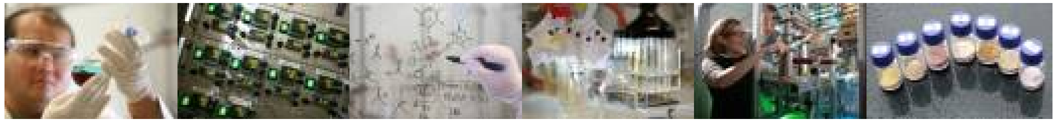

Analytics and Purity in Ionic Liquids

Dr. Peter Schulz

FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

Lehrstuhl für Chemische Reaktionstechnik

Outline

- Analysis of Ionic Liquids
  - Karl Fischer titration
  - Liquid Chromatography
  - Electron Spray Mass Spectroscopy
  - X-ray Photoelectron Spectroscopy
- Recycling – Purifying of Ionic Liquids
  - Distillation
  - Zone melting
  - NMR – spectroscopy
  - Headspace Gas chromatography
  - Inductively Coupled Plasma Optical Emission Spectrometry

Purity of Ionic Liquids

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- How to obtain ultra-pure Ionic Liquids
  - by own synthesis
  - using pure starting materials
    - freshly distilled under inert atmosphere
    - freshly recrystallized
    - Avoiding of grease
  - work-up
    - precipitation (AgCl ↓ in dry acetone)
    - washing with water
    - washing with organic solvent (cyclohexane or Et_2O)
    - heating and evaporation

Analysis of Ionic Liquid

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Analytical method	Abbreviation	Impurities to detect
Karl Fischer Titration	KF	water
Nuclear Magentic Resonance	NMR	organics
Inductively Coupled Plasma Optical Emission Spectrometry	ICP OES	metal
High pressure liquid chromatography (ion chromatography)	HPLC IC	organics ions
Electon Spray Mass Spectromety	ESI-MS	*structure analysis*
X-Ray Photoelectron Spectroscopy	XPS	*empirical formula* contaminants surface
Headspace Gaschromatography	HS-GC	volatile organics

Impurity is water
Karl-Fischer Titration

- Volumetric: water content: 0.1% -100%
- Coulometric: water content: <1%

$$I_2 + SO_2 + H_2O \rightleftharpoons SO_4^{2-} + 2I^- + 4H^+ \quad (1)$$

$$SO_2 + 2H_3COH \rightleftharpoons H_3CO\text{-}SO_2^- + H_3COH_2^+ \quad (2)$$

$$B + SO_2 + H_3COH \rightleftharpoons H_3CO\text{-}SO_2^- + BH^+ \quad (3)$$

$$H_2O + I_2 + BH^+ + H_3CO\text{-}SO_2^- + 2B \rightarrow H_3CO\text{-}SO_3^- + 3BH^+ + 2I^- \quad (4)$$

- Aldehyd and keto-functionalized ILs need special reagent (e.g. Hydranal®-Coulomat CG-K or AQUAMICRON® AKX/CXU)

Analysis of Ionic Liquid
Origin of Impurites

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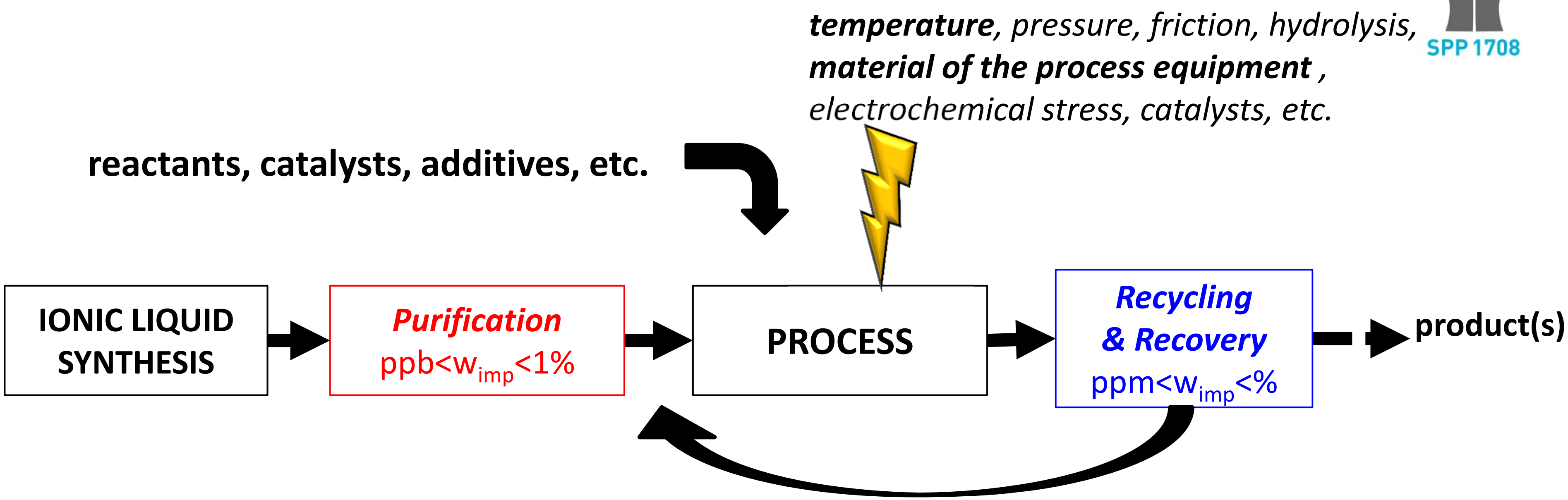

- unconverted reactants
- impurities contained in reactants
- by-products of the quaternization
- impurities from metathesis
- decomposition products (IL)
- application-specific imp.
  e.g. from educt-IL-reactions
- brownish color

- P. Keil, M. Kick, A. König: Long-Term Stability, Regeneration and Recycling of Imidazolium-based Ionic Liquids; Chemie Ingenieur Technik, 84 (2012), No. 6, 859–866.
- Keil, P.; A. König: *Analysis of decomposition products in thermally stressed ionic liquids*, in *EUCHEM*. 2012: Wales.

Analysis of Ionic Liquid
Origin of Impurites

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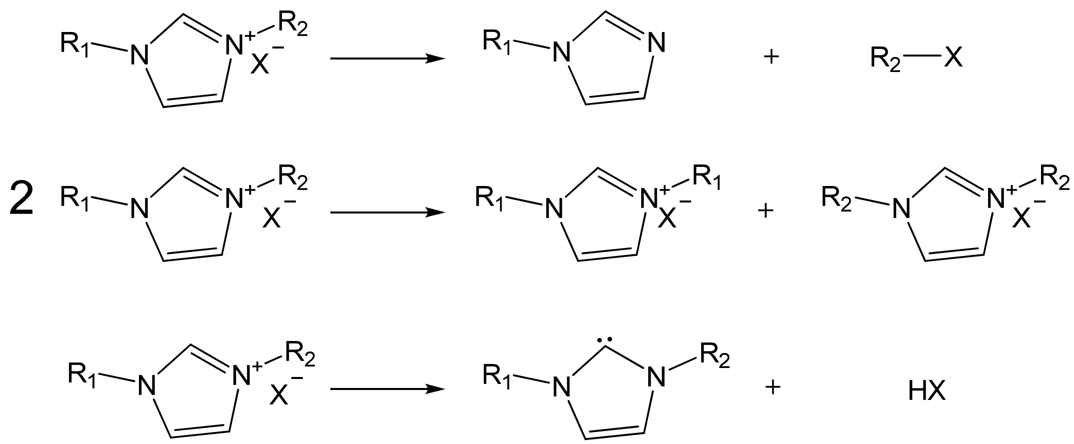
Thermal Decomposition of Imidazolium-based Cations

dealkylation [1]

scrambling of alkylchains [2]

deprotonation & consecutive reactions [3]

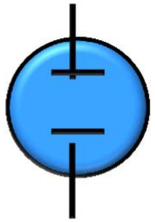


[1] Chan, B., N. Chang, and M. Grimmett, Australian Journal of Chemistry, 1977. 30(9): p. 2005-2013.
[2] Meine, N., F. Benedito, and R. Rinaldi, Green Chemistry, 2010. 12(10): p. 1711-1714.
[3] Holloczki, O., et. al., New Journal of Chemistry, 2010. 34(12), p. 3004-9

Analysis of Ionic Liquid
coupled chromatography systems IC-IC/LC-MS^3

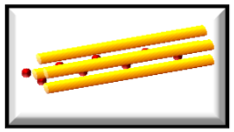
HPLC
Ultimate3000
(Dionex)

IC^2 anions + cations
***ICS-3000* (Dionex)**



- 2D-chromatography
- matrix elimination techniques
- high analyte concentrations
- up to 80% organic solvent

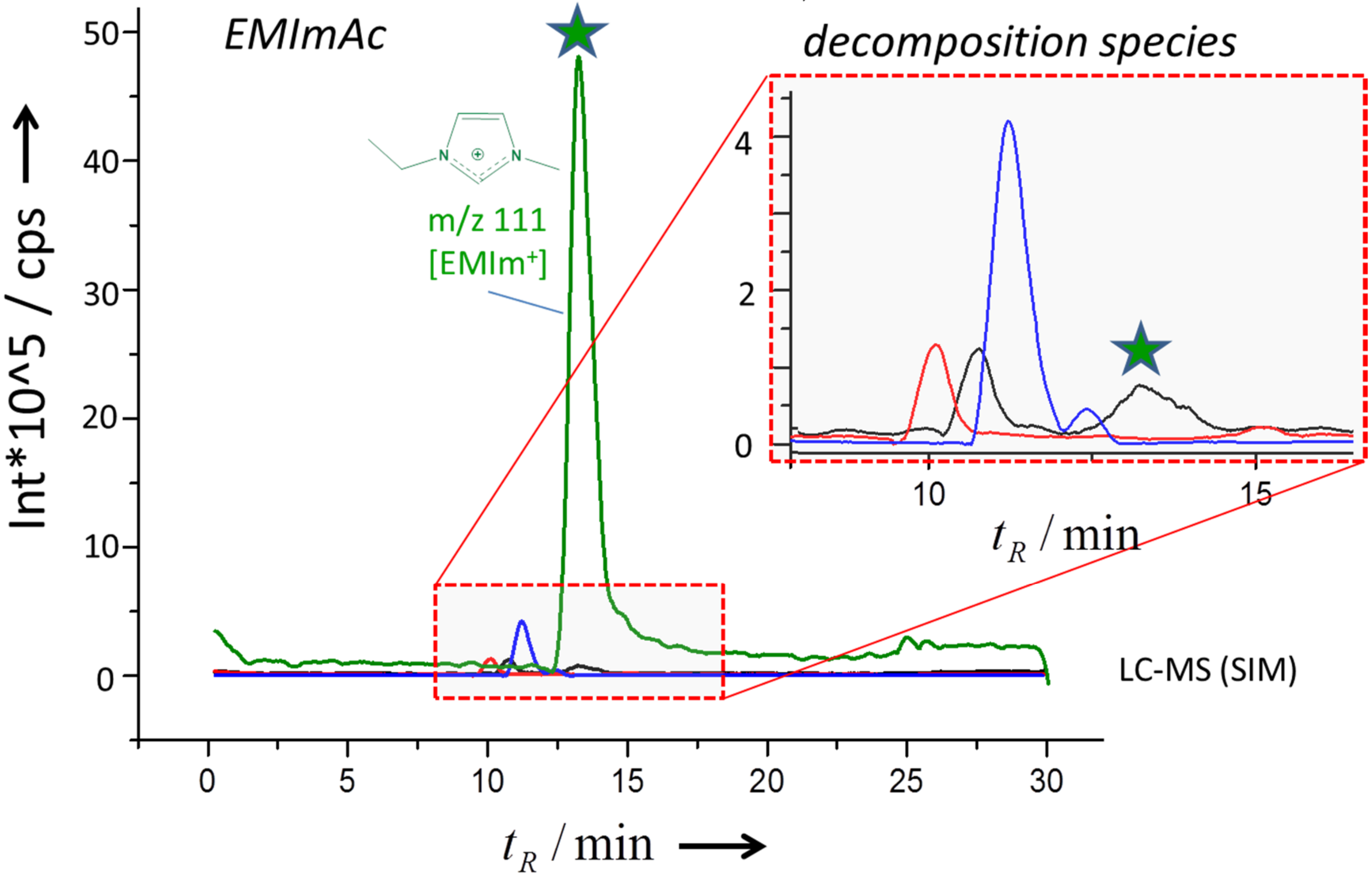
direct infusion by syringe



Triple Quad MS^3 + IonTrap
***QTrap* (ABI Sciex)**

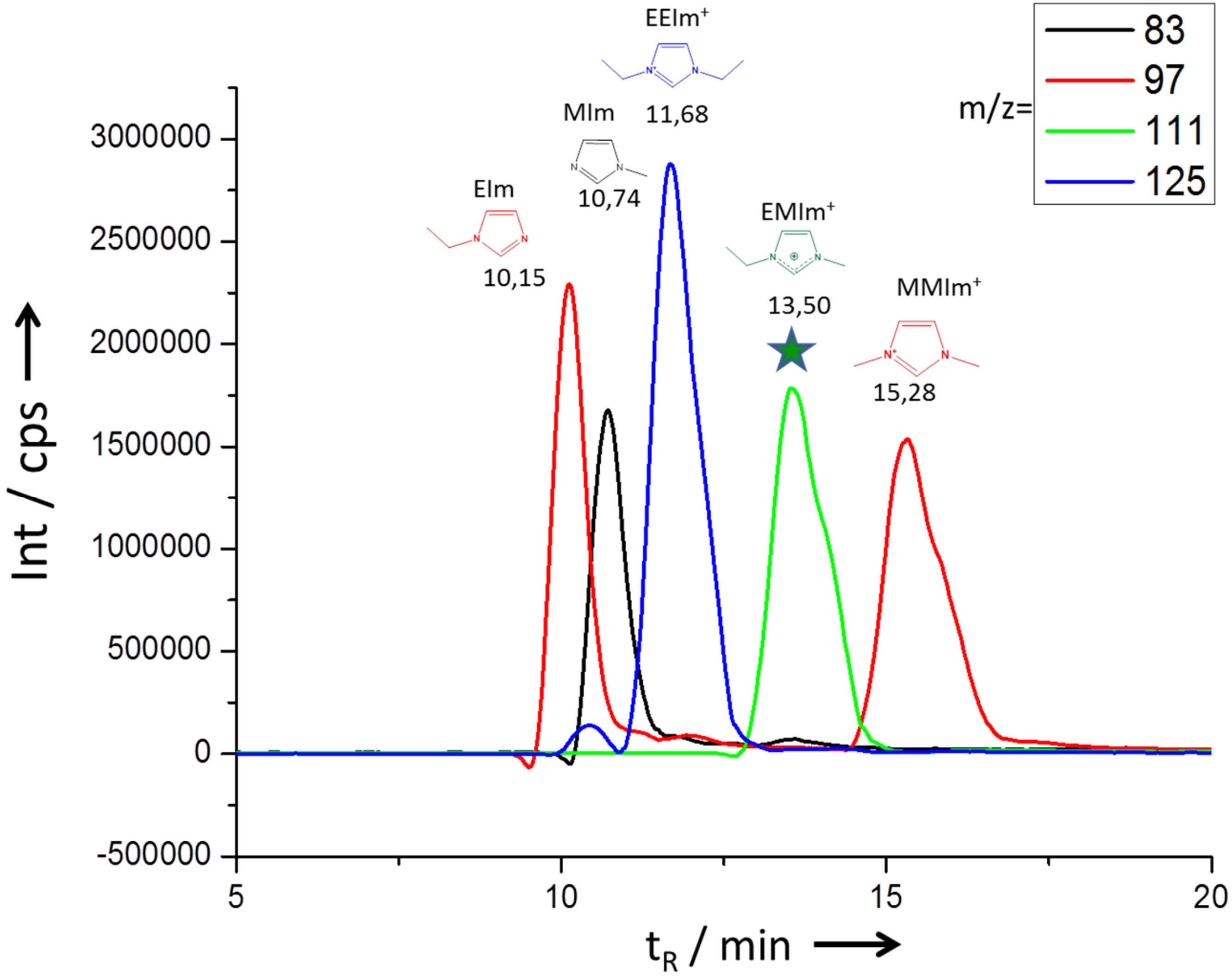
Analysis of Ionic Liquid
thermal stress

EMImAc: T=100°C, Δt = 64 d

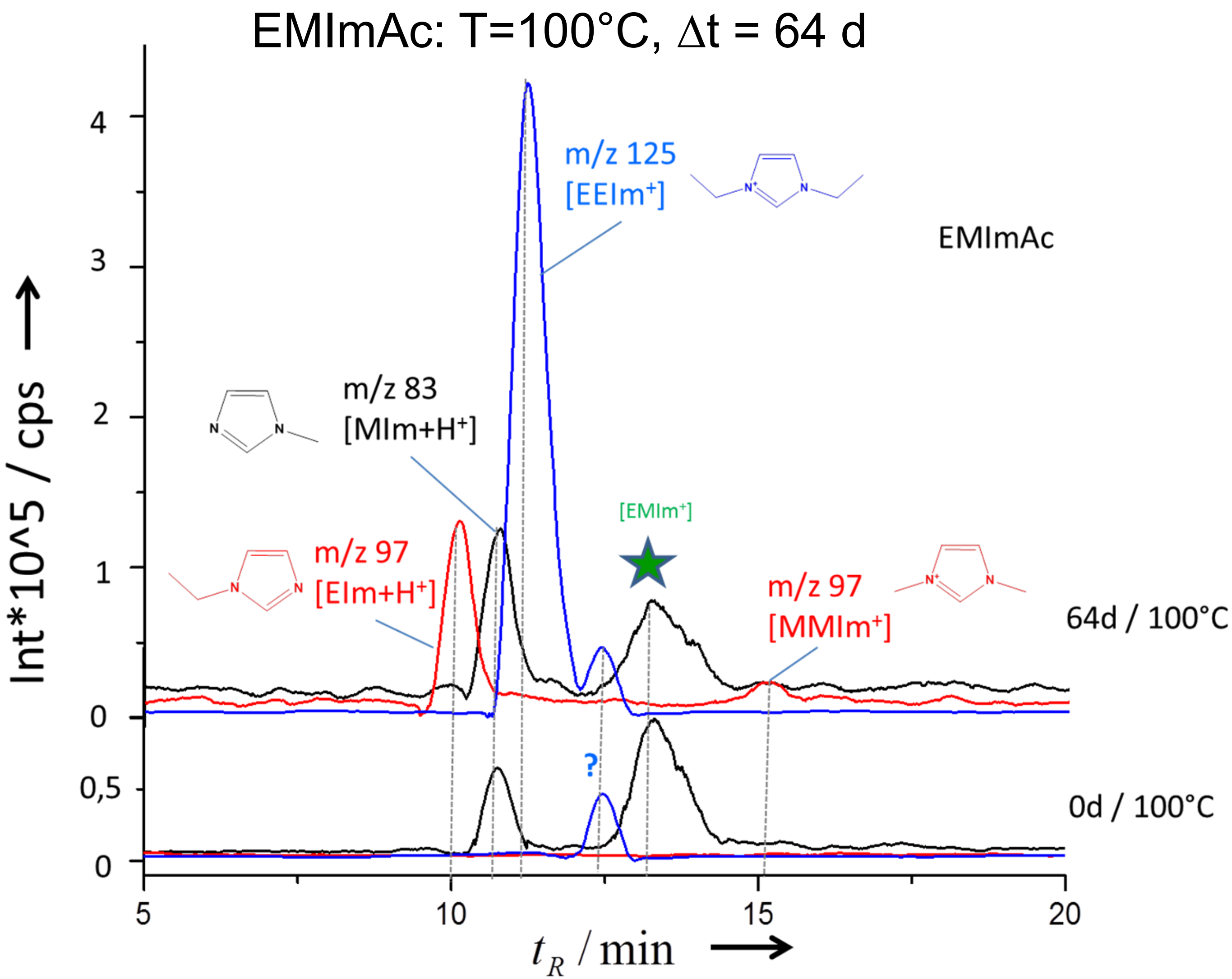


P. Keil, M. Kick, A. König: Long-Term Stability, Regeneration and Recycling of Imidazolium-based Ionic Liquids; Chemie Ingenieur Technik, 84 (2012), No. 6, 859–866.

Analysis of Ionic Liquid
detected & quantified species

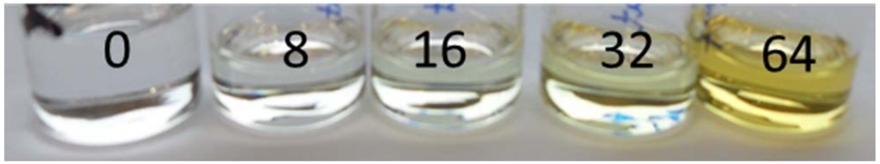


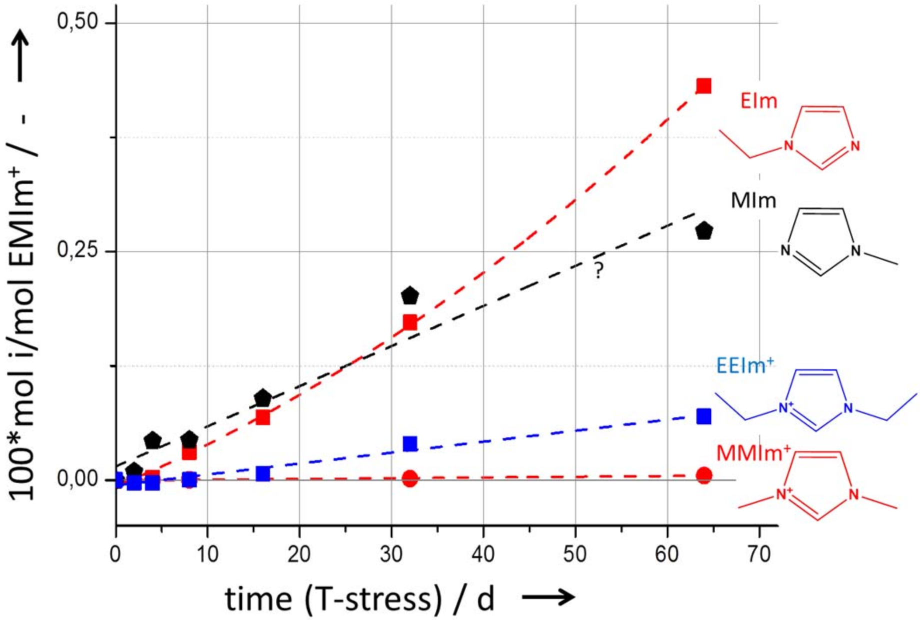
Analysis of Ionic Liquid
thermal stress



Analysis of Ionic Liquid
thermal stress

Thermal Decomposition of EMImAc = f (T, t)

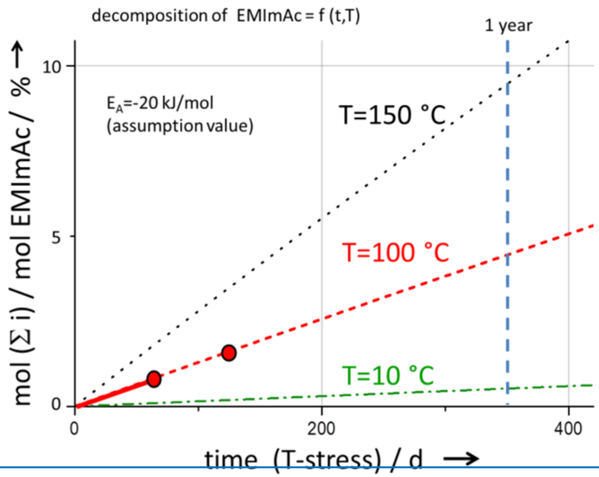




proposed decomp. Kinetics

$$dn_i / dt = k_i * n_{EMImAc}$$

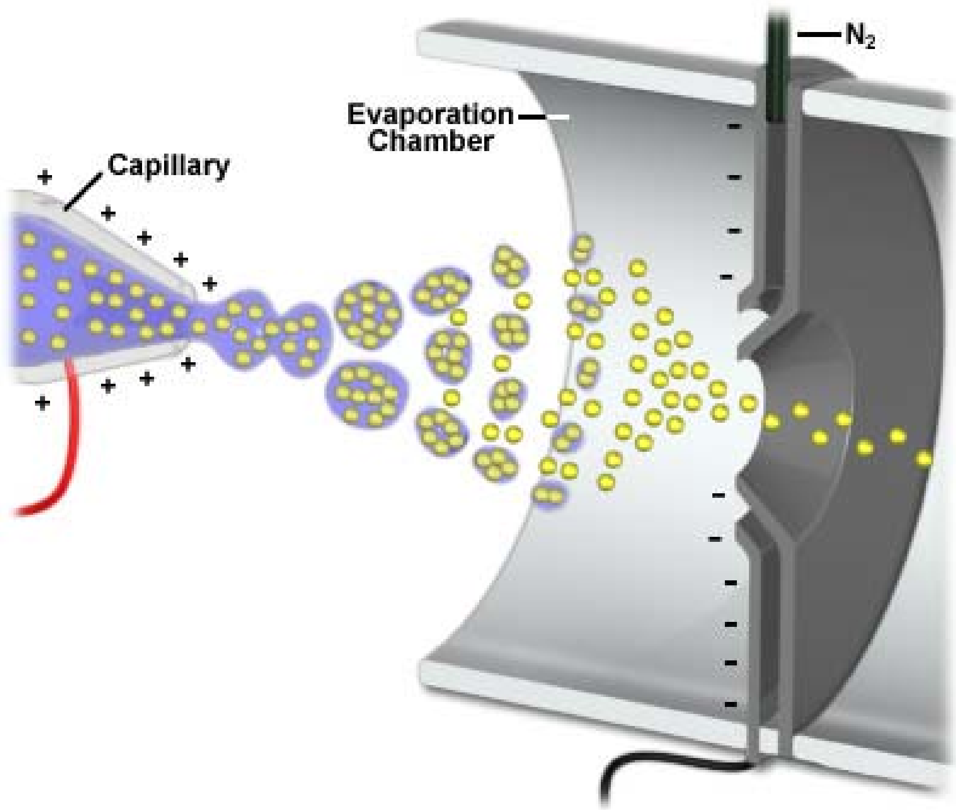
species i	k_i mol(i)/mol(EMImAc)*d
EIm	6,7E-05
MIm	4,4E-05
$EEIm^+$	1,1E-05
$MMIm^+$	7,8E-07



P. KEIL, M. KICK, A. KÖNIG: LONG-TERM STABILITY, REGENERATION AND RECYCLING OF IMIDAZOLIUM-BASED IONIC LIQUIDS; CHEMIE INGENIEUR TECHNIK, 84 (2012), NO. 6, 859–866.

Electrospray ionization mass spectrometry

ESI-MS



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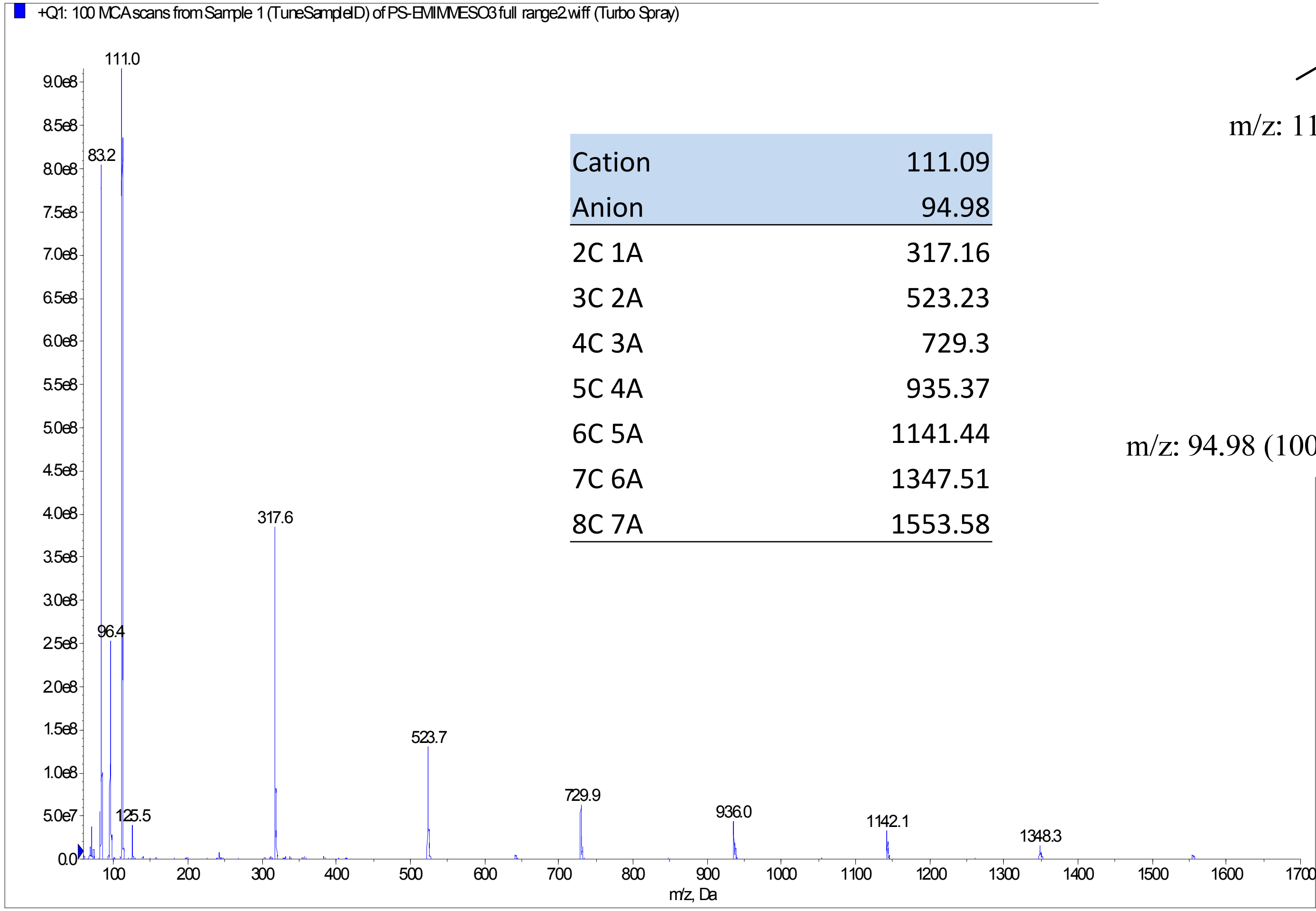
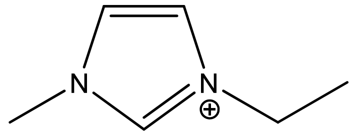
ESI-MS

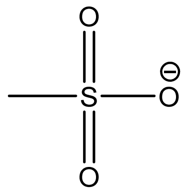
[EMIM][$MeSO_3$] in EtOH (~1mmol/l); positive range potential difference = **4.5 kV**



Cation	111.09
Anion	94.98
2C 1A	317.16
3C 2A	523.23
4C 3A	729.3
5C 4A	935.37
6C 5A	1141.44
7C 6A	1347.51
8C 7A	1553.58



m/z: 111.09 (100.0%), 112.10 (6.6%)



m/z: 94.98 (100.0%), 96.98 (5.1%), 95.98 (2.0%)

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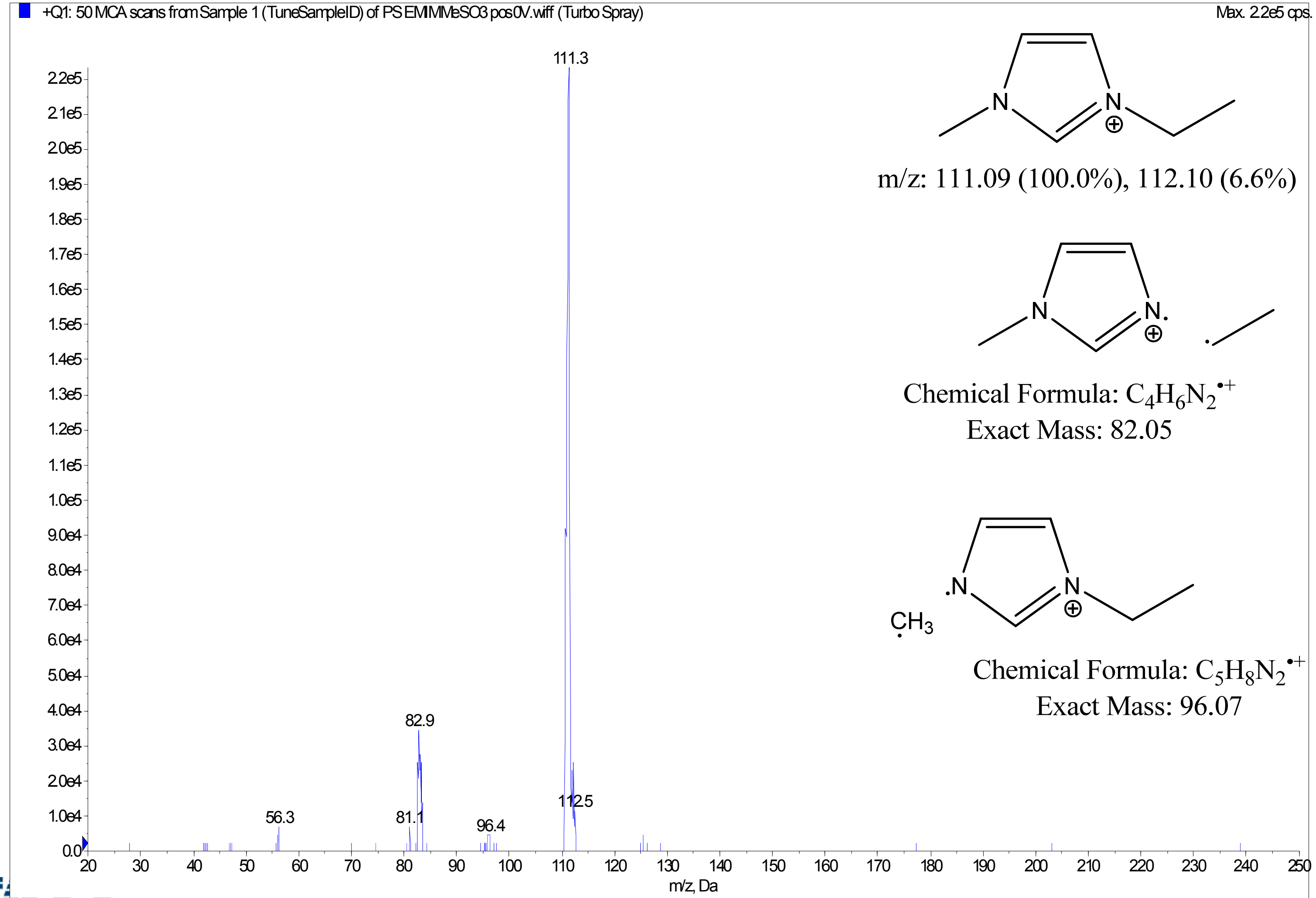
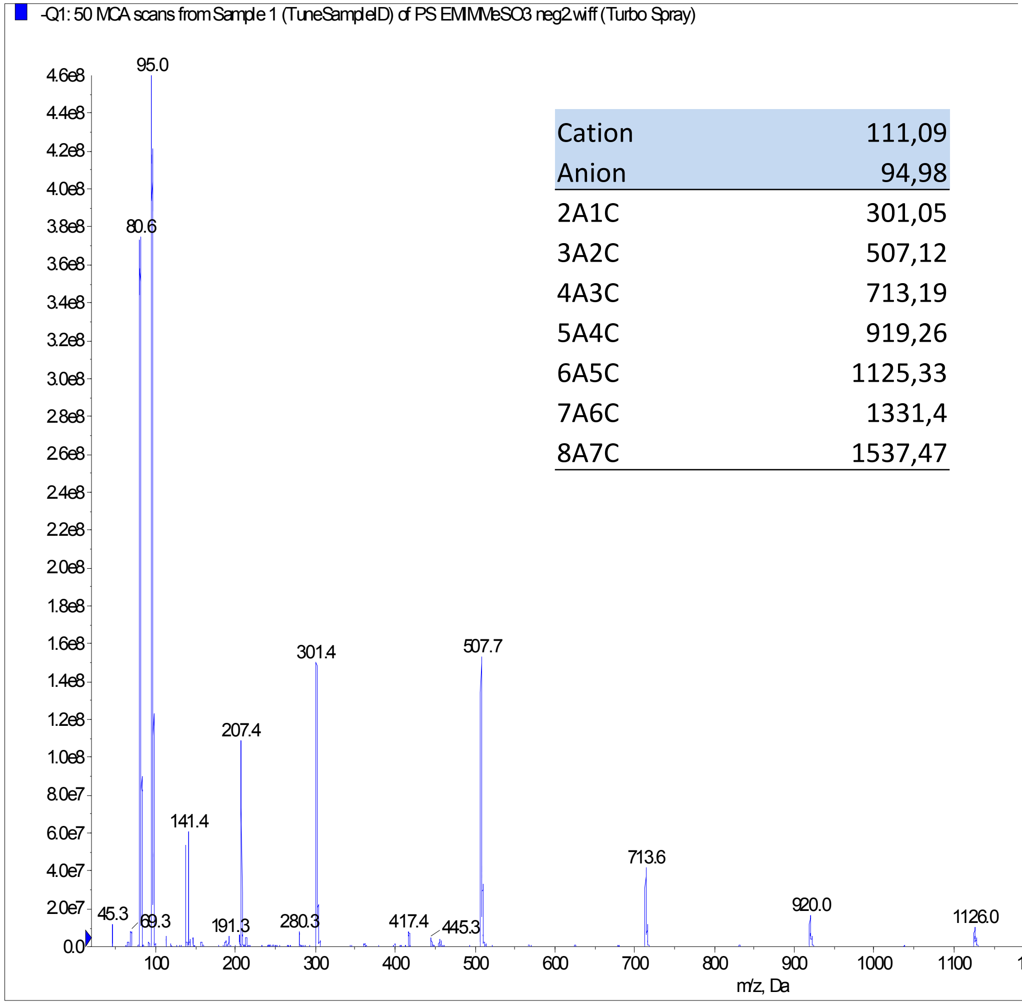
ESI-MS

[EMIM][$MeSO_3$] positive range potential difference = **0 kV**

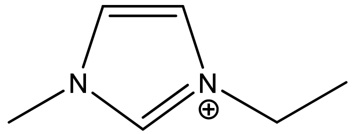


ESI-MS

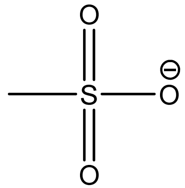
[EMIM][$MeSO_3$] in EtOH (~1mmol/l); negative range potential difference = **-4.5 kV**



Cation	111,09
Anion	94,98
2A1C	301,05
3A2C	507,12
4A3C	713,19
5A4C	919,26
6A5C	1125,33
7A6C	1331,4
8A7C	1537,47



m/z: 111.09 (100.0%), 112.10 (6.6%)



m/z: 94.98 (100.0%), 96.98 (5.1%), 95.98 (2.0%)

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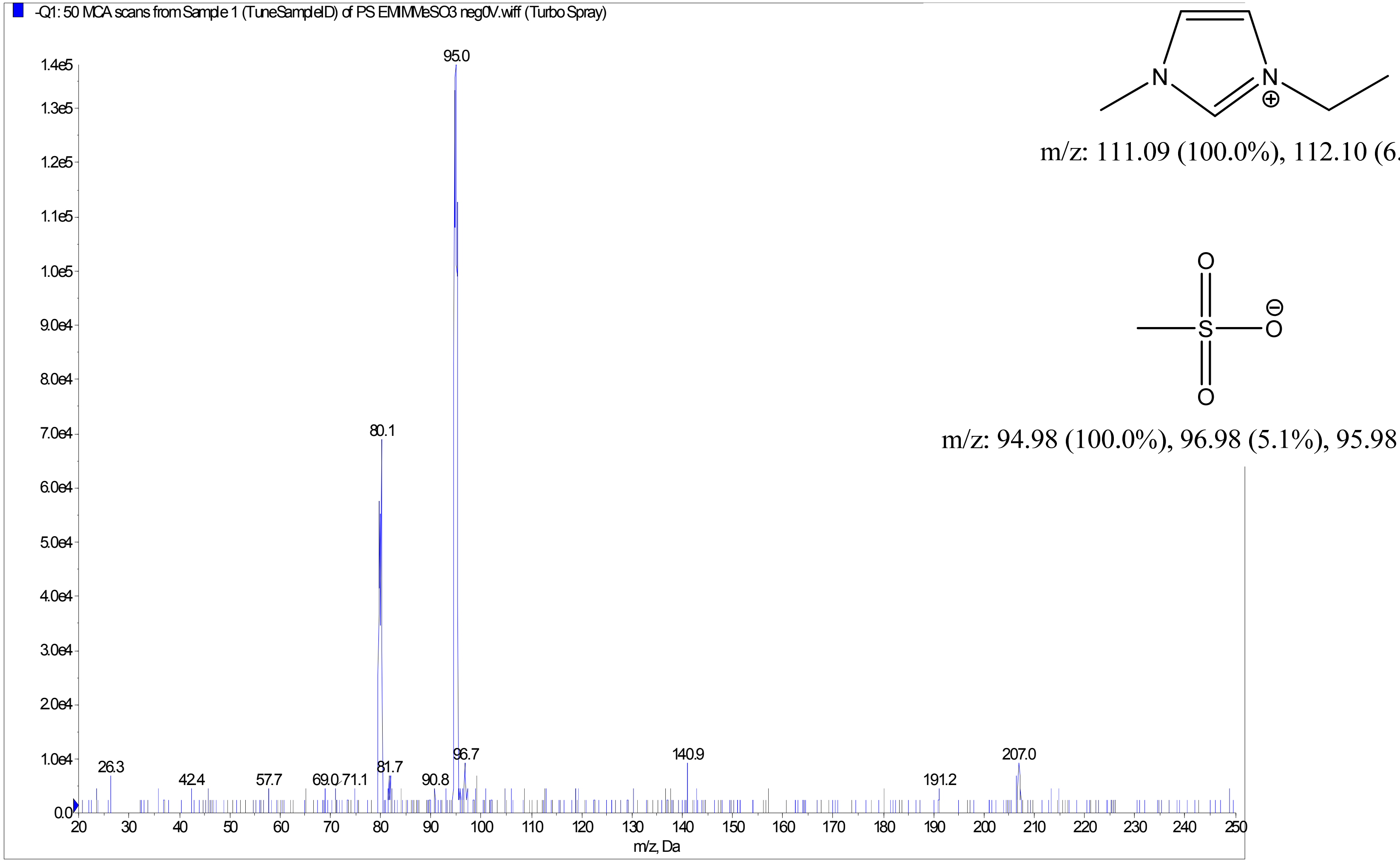
ESI-MS

[EMIM][$MeSO_3$] in EtOH (~1mmol/l); negative range potential difference = **0 kV**



m/z: 111.09 (100.0%), 112.10 (6.6%)

m/z: 94.98 (100.0%), 96.98 (5.1%), 95.98 (2.0%)

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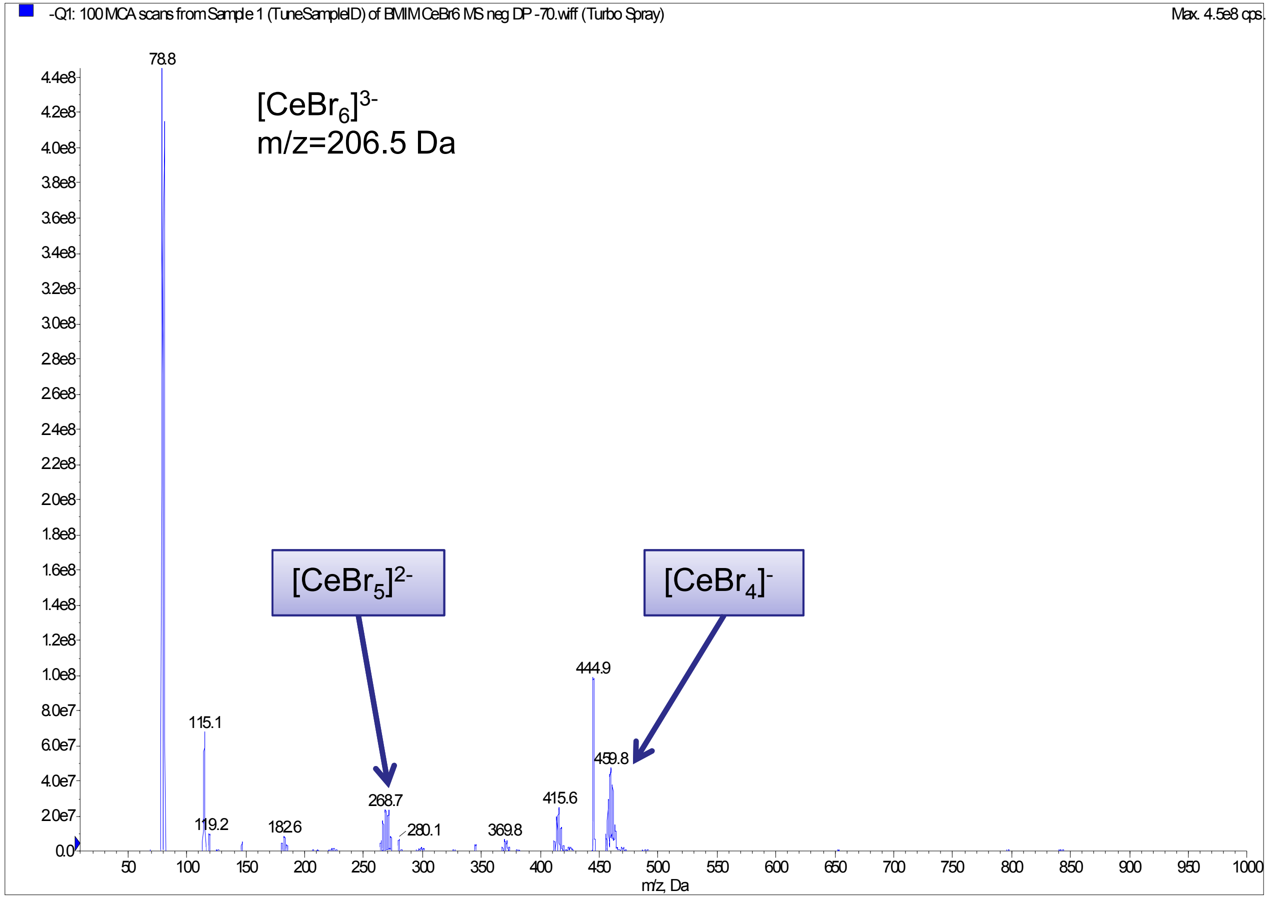
ESI-MS

- Anion speciation in halometallates with ESI-MS leads to confusing results



ESI-MS spectrum of $[BMIM]_3[CeBr_6]$

ESI-MS

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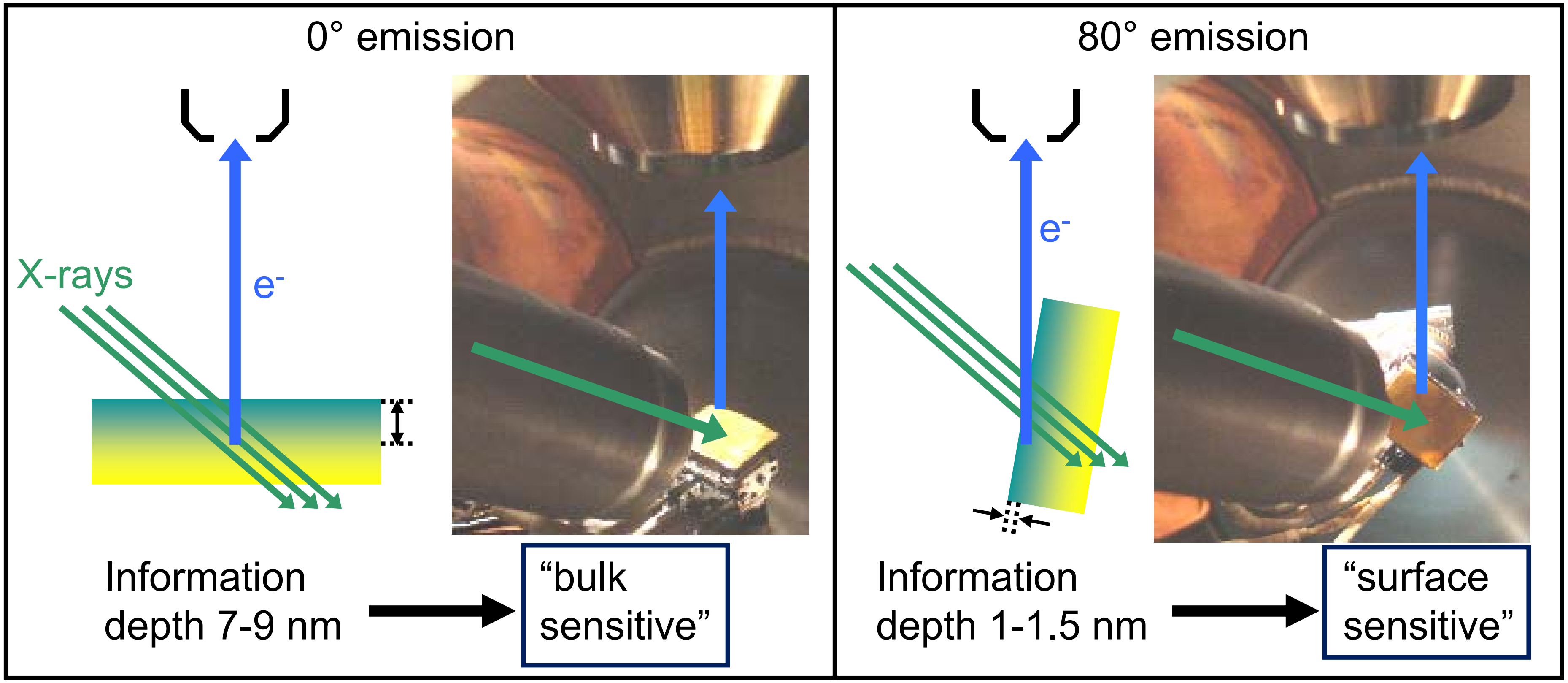
- Good for IL characterization
- Does not give a picture of IL´s aggregation in solution
- Straightforward for cation characterization
- Not always clearly for anion characterization i.e.:
  - halometallate
  - inorganic anions like halogens
  - Phosphonates
- Not combinable with trace analysis on the same instrument

AR-XPS of ionic liquids

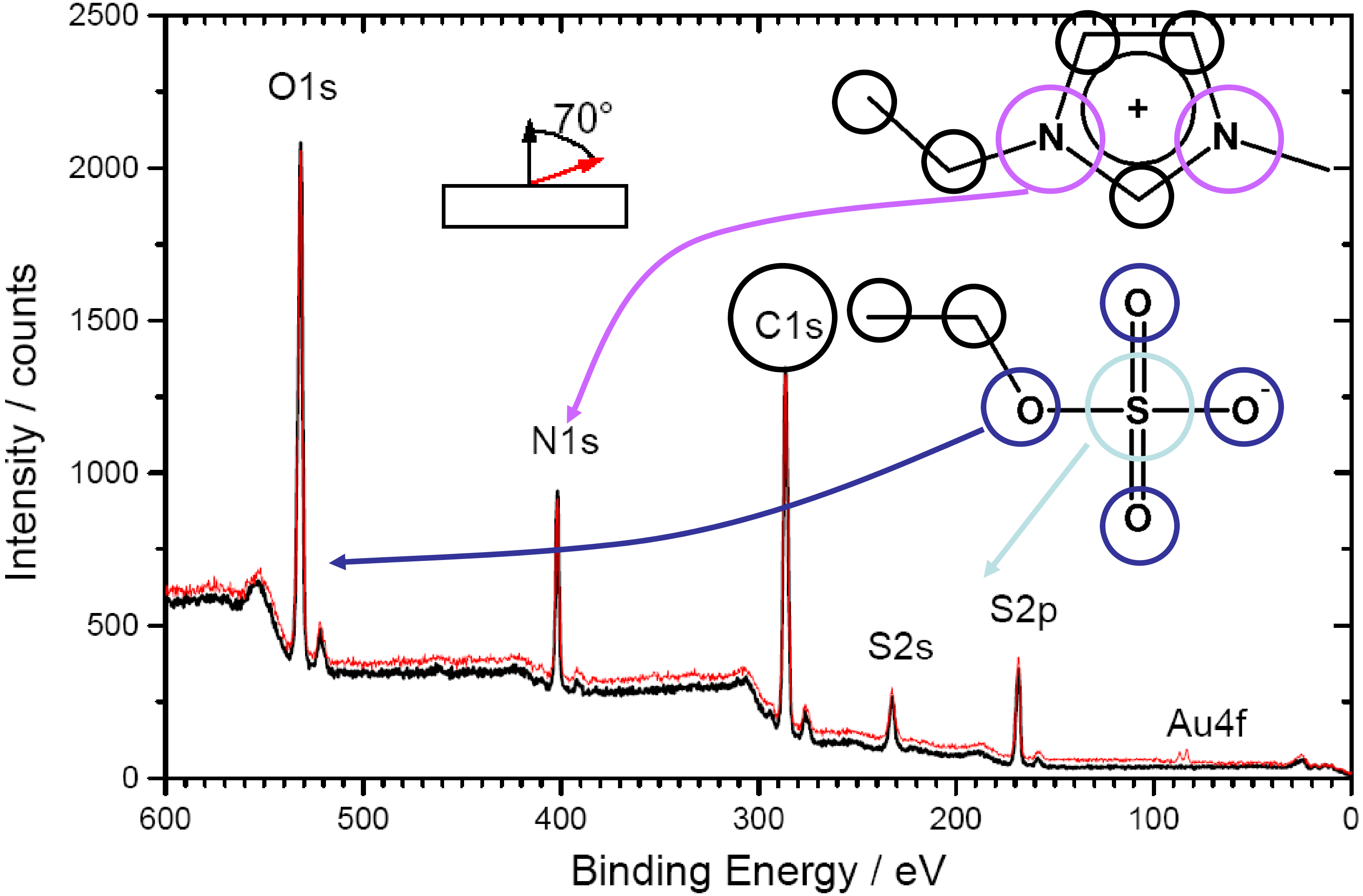
Key message

- 0° ⇒ 70° / 80° Intensity of one element increases ⇒ enhancement of that element in near-surface region (full analysis ⇒ surface composition)



Analysis of Ionic Liquid
Survey XP spectrum of [EMIM][EtSO$_4$]

Preparation: ***- Synthesis (ultra-clean conditions, purification of starting materials)***
- 0.1 ml on Au-support, 12 hours in UHV prior to XPS



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J.M. GOTTFRIED ET AL., Z. PHYS. CHEM. 220 (2006) 1439.

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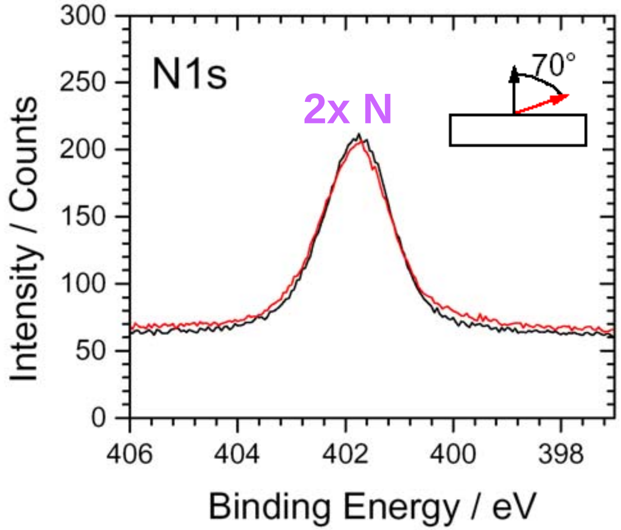
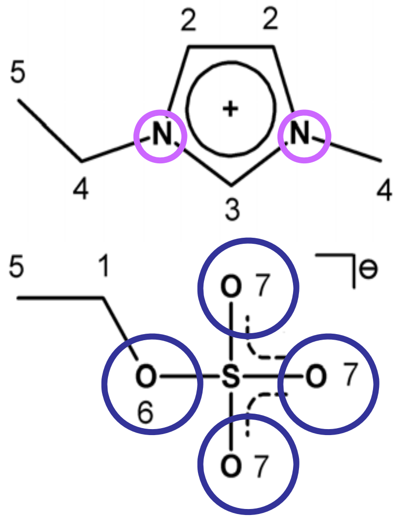
Analysis of Ionic Liquid, XPS

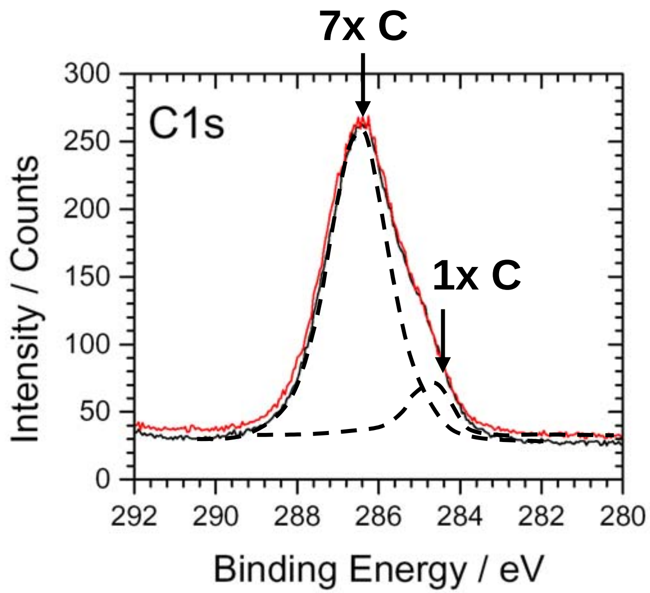
Detailed core level spectra of [EMIM][$EtSO_4$]

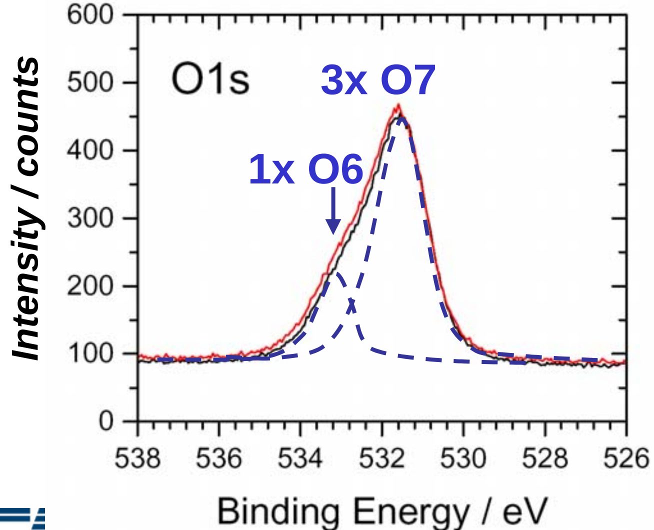
0° … "bulk sensitive"

70° … "surface sensitive"









➔ ***Identification of functional groups***

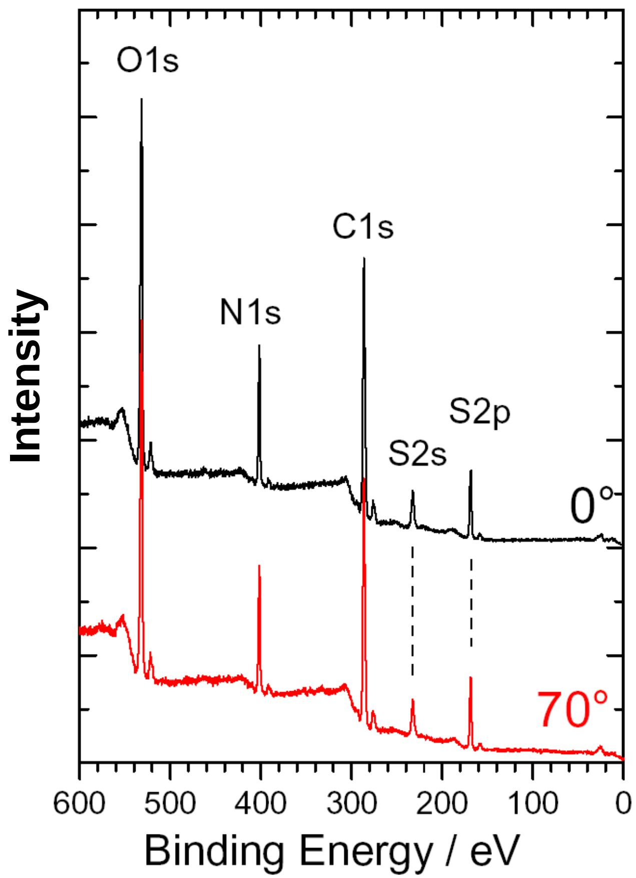
➔ ***No angular dependence of intensities***

J.M. GOTTFRIED ET AL., Z. PHYS. CHEM. 220 (2006) 1439.

Analysis of Ionic Liquid, XPS

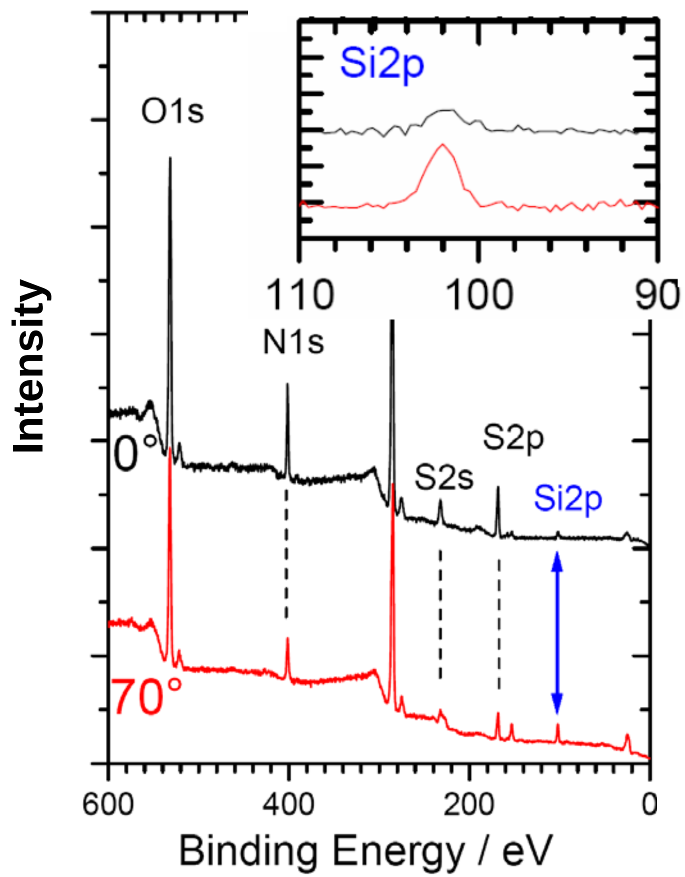
Clean vs. contaminated IL surface: Survey scan

Surface-clean sample:
Home-made [EMIM] [EtSO$_4$]



➔ ***As before***

Surface-contaminated sample:
ECOENG 212, purity > 98%



➔ ***Si-containing contaminations***

➔***Differential intensity variations***

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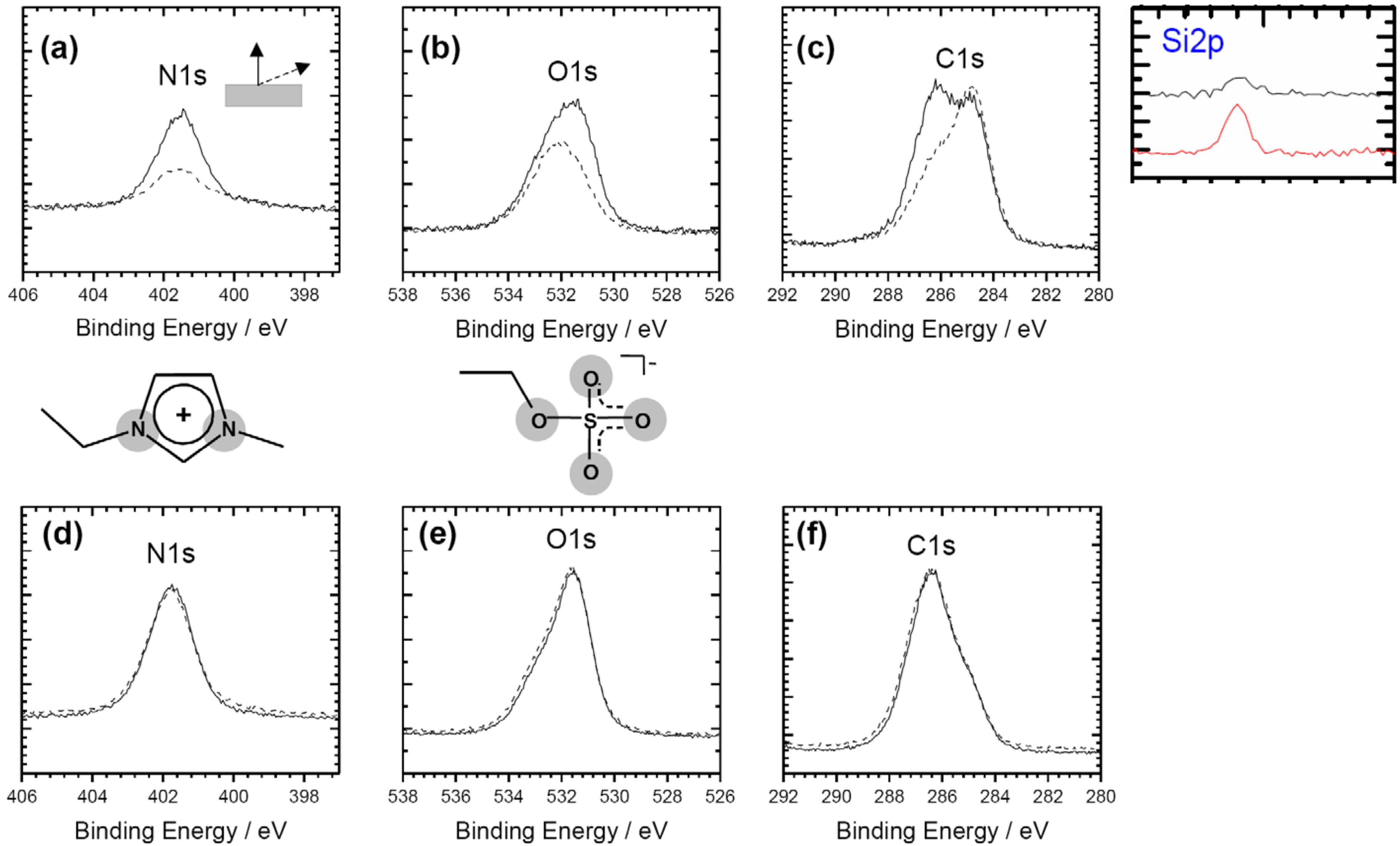
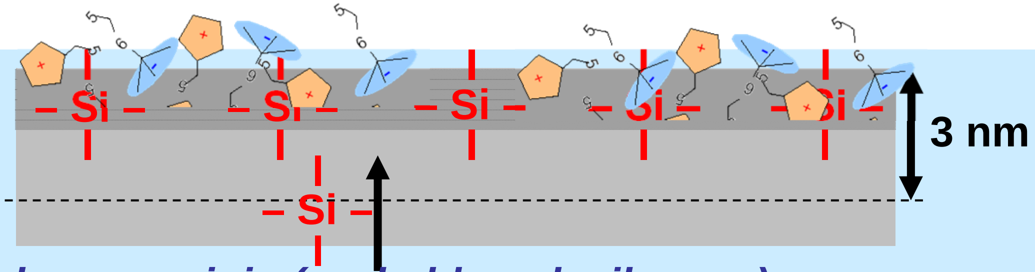
Analysis of Ionic Liquid, XPS
Contaminated vs clean surface



➔Commercial IL:
pronounced change in intensity with emission angle

Analysis of Ionic Liquid, XPS
Clean vs. contaminated IL surface: Survey scan



→ ***Si-impurities of unknown origin (probably polysiloxane)***

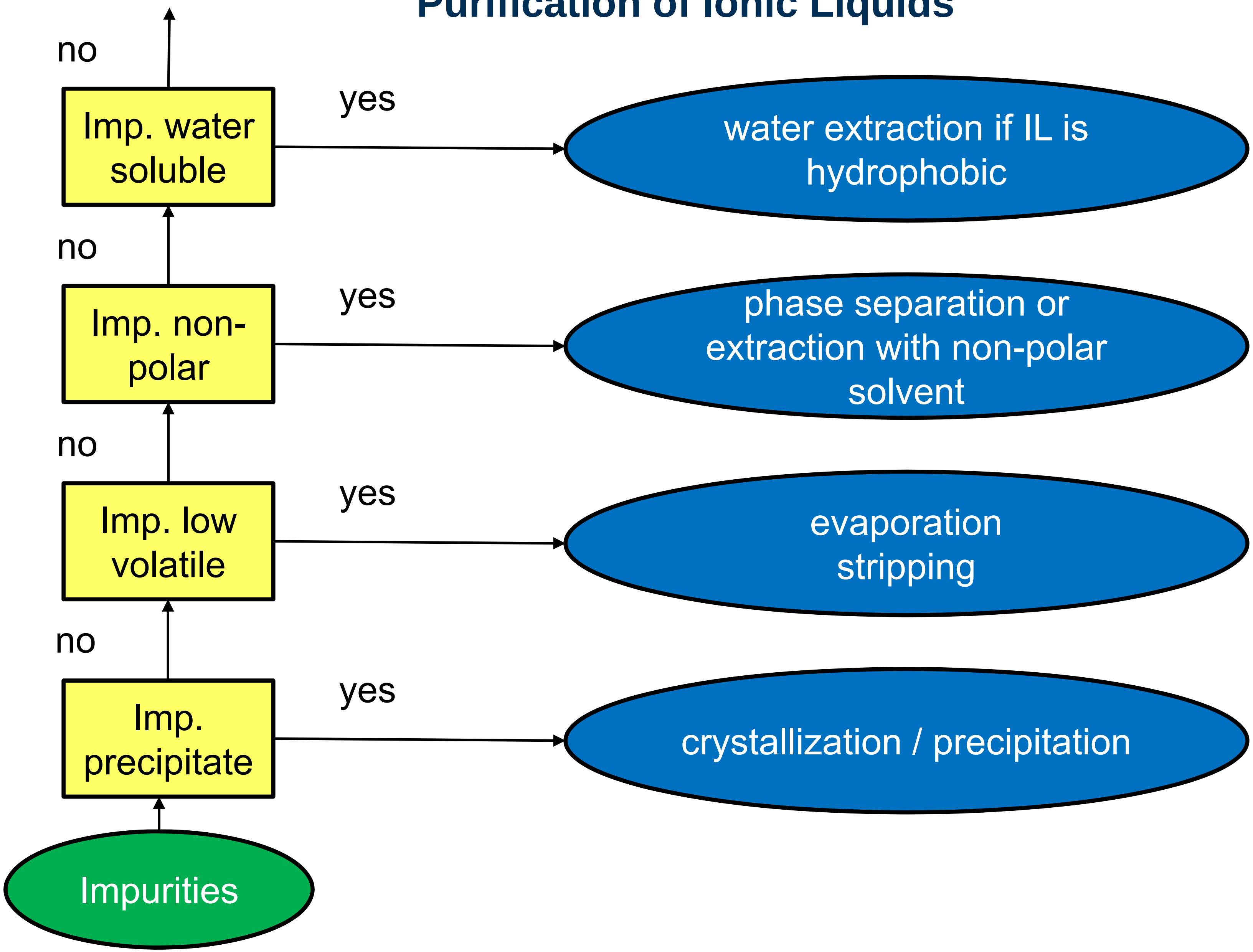
→ ***Bulk concentration below detection limits of ICP-AES: Si << 5 ppm***

→ ***Extreme surface enrichment***

J.M. Gottfried et al., Z. Phys. Chem. 220 (2006) 1439.

- Surface enrichment on surface towards vacuum
- Enrichment to other phase boundary possible

Purification of Ionic Liquids



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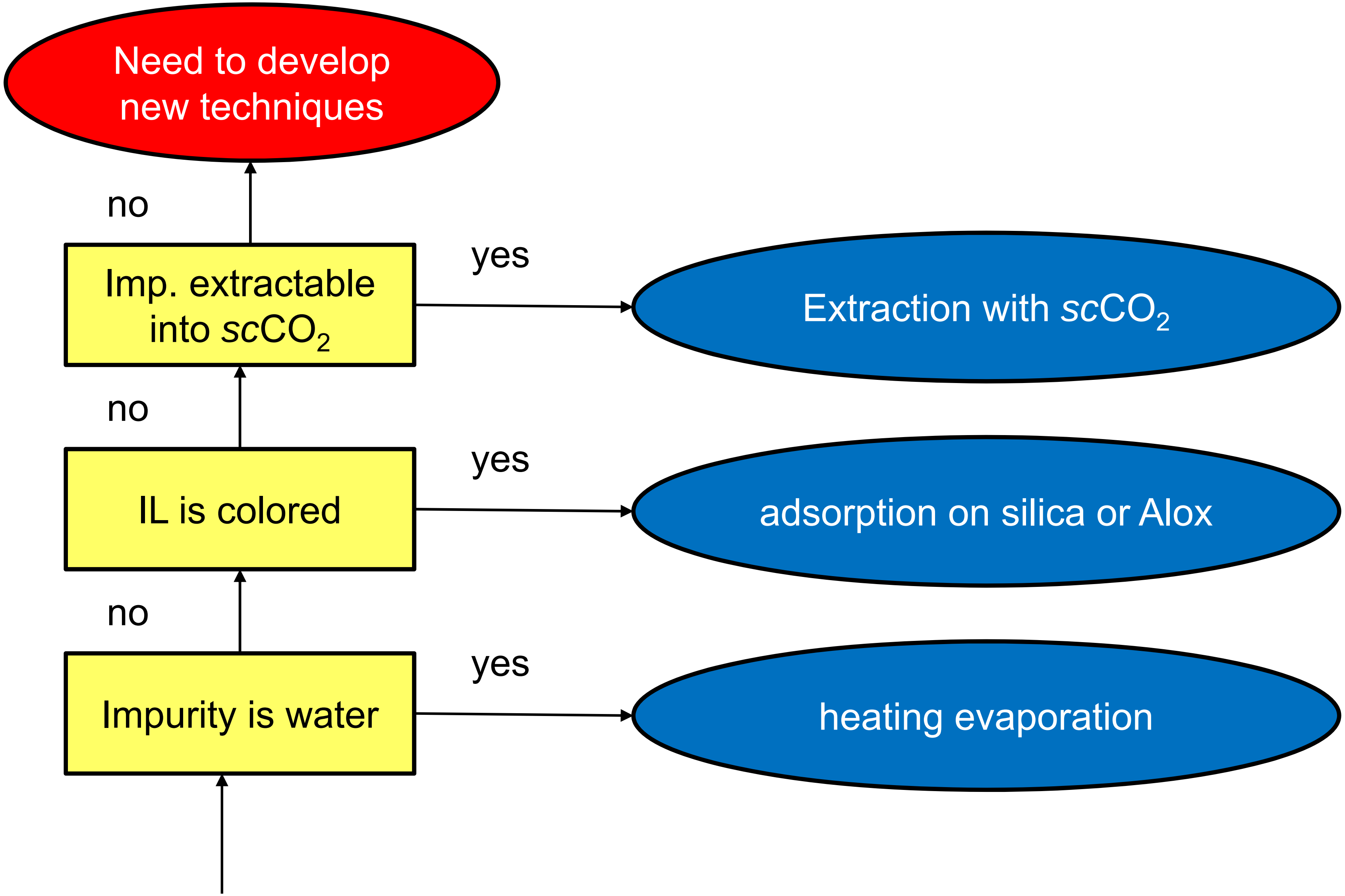
Purification of Ionic Liquids



Ionic Liquid Recyling

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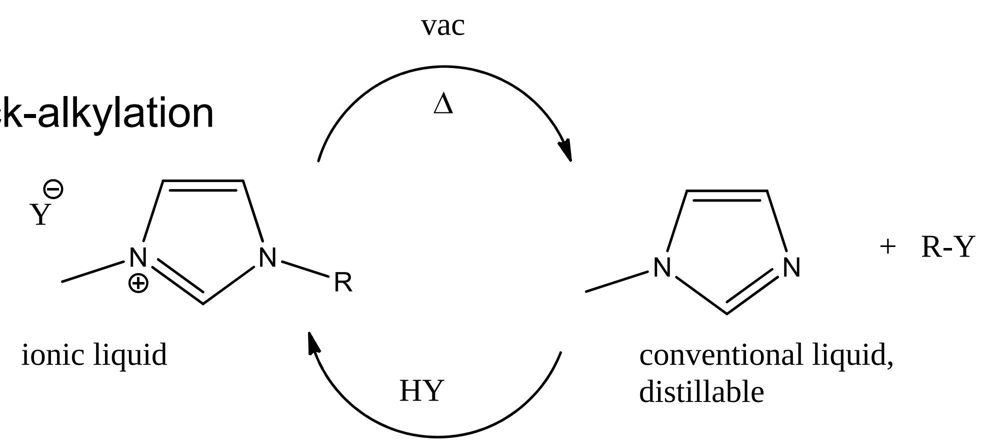
Impurity	Cleaning method	Reference
water	Heating and evaporation, Electrochemical	Md. Mominul Islam, Takeyoshi Okajima, Shimpei Kojima, Takeo OhsakaChem. Comm. **(2008)**, (42), 5330-2.
salts, halids	Extraction with water, distillation	Ionic Liquids - Classes and Properties Edited by Scott T. Handy, ISBN 978-953-307-634-8, 360 pages, Publisher: InTech, Chapters published Chapter 11 by Samir I. Abu-Eishah
organic compounds	extraction with unpolar solvent or *sc*CO_2	
colour	adsorption on Silica or Alox	
solids	filtration	

Further methods

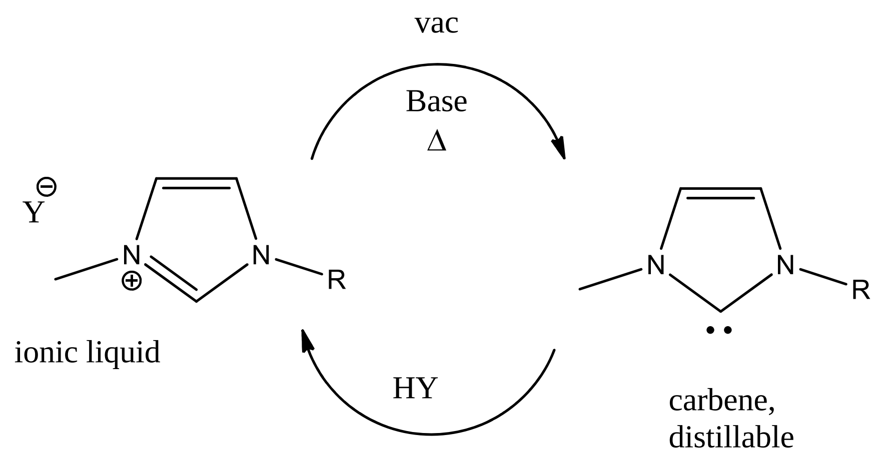
Distillation	Volatile Ionic Liquids	*Seddon et al. Nature* **439**, 831-834 (16 February **2006**)
	Protic Ionic Liquids	Marina M. Seitkalieva, Vadim V. Kachala, Ksenia S. Egorova, and Valentine P. Ananikov ACS Sustainable Chemistry & Engineering **(2015)** 3 (2), 357-364
	By Reversible Amide O Alkylation	Chen, Z.-J., Xi, H.-W., Lim, K. H. and Lee, J.-M. **(2013)** Angew. Chem., 125: 13634–13638.
Melt Crystallization Zone Melting		A. König, M. Stepanski, A. Kuszlik, P. Keil, C. Weller, Chemical Engineering Research and Design, 86, 7, **(2008)**, 775-780 J. L. Solà Cervera, P. Keil, A. König1Chemie Ingenieur Technik **(2012)**, 84, No. 6, 859–866

Ionic Liquid Recycling – IL distillation

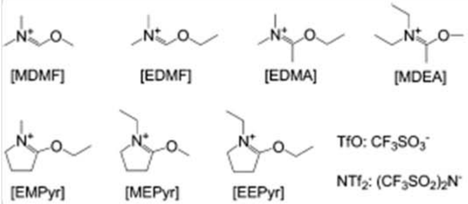
- Ion pair in gas phase
- Deprotonation (R = H) or back-alkylation



- Carbene formation



Ionic Liquid Recycling – IL distillation

Distillable IL	Conditions	Lit
$[C_nMIM][NTf_2]$	300°C, 0,1 mbar, 5h	*Nature* **(2006)** 439, 831-834
$[TMGH][CO_2Et]$ and homologue	100-200°C, 0,75 mbar, 30 min	Angew. Chem. Int. Ed. **(2011)**, 50, 6301 –6305
N,*N*-dimethylammonium *N'N'*-dimethylcarbamate		Green Chem. **(2010)**, 12, 1023–1028.
[DMEA][HCOO]	122°C 0,5 mbar	Sustainable Chem. Eng. **(2014,)** 2, 1888 – 1894
[HMIM]Cl	150°C 0,5 mbar	WO 2005/068404
	175 - 210°C 0,002-0,5 mbar	Angew. Chem., **(2013)** 125: 13634–13638.
IL -> carbene		New J. Chem., **2010**, 34, 3004-3009 WO 01/77081; WO 05/019183 by BASF
$[C_nMIM][NTf_2]$, ~[EtSO4], $\sim[BF_4]$, $\sim[PF_6]$, $\sim[CF_3SO_3]$	Data, Heat of evaporation	Phys. Chem. Chem. Phys., **(2007)**, 9, 982-990
$[C_nMIM][NTf_2]$	Prediciton	Phys. Chem. Chem. Phys., **(2007)**, 9, 4653-4656

Ionic Liquid Recycling – IL distillation

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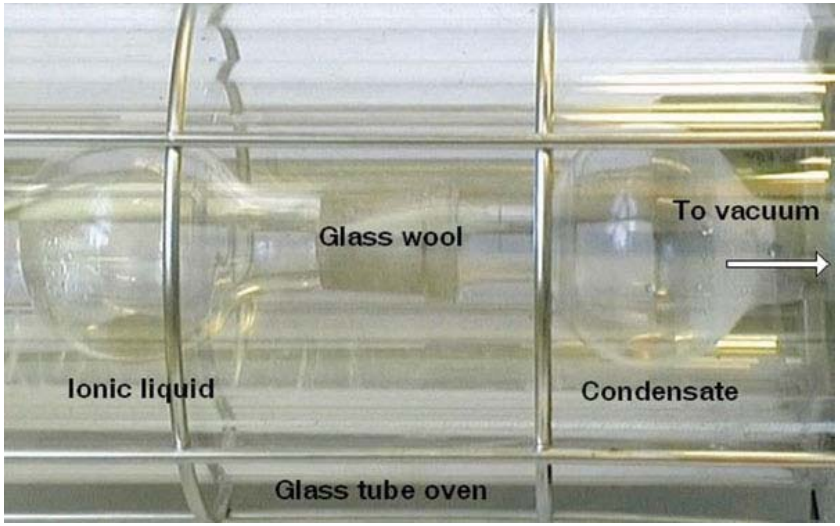
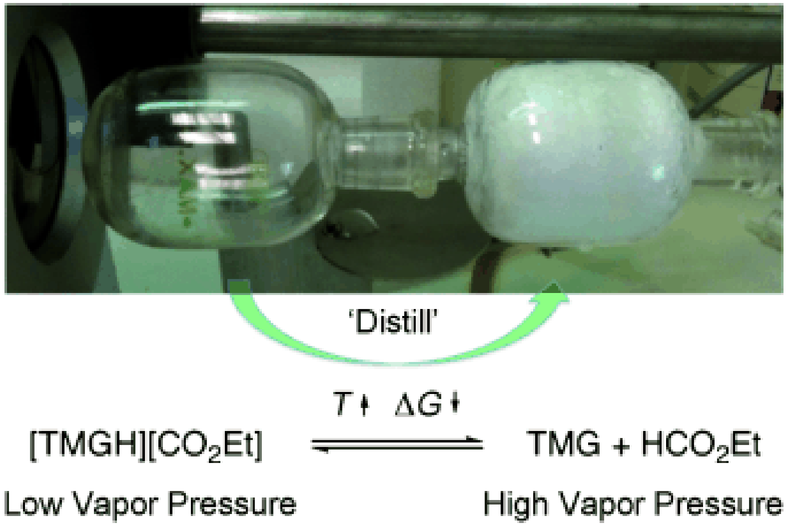
- Evaporation by
  - „Kugelrohr“ distillation





  - or apparatus for sublimation

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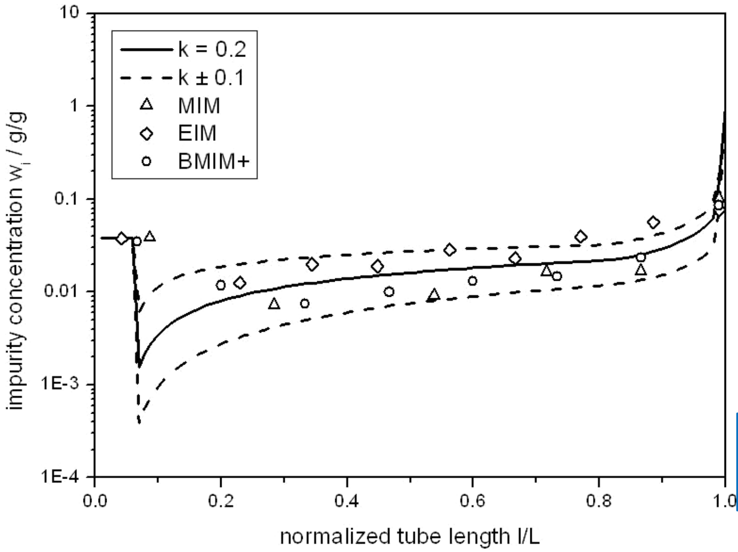
Melt crystallization

- impurities can be structural similar or not, volatile or nonvolatile, charged or uncharged
- IL has to crystallize
- solid-liquid phase behavior of the system IL/impurity has to be appropriate
- impurity is depleted in the solid phase
- Zone melting is a short cut method to prove if melt crystallization is possible

EMIM Cl after 2 passes



Concentration profiles for MIM, EIM and BMIM+ in EMIM Cl determined by zone melting with a linear growth rate dL/dt = 1.44mm/h (symbols) and modeled concentration profile for effective distribution coefficients k = 0.2 (solid line) and k = 0.2 ± 0.1 (dashed line

J. L. Solà Cervera, P. Keil, A. König Chemie Ingenieur Technik (2012), 84, No. 6, 859–866

Zone melting

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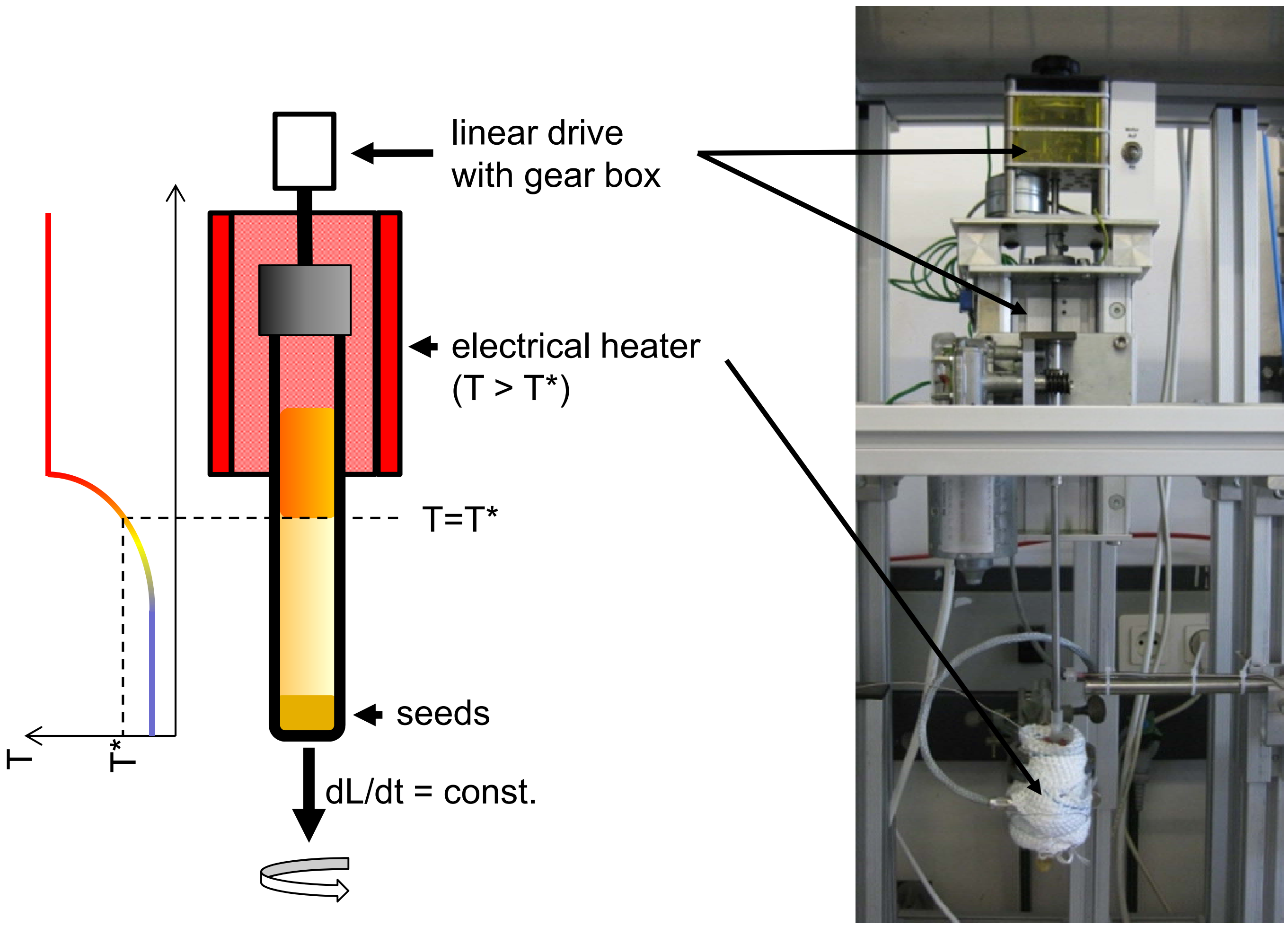
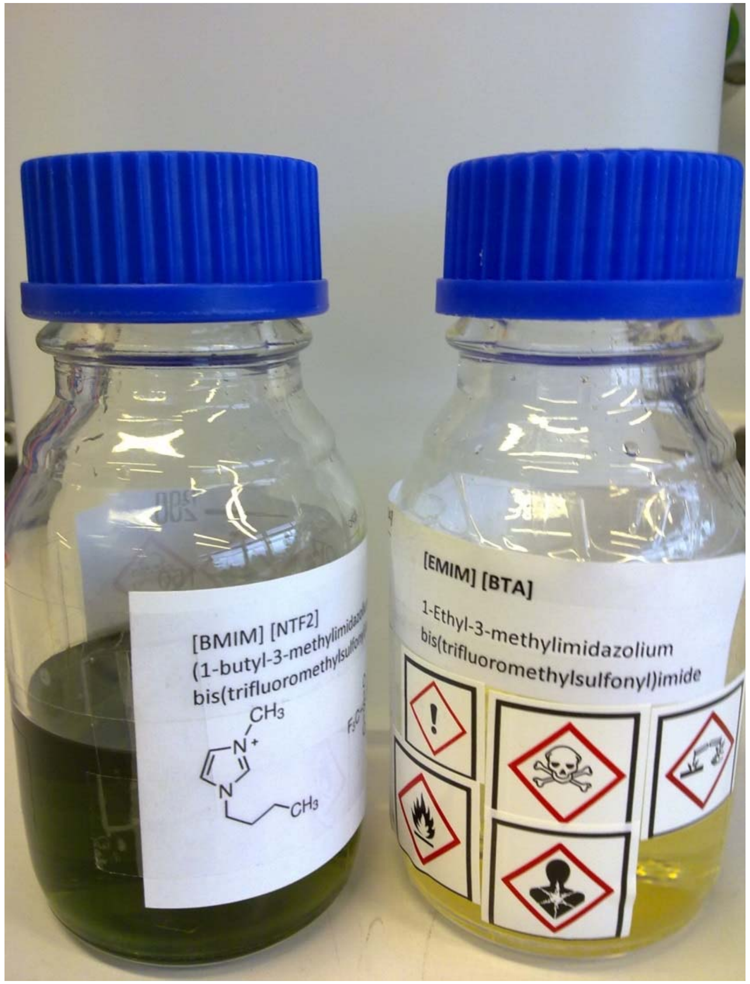


Ionic Liquid Recycling

- Recycling of [BMIM][NTf_2] and [EMIM][Tf_2]
  - Extraction
    - 50 ml IL with 3x 150 ml dist. water
    - 2x 100 ml cyclohexane
  - Adsorption
    - 30 ml IL + ~ 3g Alox/Silica 100,
    - 24 @ 60 °C stirring
  - Filtration
    - BMIM ALOX+ EMIM AlOX washed with ethyl acetate
  - Drying at 60°C / vacuum overnight



Ionic Liquid Recycling

- **ICP:**
- [BMMIM][NTf_2] (114,9 mg in 100 ml) / mgL^{-1}:
  - before

Al	Cr	Mn	Co	Fe	Cu	Mo
1,9	0.11	0,25	-0,12	-0,08	0,23	-0,004

  - after

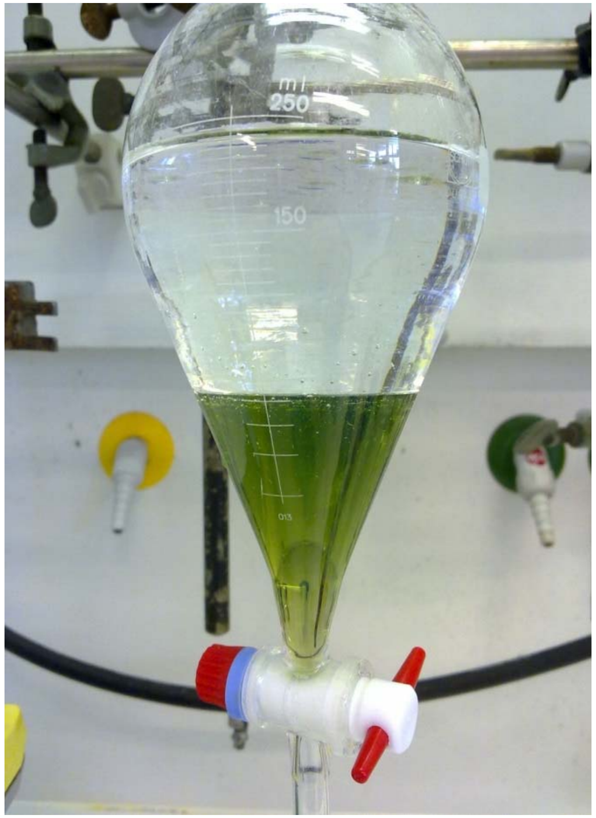
Al	Cr	Mn	Co	Fe	Cu	Mo
-0.088	-0,45	-0.714	-0.71	-0.65	-0.80	-0.64

- [EMIM][NTf_2] (114,6 mg in 100 ml) / mgL^{-1} :
  - before

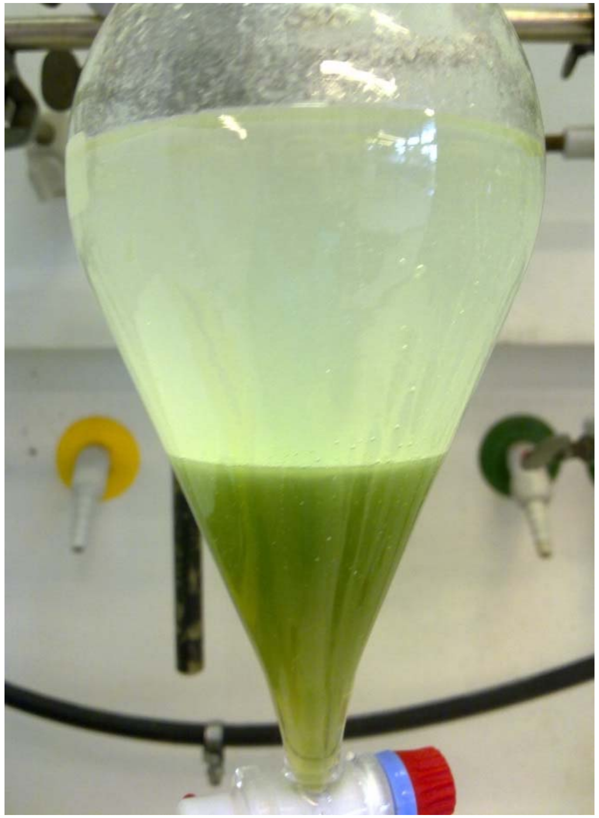
Al	Cr	Mn	Co	Fe	Cu	Mo
1,73	-0,1	-0,26	-0,1	-0,08	-0,05	-0,005

Ionic Liquid Recycling

- before extraction with water

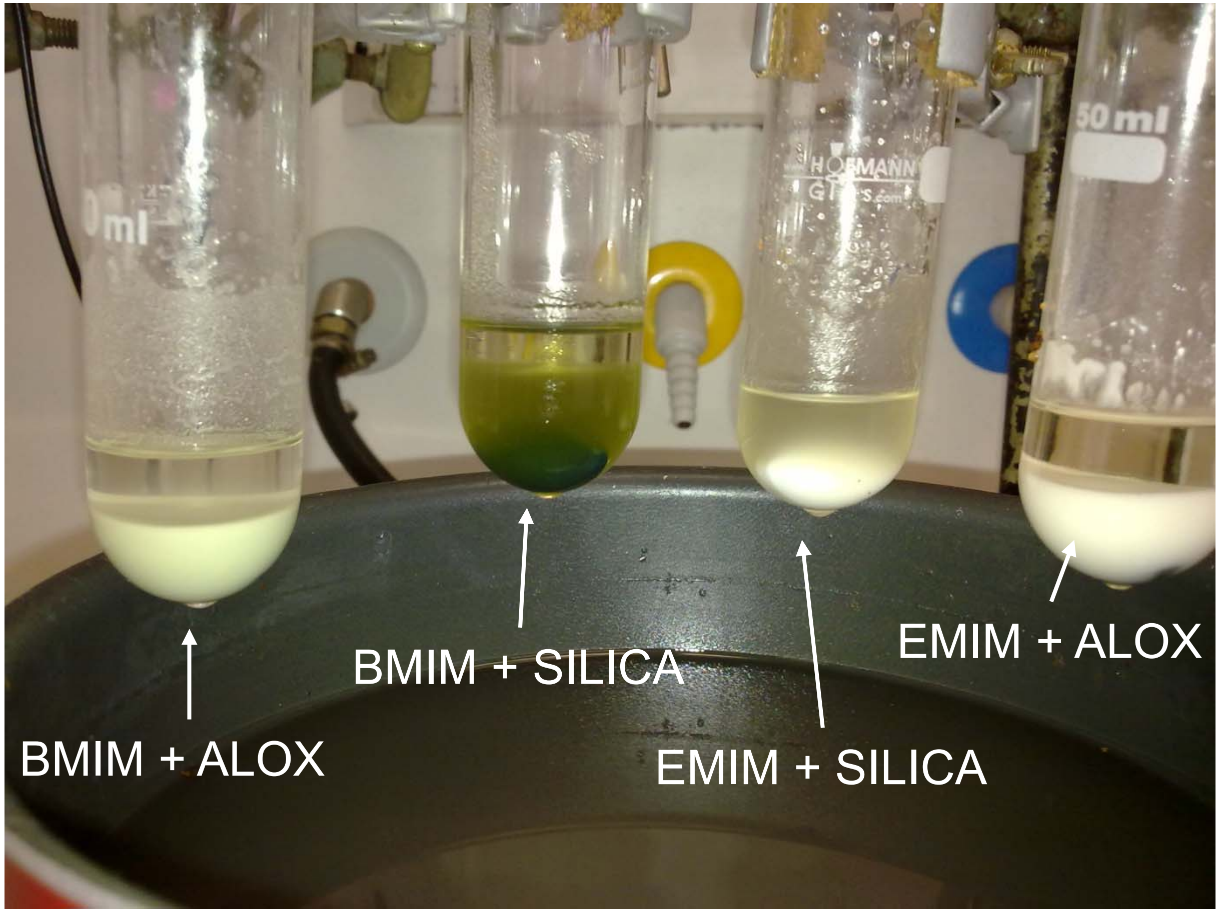


- after extraction with water



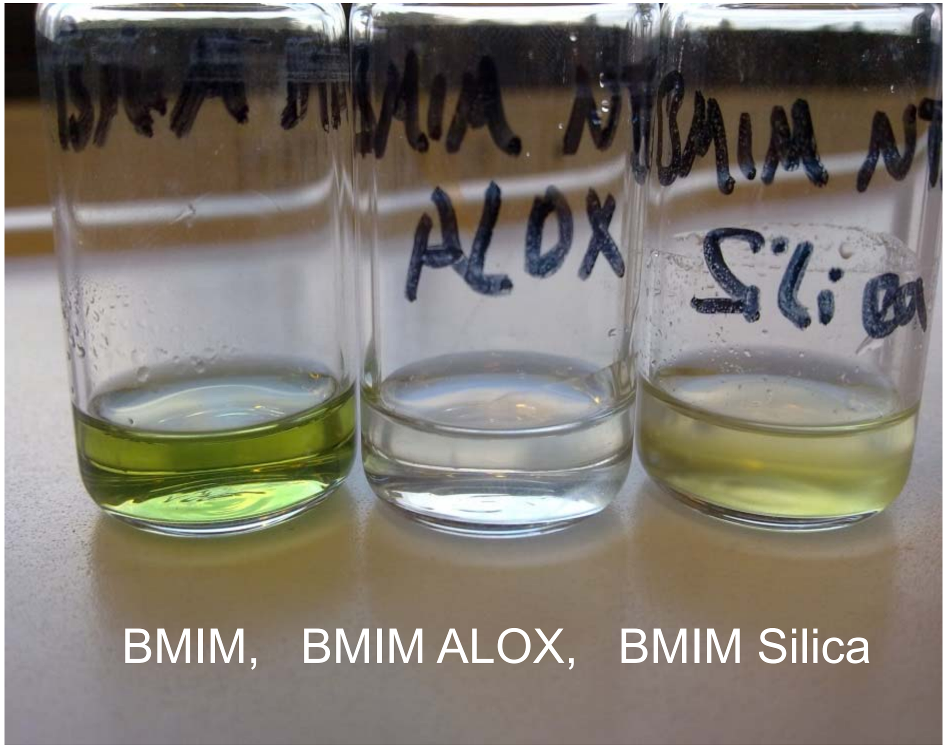
Ionic Liquid Recycling

- after adsorption on silica / ALOX (24h stirring @ 60°C):



Ionic Liquid Recycling

- Optical result:



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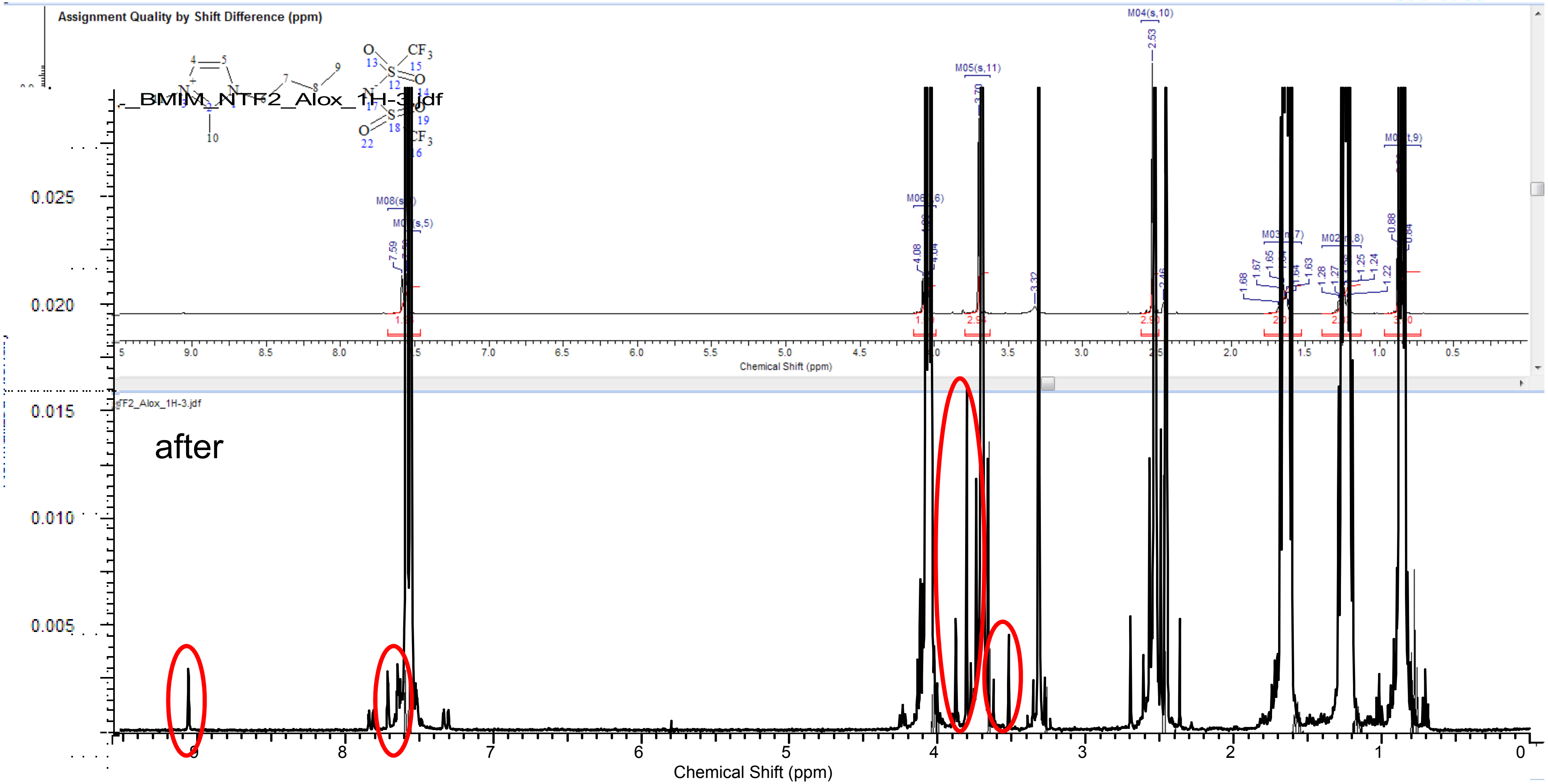
Ionic Liquid Recycling
^{1}H- NMR-spectroscopy

- before



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Ionic Liquid Recycling
^{13}C- NMR-spectroscopy

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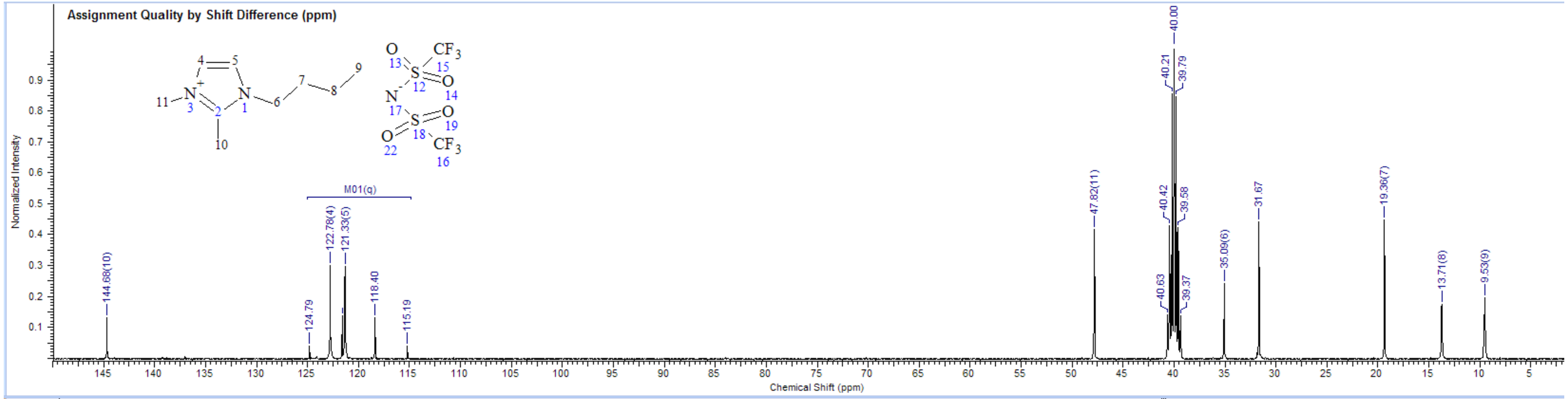
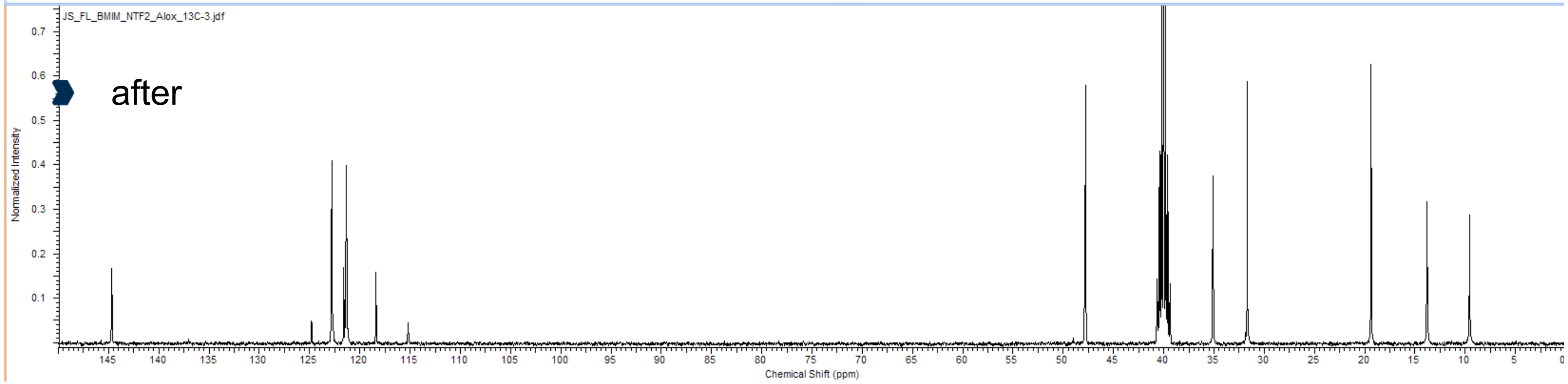
- before



- after



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Headspace Gaschromatographie

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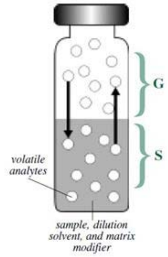
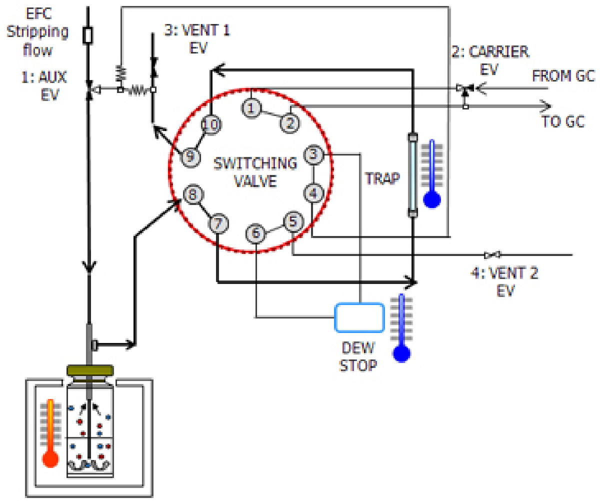
- Chromatography of compounds, which can be evaporated without decomposition
- Injection by syringe or valve
  - syringe:



Headspace Gaschromatographie

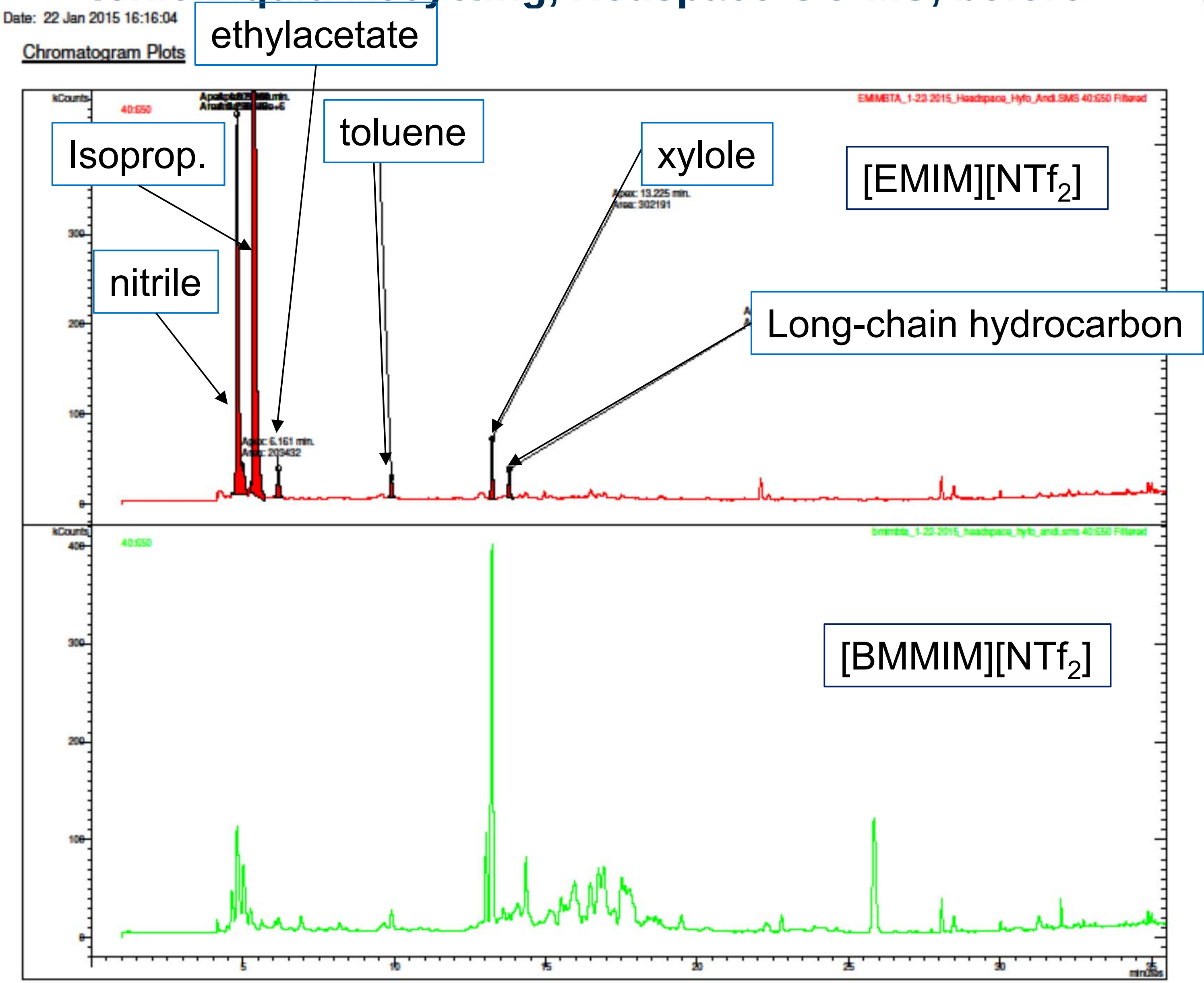
- Chromatography of compounds, which can be evaporated without decomposition
- Injection by syringe or valve
  - valve:



Ionic Liquid Recycling, Hedspace GC-MS, before

Print Date: 22 Jan 2015 16:16:04

Chromatogram Plots



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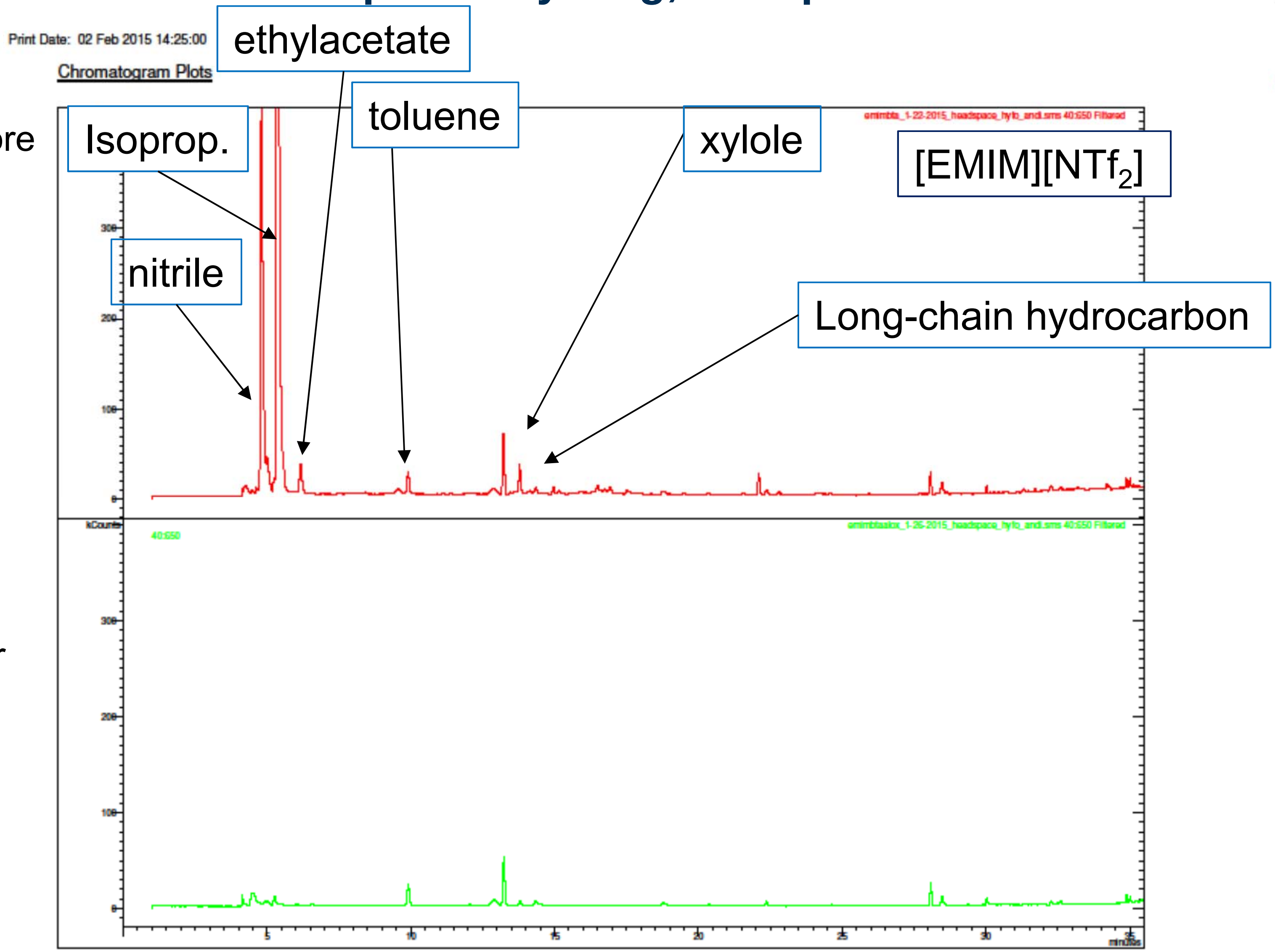
Ionic Liquid Recycling, Hedspace GC-MS

- before
- after



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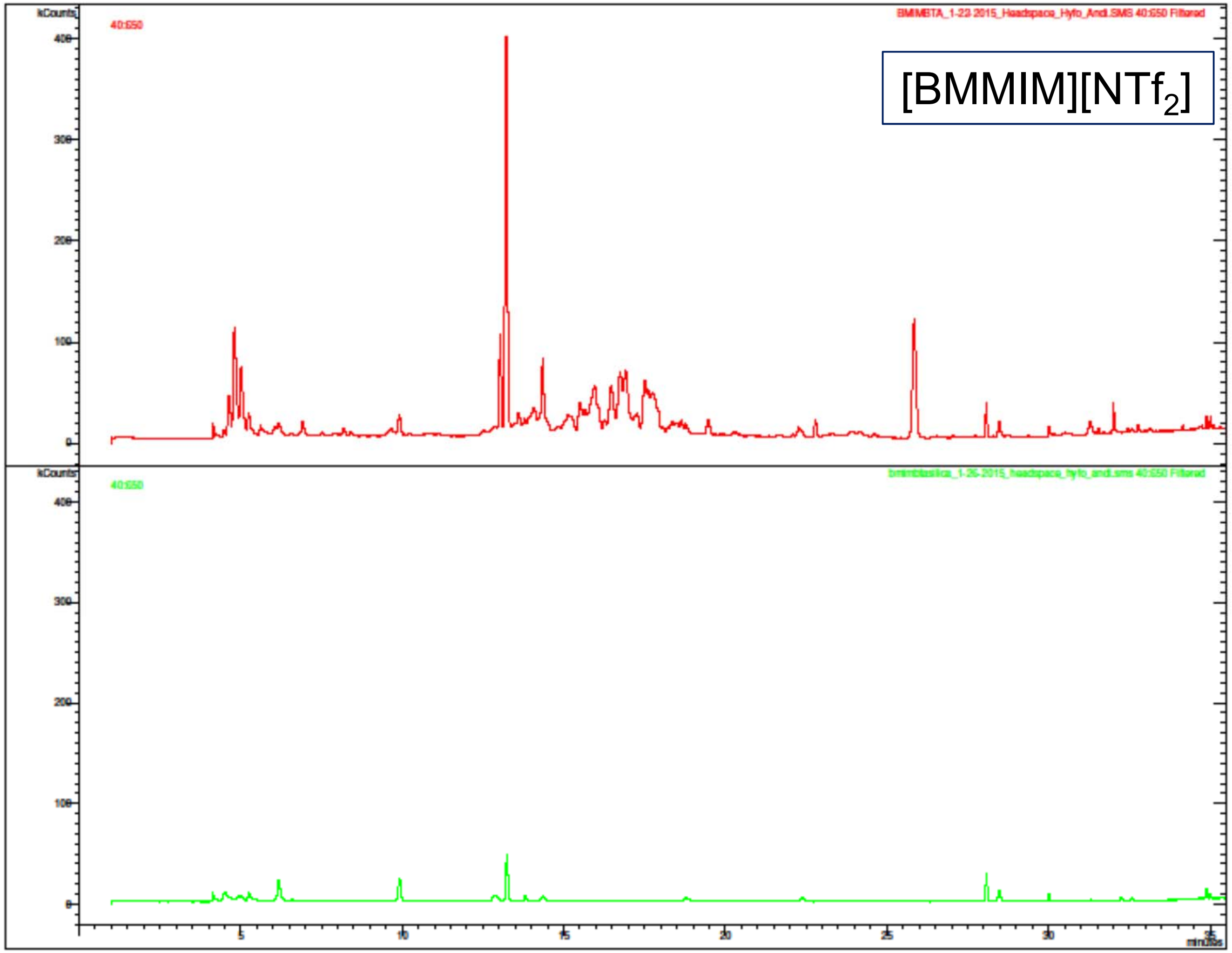
Ionic Liquid Recycling, Hedspace GC-MS

Print Date: 02 Feb 2015 14:21:42

Chromatogram Plots

- before
- after



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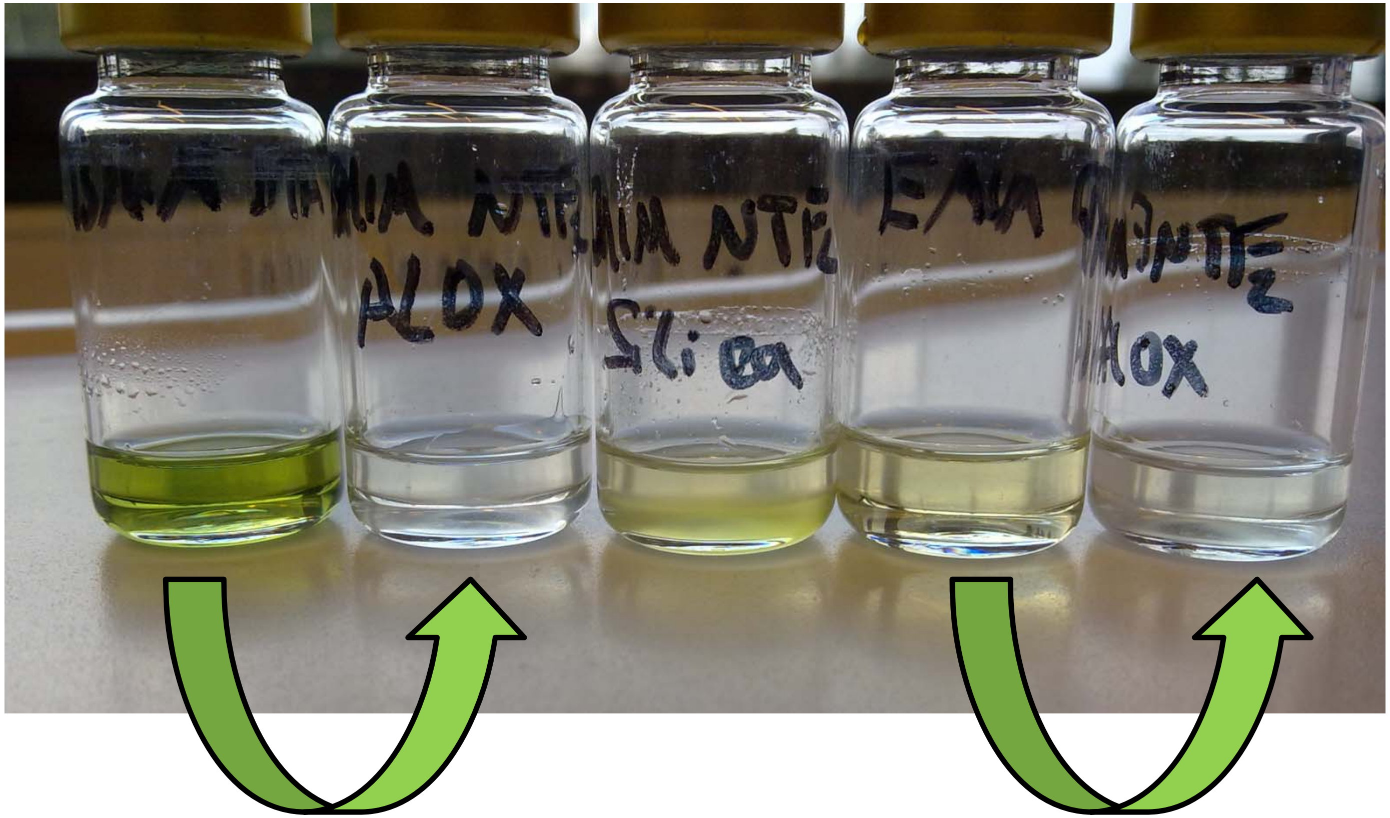
IL Recycling



- Recycling possilble but you have to consider the application

Conclusion

- To obtain ultra pure Ionic Liquid, you have to synthesize them by yourself
  - purification of starting material
  - working under inert atmosphere
  - avoiding grease, silica, carbon and alox
- Purification, recycling
  - possible
  - easy for hydrophobic ILs, demanding for hydrophilic ILs
  - success dependent on the application

Thanks to

- Prof. Wasserscheid
- Prof. König
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- Thank you for your attention