was achieved for low ppb levels (low ppm in original samples). This method has been successfully applied to analyze commercially available ionic liquids including lidocaine chloride, 1-butyl-3-methylimidazolium hexafluorophosphate and 1-ethyl-3-methylimidazolium tosylate.

INSTRUMENTATION

Ion Chromatography

System:	ICS-2000 Reagent-Free™ Ion Chromatography (RFIC™)	
Column:	IonPac AS20 hydroxide selective anion-exchange column	
Flow Rate:	0.25 mL/min	
Temperature:	35 °C	
Mobile Phase:	Hydroxide gradient electrolytically generated from EG II KOH cartridge	
	Time /min	hydroxide concentration
	-5	10 mM
	0	10 mM
	6	30 mM
	14	60 mM
	16	100 mM
	30	100 mM
	30.5	10 mM
Detection:	Suppressed Conductivity MSQ Plus™ mass spectrometer	

Mass Spectrometry

Interface:	Electrospray Ionization (ESI)
Probe Temperature:	500 °C
Nebulizer Gas:	Nitrogen at 85 psi
Needle Voltage:	1.0 kV
Scan Mode:	Selected Ion Monitoring (SIM) See Table 1 for details.

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CHEMICALS AND REAGENTS

Ionic liquids selected in this study were purchased from Sigma-Aldrich, including lidocaine (chloride salt, L5647), 1-butyl-3-methylimidazolium hexafluorophosphate (70956), and 1-ethyl-3-methylimidazolium tosylate (89155). Salts of counterions and inorganic ions were purchased from Aldrich and Fluka. Acetonitrile was obtained from Burdick & Jackson (HPLC/UV grade, Honeywell, Muskegon, MI).

RESULTS AND DISCUSSION

Chromatography

Previously reported methods used a reversed-phase column to analyze organic cations or anions, and an ion-exchange column to analyze inorganic counterions and impurities, such as tetrafluoroborate (BF_4^-), methanesulfonate (MSA, CH_3SO_3^-), hexafluorophosphate (PF_6^-), chloride (Cl^-), bromide (Br^-) and iodide (I^-). A previous study using an Acclaim® Trinity P1 column simultaneously separated cationic/anionic liquids, counterions, and inorganic ions with the capability to quantify parts-per-million (ppm) level impurities in the final diluted solution (in press). This present study focuses on the quantitative determination of anionic impurity profiles in ionic liquids which includes additional commonly encountered anions: fluoride (detected as HF_2^-), acetate (CH_3COO^-), butanesulfonate ($\text{CH}_3(\text{CH}_2)_3\text{COO}^-$), trifluoroacetate (TFA, CF_3COO^-), nitrate (NO_3^-), sulfate (detected as HSO_4^-), triflate (CF_3SO_3^-), phosphate (detected as H_2PO_4^-), thiocyanate (SCN^-) and perchlorate (ClO_4^-). A multistep gradient (details described in experimental section) was applied to chromatographically separate all analytes (Figure 1).

The authors chose ion chromatography for quantification purposes due to the significantly improved sensitivity for anionic species observed with IC-MS compared to the LC-MS method. This can be explained by comparing the eluents entering the MS detector: for IC-MS methods, the eluent is virtually only analytes in deionized water. This keeps the electrospray current at a very low level and analytes can be ionized and detected very efficiently. In comparison, for the LC-MS method, analytes are eluted in a mobile phase of higher ionic strength (5 mM total acetate), where analytes are detected with much less efficacy.

Quantitative Analysis

Calibration and Calibration Range

Calibration standards were prepared from 2 ppb to 1000 ppb at 8 levels: 2 ppb, 5 ppb, 10 ppb, 20 ppb, 50 ppb, 100 ppb, 500 ppb, and 1000 ppb. Due to low level impurities of some anions (such as chloride, bromide, and sulfate) found in ionic liquid standards, calibration standard sets were prepared individually for those anions with each standard solution containing only one analyte. Different standard curve fitting parameters (linear, quadratic or cubic) were applied to achieve the best correlation coefficient (R^2). As shown in Table 2, $R^2 > 0.99$ was achieved for each analyte from the lowest calibration level with $S/N > 10$ to 1000 ppb.

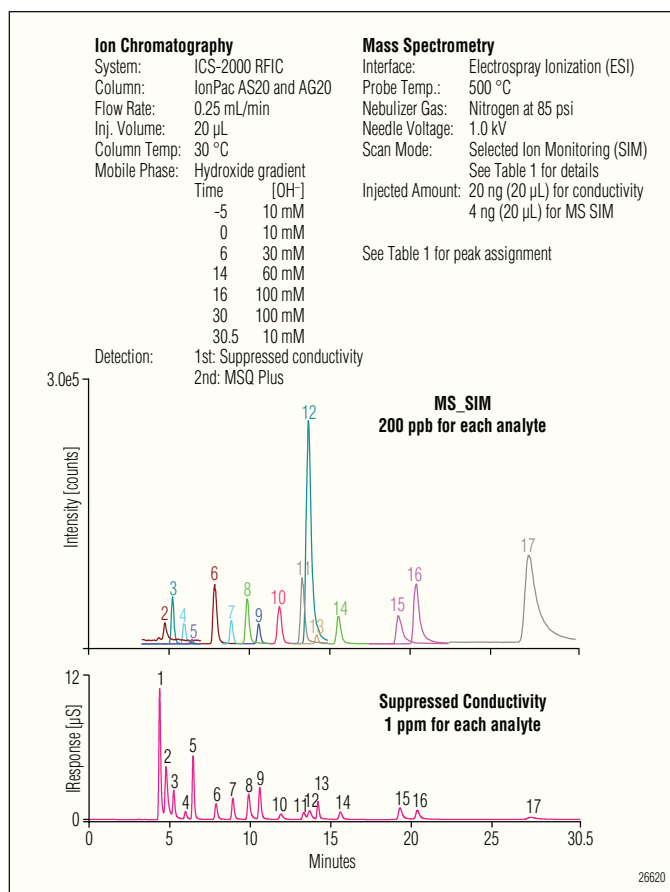


Figure 1. Suppressed conductivity and MS SIM chromatograms for ionic liquids and anions.

Table 1. Ionic Liquids, Counterions, and Impurities

Peak	Analyte	Formula	Ret. Time	SIM	Scan Event	Cone Voltage
1	Fluoride	$[\text{F}+\text{HF}]^-$	4.4	39.0	3.5-7.2	25
2	Acetate	CH_3COO^-	5.0	59.1	3.5-7.2	50
3	Methanesulfonate	CH_3SO_3^-	5.3	95.0	3.5-7.2	60
4	Butanesulfonate	$\text{CH}_3(\text{CH}_2)_3\text{SO}_3^-$	6.0	137.2	3.5-7.2	60
5	Chloride	Cl^-	6.5	35.0	3.5-7.2	80
6	Trifluoroacetate	CF_3COO^-	7.9	113.1	7.2-9.5	30
7	Bromide	Br^-	9.0	78.9	8.5-9.5	100
8	Nitrate	NO_3^-	9.9	62.0	9.5-11.4	75
9	Sulfate	HSO_4^-	10.7	97.1	9.5-11.4	50
10	Tosylate	$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$	12.0	171.0	11.4-12.8	60
11	Tetraborate	BF_4^-	13.4	87.0	12.8-15.1	50
12	Triflate	CF_3SO_3^-	13.8	149.1	12.8-15.1	60
13	Phosphate	H_2PO_4^-	14.3	97.1	12.8-15.1	50
14	Iodide	I^-	15.7	127.0	15.1-17.6	90
15	Thiocyanate	SCN^-	19.4	58.0	17.6-22.6	50
16	Perchlorate	ClO_4^-	20.5	99.0	17.6-22.6	80
17	Hexafluorophosphate	PF_6^-	27.7	145.1	22.6-30.5	80

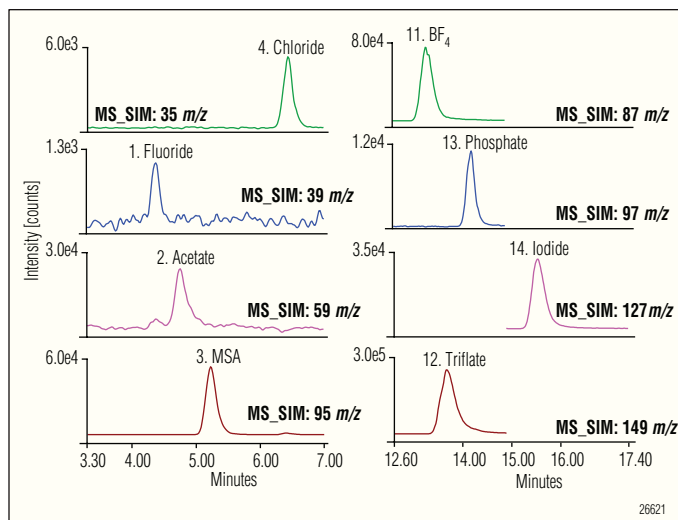


Figure 2. MS SIM chromatograms show differentiation of closely eluted analytes.

Table 2. Calibration, Range, and Method Detection Limits (MDL)							
Peak	Analyte	Calibration Range (ppb)		Fitting	R ²	%RSD ^b	MDL ^c
1	Fluoride ^a	100	1000	Linear	0.997	9.35	29.39
2	Acetate ^a	50	1000	Linear	0.999	NC ^d	NC ^d
3	Methanesulfonate	5	1000	Quadratic	0.999	5.40	3.39
4	Butanesulfonate	5	1000	Linear	0.999	3.90	2.62
5	Chloride	2	1000	Quadratic	0.996	5.55	3.49
6	Trifluoroacetate	5	1000	Cubic	1.000	1.72	1.16
7	Bromide	2	1000	Cubic	0.997	2.95	1.85
8	Nitrate	2	1000	Cubic	0.994	2.86	1.80
9	Sulfate	5	1000	Quadratic	0.998	9.75	6.13
10	Tosylate	5	1000	Quadratic	0.999	1.55	1.04
11	Tetraborate	5	1000	Cubic	1.000	4.99	3.36
12	Triflate	5	1000	Cubic	0.998	2.11	1.42
13	Phosphate	5	1000	Quadratic	1.000	4.99	3.36
14	Iodide	5	1000	Cubic	1.000	4.42	2.78
15	Thiocyanate	5	1000	Cubic	1.000	1.69	1.06
16	Perchlorate	5	1000	Cubic	0.999	4.54	2.85
17	Hexafluorophosphate	5	1000	Quadratic	0.998	4.76	2.99

^aData obtained from previous experiments

^b%RSD calculated based on experiments with n > 5

^cMDL calculated by $MDL = S \times t_{(99\%, n-5)}$

^dNC not calculated

Method Detection Limits (MDL)

Method detection limits were statistically calculated by equation $MDL = S \times t_{99\%}$, where S is the standard deviation and t is the student's t at 99% confidence interval ($n > 5$). Results shown in Table 2. MDLs were achieved at low ppb levels for each analyte, ranging from 1.04 ppb (tosylate) to 6.13 ppb (sulfate). The detection limit using the IC-MS method is significantly lower than the MDL using an LC-MS method with a trimode column (in press), making IC-MS the preferred method for low-level quantification.

Analysis of Commercial Ionic Liquids

Three commercially available ionic liquids (dissolved in DI water at 2 mg/mL) were analyzed for impurities by the IC-MS method. Eight anions were detected in these ionic liquids at very low ppm levels. Acetate, chloride, bromide, sulfate, and PF_6^- were observed in individual or all samples at quantifiable levels (> 2.5 ppm in the original sample). Chloride (in two of the three samples) and bromide (in all samples) were observed as the major impurities. Figure 3 shows the conductivity and MS SIM traces of 1-butyl-3-methylimidazolium/ PF_6^- and the detected anions.

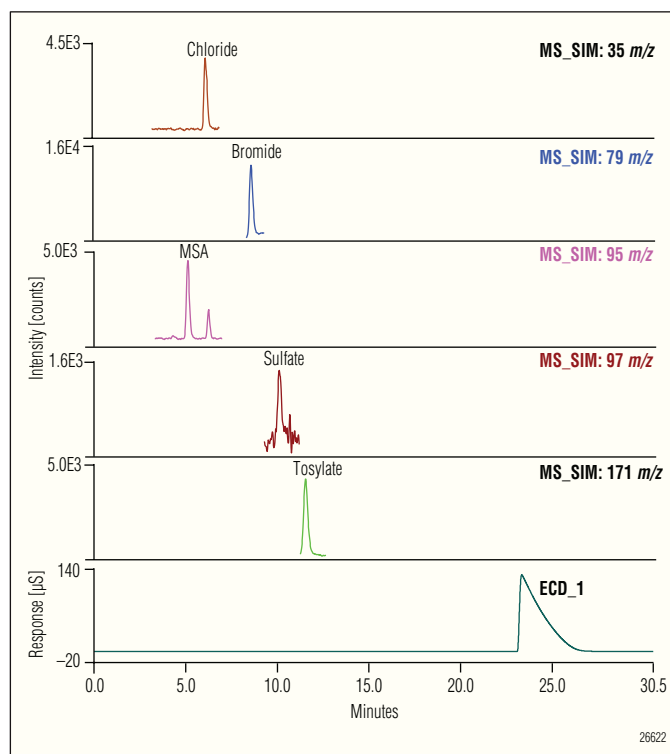


Figure 3. PF_6^- and impurity anions by IC-MS and conductivity.

Table 3. Quantification of Anions in Commercial Ionic Liquids

Analyte	Lidocaine/HCl	1-butyl-3-methyl-imidazolium/PF ₆ ⁻	1-ethyl-3-methyl-imidazolium Tosylate
Acetate	25.99	ND	ND
Methanesulfonate	ND	BRL	ND
Chloride	—	12.55	13.23
Bromide	7.7	7.69	3.41
Nitrate	BRL	BRL	BRL
Sulfate	BRL	BRL	5.65
Tosylate	BRL	BRL	—
Hexafluorophosphate	BRL	—	14.08

ND: Not detected

BRL: Detected but below lowest quantification level. (<2.5 ppm in original sample)

CONCLUSIONS

This study describes an IC-MS method for quantitative analysis of anionic ionic liquids, counterions, and impurities. Low ppb-level quantification was achieved for diluted solutions (low ppm level in original sample) with good coefficient of determination ($R^2 > 0.99$). Three commercially available ionic liquid samples were analyzed by this method with the major impurities of chloride and bromide quantified at ppm levels. The results shown here demonstrate that this method can be used for quality assurance of ionic liquids, contamination analysis, and residue assessment of removal processes.

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