On-site Applications of MIMS and the Importance of Interface Design as Exemplified by Highly Unusual “Fragments” in MIMS Mass Spectra of Chloramines and Bromamines

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An industrial MIMS mass spectrometer

Does this plant contain bioactive compounds?

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Outline of the presentation

1. The diversity of MIMS applications: An overview

2. Examples of MIMS applications to gaseous, liquid and solid samples
    a) Surveillance of exhaust from power stations
    b) Surveillance of air quality in the field
    c) On-line investigations of chemical reactions
    d) Identification of new natural compounds
    e) Hot cell MIMS for direct analysis of solid samples
    f) Quantitative hot cell MIMS with MEPS pre-concentrating

3. Investigation of disinfection processes in water
    a) Monitoring of haloamines: An example of the importance of variations in interface setup

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The basics of MIMS

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The MIMS instrument

A solid water tight phrame with all basic control units available

Membrane interface prepared for easy shift from one type of application to another

Easy access and maintenance with plexiglass window

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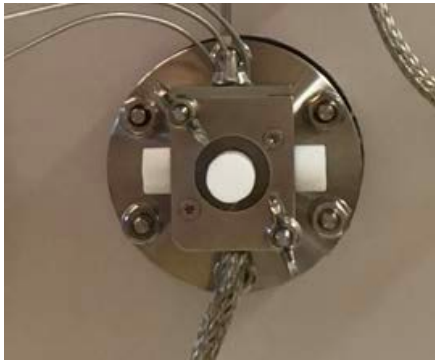
Interface setup

Membrane inlet detached

Inside of vacuum flange

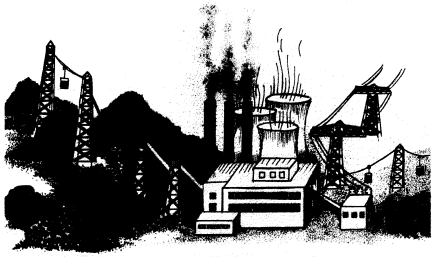
Outside of vacuum flange with membrane inlet mounted



On-site applications
An overview

Ground water, DK

Powerstations, DK



Off odours from pig manure, DK

Nuclear power stations, Olkilouto, FIN

Swimming pools, DK, DE, CH, AUS

Dairy flavors, DK

Yangtze river, CHN

Soil pollution, SE

Waste sampling. Half masks was needed because of the odour.

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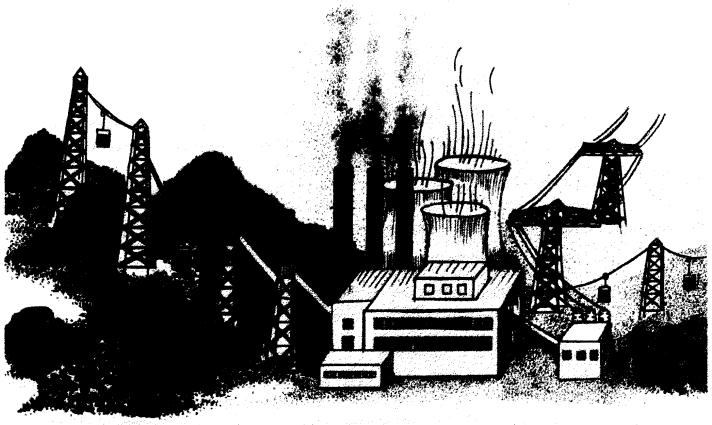
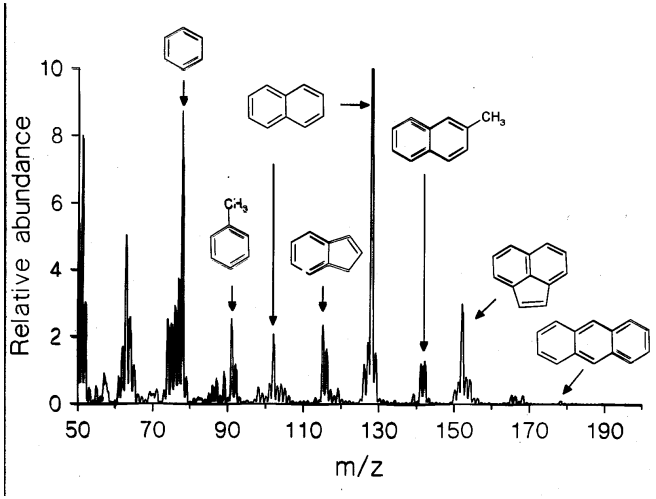
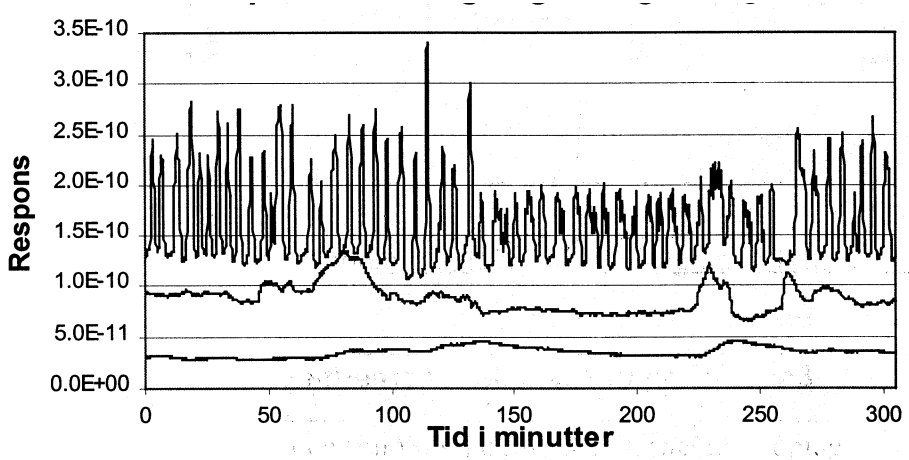
On-line monitoring of ”clean” gas from a power station

Clean exhaust ?







Oxygene

Toluene

Naphthalene

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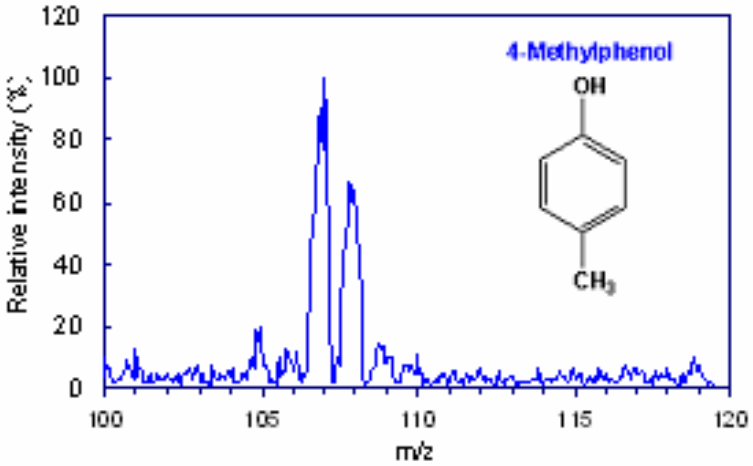
Detection of off-odours near pig farms

Typical off odours :

- Phenols (4-Methyl-phenol)
- Reducing sulphur compounds
  - (Dimethyl sulfide)
- Indoles
- Short chain fatty acids
- Aldehydes (3-methylbutanal)



Pictures: Courtesy of Danish Technological Institute

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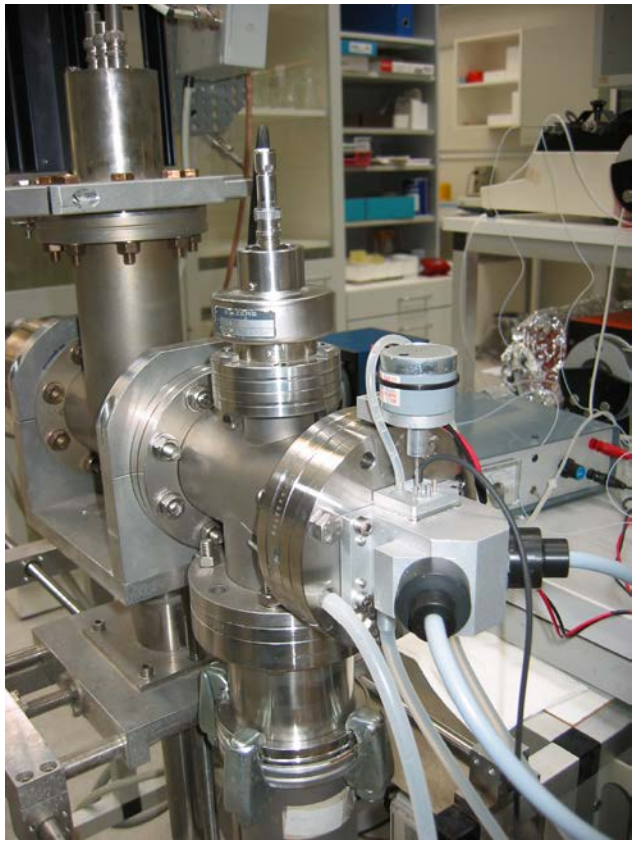
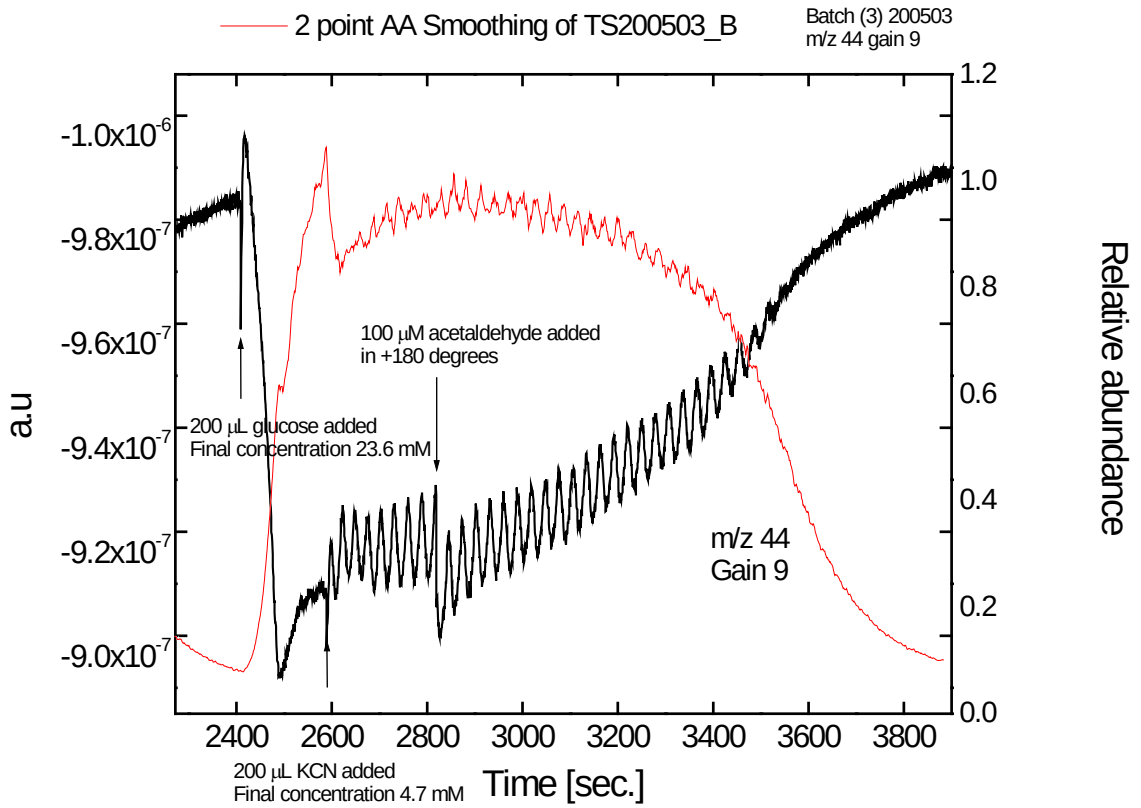
Combined reactor cells with MIMS and a UV absorbanse/fluorescence

On-line monitoring of oscillations in yeast cultures using combined MIMS and fluorescence





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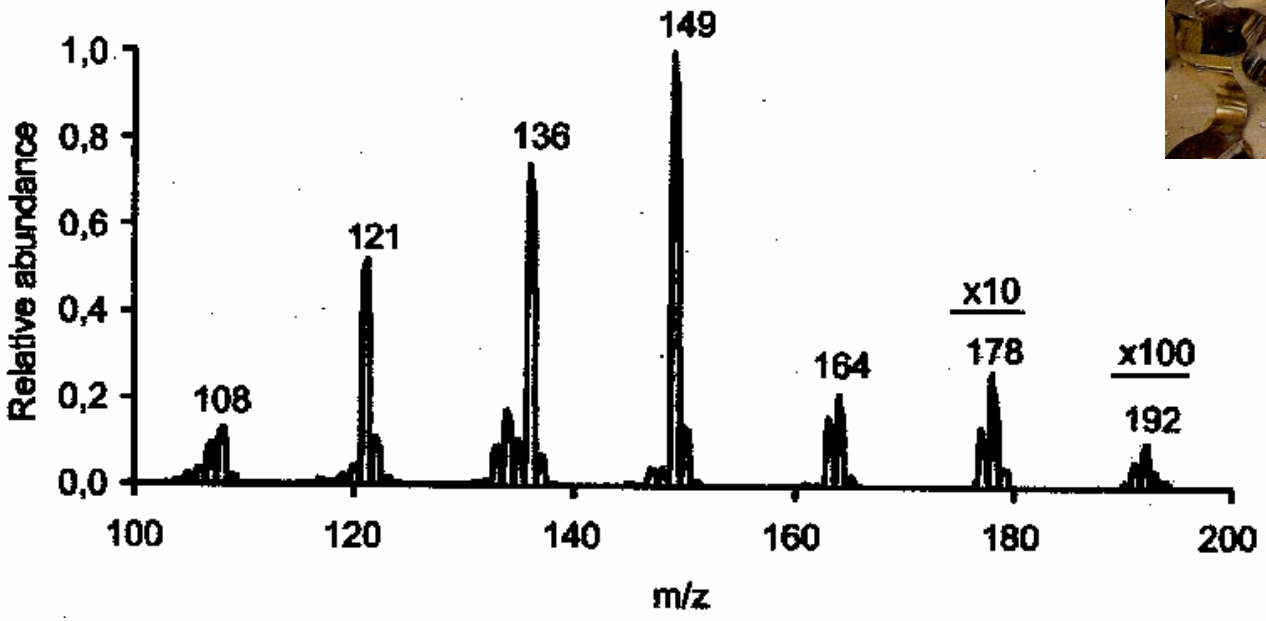
Identification of novel natural compounds in microbial cultures

Fermentation of Paenibacillus polymyxa: What is this?



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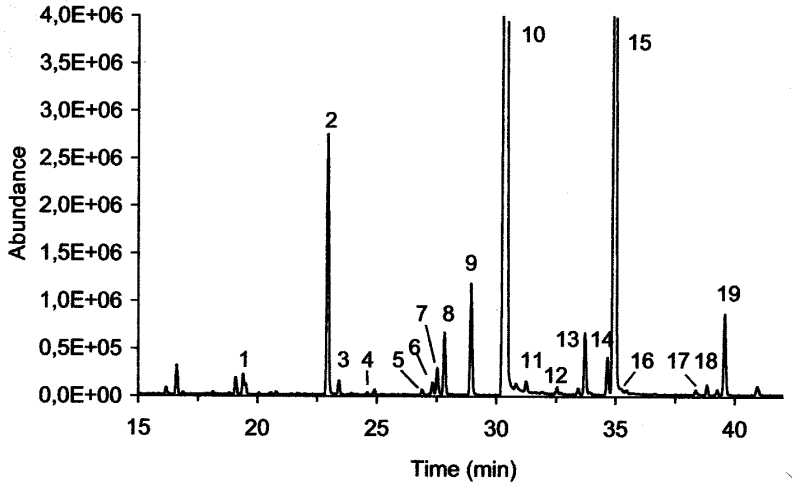
Identification using advanced MS techniques

Total ion chromatogram, GC



GC-EI-MS spectrum of **10**

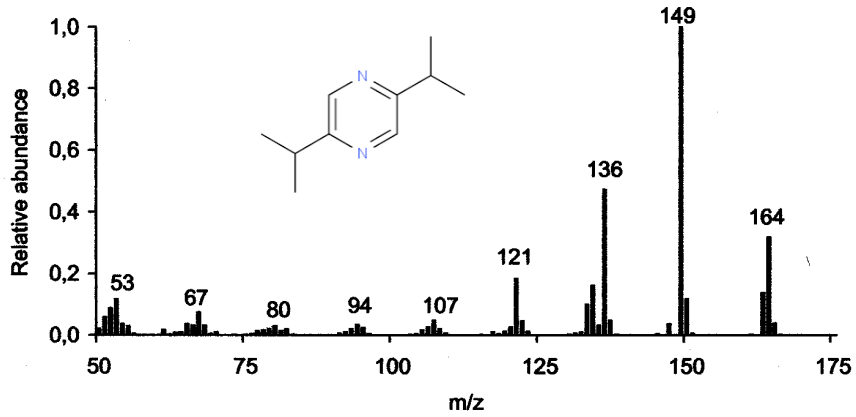


Fig. 4. EI-MS spectrum of the unknown compound **10**.

HRMS data, Q-TOF with Micromass MS-Nose

Table 1
HRMS data of the pseudomolecular ions $(M+H)^+$, and predicted molecular formula for the observed masses of unknown volatile metabolites produced by *P. polymyxa* ATCC 10401

	Observed mass (Da)	Error (ppm)	Calculated mass (Da)	Formula
2	123.0917	4.3	123.0922	$C_7H_{11}N_2$
3	137.1080	0.7	137.1079	$C_8H_{13}N_2$
4	151.1232	2.3	151.1235	$C_9H_{15}N_2$
5	165.1389	1.5	165.1392	$C_{10}H_{17}N_2$
6	179.1548	0.0	179.1548	$C_{11}H_{19}N_2$

19 pyrazine metabolites, where off 7 are novel natural products

Table 2
EI-MS and identity of pyrazines biosynthesised by *P. polymyxa* ATCC 10401 when cultivated in TSB medium

Metabolite	Retention time (min)	*m/z* of fragment ions (% relative intensity)	Identification
1	19.40	122 (M^+, 22), 107 (100), 94 (33), 80 (13), 53 (22)	2-Isopropylpyrazine
2	22.91	136 (M^+, 35), 121 (100), 108 (44), 94 (9), 66 (11), 53 (12)	2-Methyl-6-isopropylpyrazine
3	23.38	136 (M^+ 38), 135 (21), 121 (100), 108 (40), 94 (8), 66 (6), 53 (10)	2-Methyl-5-isopropylpyrazine
4	23.92	136 (M^+ 12), 121 (20), 108 (4), 94 (100), 67 (7), 52 (4)	2-Isobutylpyrazine
5	26.85	150 (M^+, 38), 149 (25), 135 (100), 122 (55), 108 (9), 80 (3), 67 (12), 53 (21)	2,3-Dimethyl-5-isopropylpyrazine
6	27.29	150 (M^+, 38), 149 (25), 135 (100), 122 (56), 108 (9), 80 (3), 67 (12), 53 (21)	2,5-Dimethyl-3-isopropylpyrazine
7	27.49	150 (M^+, 10), 135 (15), 122 (1), 108 (100), 94 (1), 80 (2), 66 (8), 53 (2)	2-Methyl-5-isobutylpyrazine
8	27.90	150 (M^+, 33), 149 (18), 135 (100), 122 (35), 107 (11), 94 (2), 80 (4), 67 (6), 53 (13)	2,6-Dimethyl-5-isopropyl-pyrazine
9	28.90	164 (M^+, 31), 163 (22), 149 (100), 136 (58), 122 (6), 107(2), 94 (2), 80 (2), 67 (6), 53 (13)	2,6-Diisopropylpyrazine
10	30.25	164 (M^+, 32), 163 (14), 149 (100), 136 (47), 121 (18), 107 (5), 94 (3), 80 (3), 67 (7), 53 (12)	2,5-Diisopropylpyrazine
11	31.88	164 (M^+ 15), 149 (25), 136 (7), 122 (100), 107 (3), 94 (2), 80 (9), 67 (3), 53 (7)	2,5-Dimethyl-6-isobutylpyrazine
12	32.50	164 (M^+ 24), 149 (36), 136 (9), 122 (100), 107 (49), 94 (4), 80 (2), 67 (5), 53 (8)	2,6-Dimethyl-5-isobutylpyrazine
13	33.67	178 (M^+ 9), 163 (16), 147 (3), 136 (100), 121 (11), 108 (2), 94 (3), 80 (1), 67 (3), 53 (4)	2-Isopropyl-6-isobutylpyrazine
14	34.61	178 (M^+ 18), 163 (47), 150 (100) 135 (57), 121 (11), 107 (3), 94 (3), 80 (4), 67 (6), 53 (14)	2-Isopropyl-5-sec-butylpyrazine
15	34.91	178 (M^+ 18), 163 (23), 150 (3), 136 (100), 121 (74), 107 (4), 94 (3), 80 (2), 67 (4), 53 (7)	2-Isopropyl-5-isobutylpyrazine
16	35.40	192 (M^+ 60), 177 (100), 164 (58), 149 (13), 135 (3), 107 (17), 94 (1), 79 (7), 67 (6), 53 (2)	2,5-Dimethyl-3,6-diisopropylpyrazine
17	38.30	192 (M^+ 10), 177 (16), 150 (100), 135 (4), 108 (30), 94 (2), 80 (3), 66 (6), 53 (3)	2,6-Diisobutylpyrazine
18	39.20	192 (M^+ 15), 177 (21), 164 (28), 150 (71), 136 (8), 121 (100), 107 (4), 94 (2), 79 (1), 67 (3), 53 (7)	2-Isobutyl-5-sec-butylpyrazine
19	39.55	192 (M^+ 14), 177 (14), 162 (1), 150 (87), 135 (5), 121 (1), 107 (100), 94 (2), 80 (4), 66 (3), 53 (4)	2,5-Diisobutylpyrazine

H.C. Beck, A.M. Hansen and **Frants R. Lauritsen**.
FEMS Microbiology Letters, **220**, 67-73, 2003.

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Hot cell MIMS for analysis of solid materials

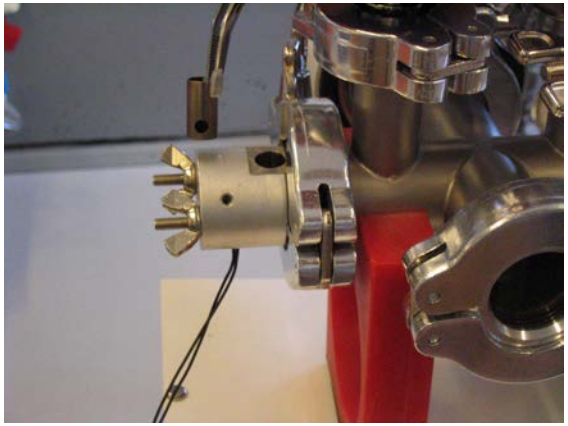
PAH contaminated soil

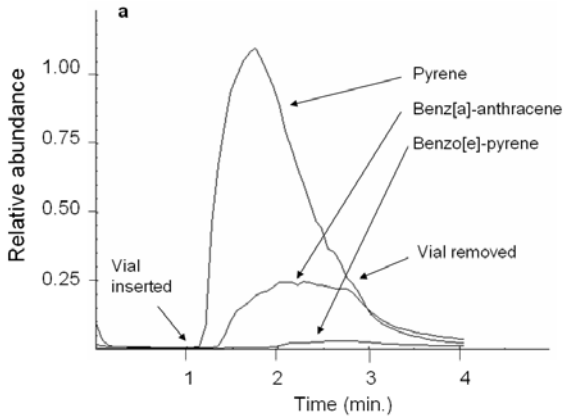
Mini MIMS, Copenhagen University

Multipole mass spectrometer

S. Boumsellek and R.J. Ferran, *J. Am. Soc. Mass Spectrom.*, 2001. **12**(6): p. 633-640.

Hot cell design



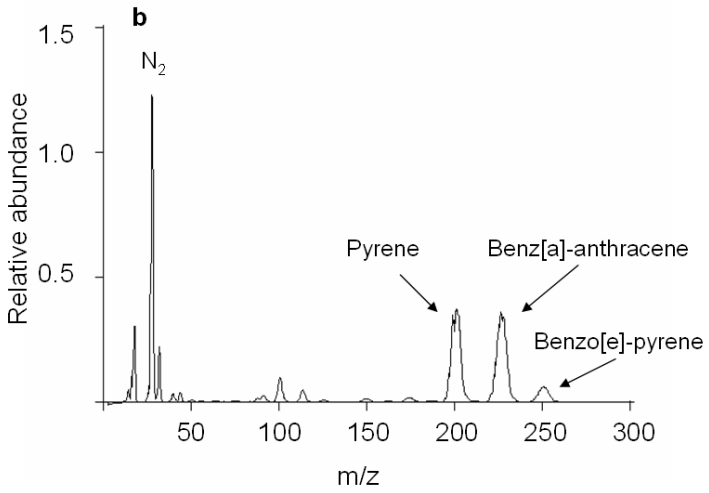


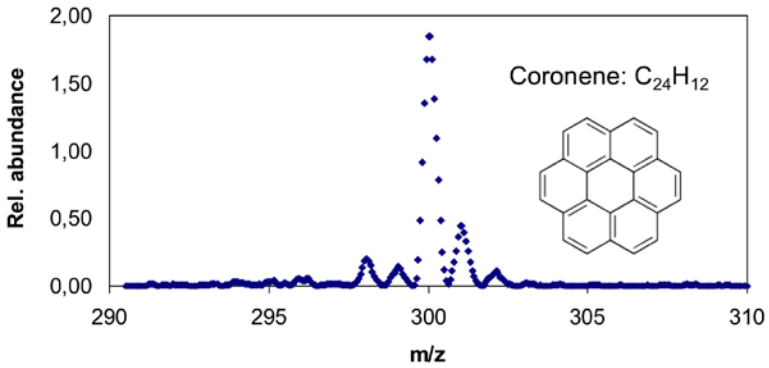
Helle Frandsen, Christian Janfelt and **Frants R. Lauritsen**
Rapid Communications in Mass Spectrometry, **21**, 1574-1578, 2007.

Direct analysis of contaminated soil

Mini MIMS (PAHs)

Industrial MIMS





Pia Kammeyer, AEC Group, CPU

Rapid Commun. Mass Spectrom. 2007, 21, 1574-1578

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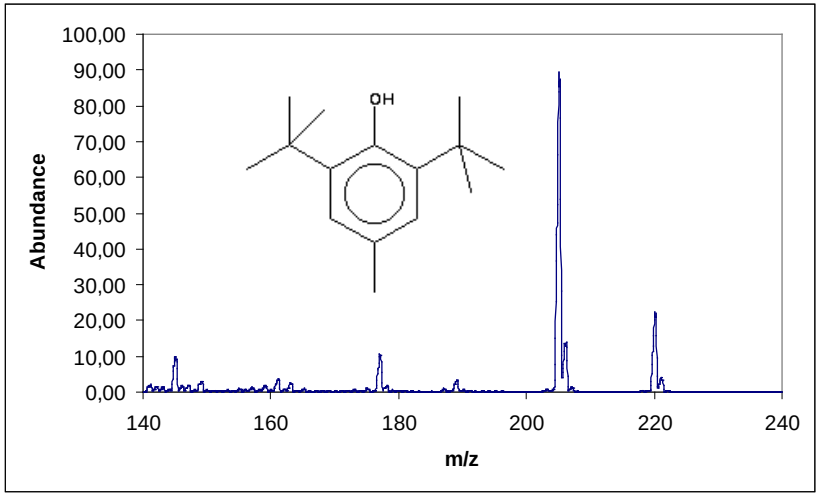
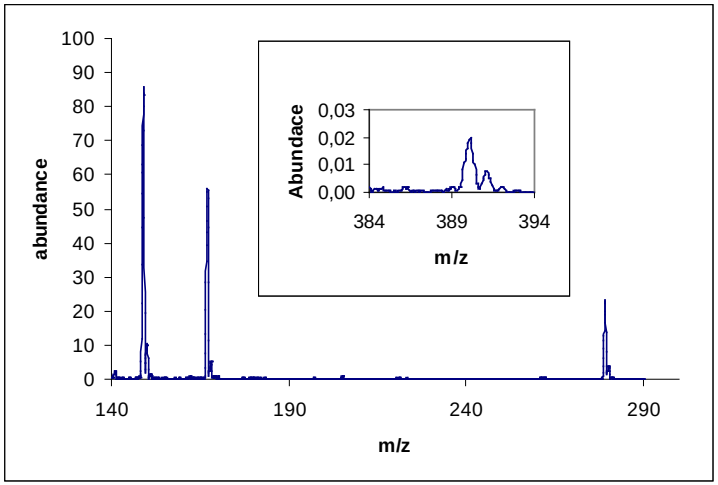
Direct analysis of plastic materials

Vacuum tube of rubber

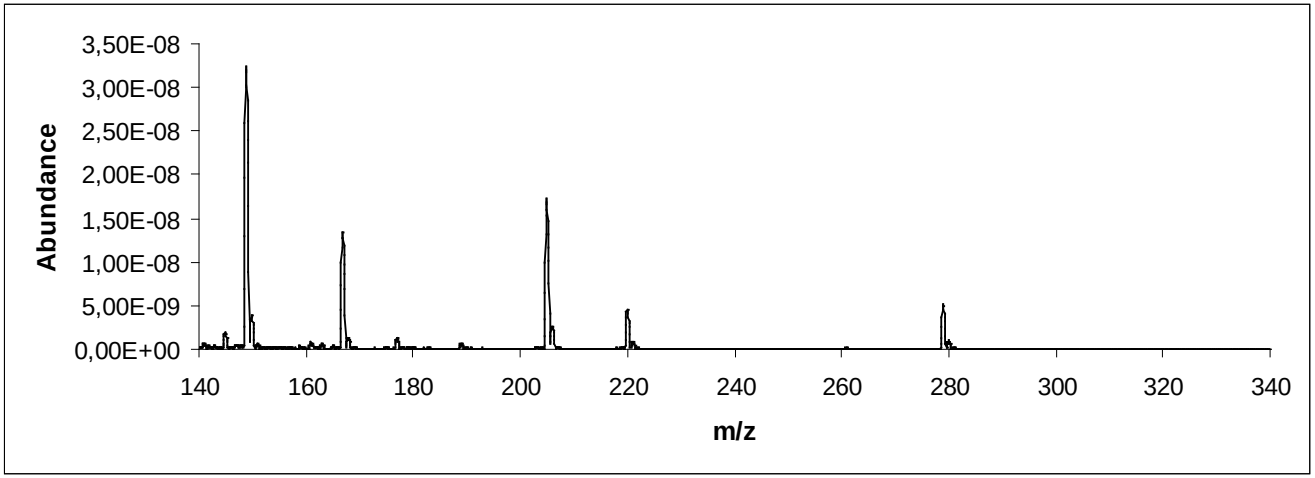


Soft PVC tube



Chen, Xia, Pedersen-Bjergaard, Svensmark, Lauritsen. Anal. Chem. 2009, 81, 4010-4014

Plastic bag for medical infusion at hospitals



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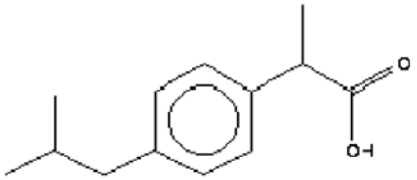
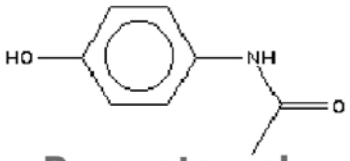
Tablets/powders with commonly used drugs in suicide attempts that can be measured with hot cell MIMS

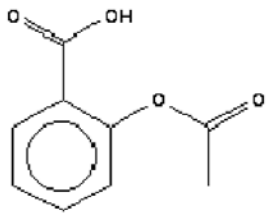
Pain killers



Ibuprofen

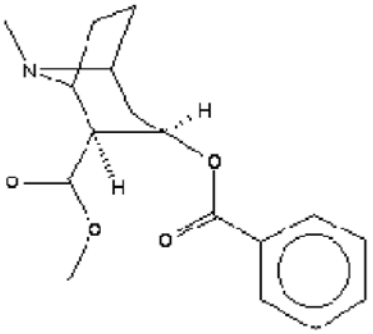


Paracetamol

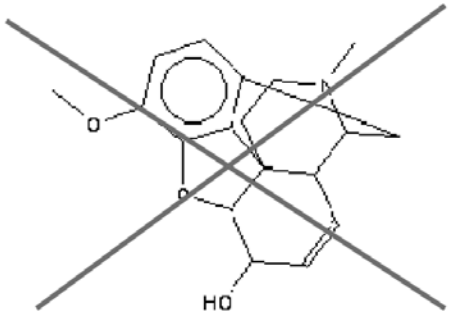


Acetyl salicylic acid

Narcotics

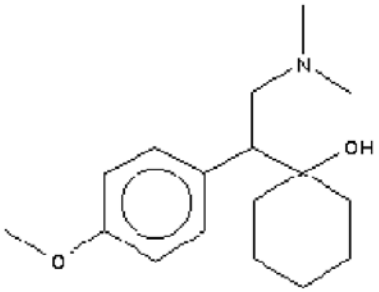


Cocaine

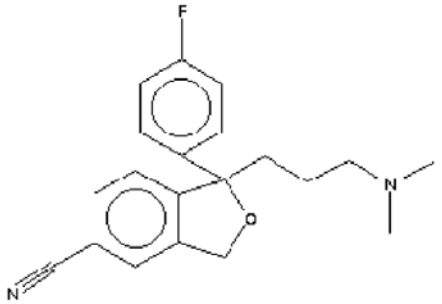


Codeine phosphate

Anti depressives



Venlafaxine



Citalopram

F.R. Lauritsen, K. Nielsen

International Journal of Mass Spectrometry, **295**, 119-123, 2010.

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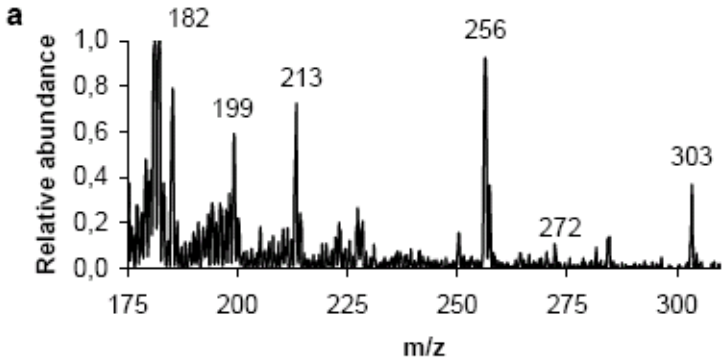
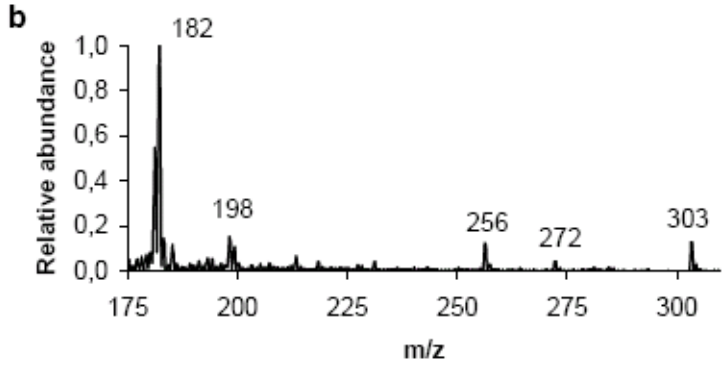
Quantitative analysis

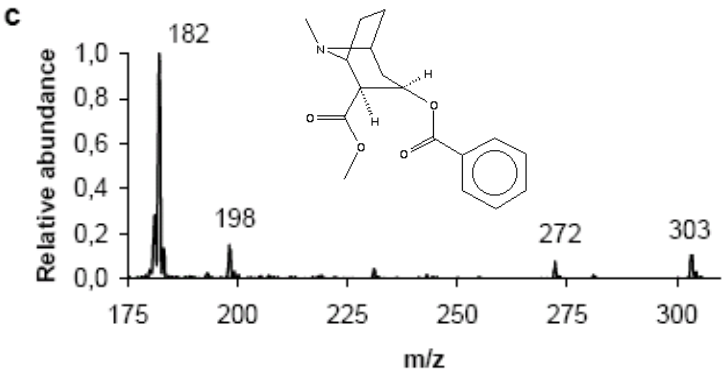
Coca plant



Direct analysis of leaves



Micro extract in methanol



Cocaine standard

Chen, Xia, Pedersen-Bjergaard, Svensmark, Lauritsen. Anal. Chem. 2009, 81, 4010-4014.

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Hot cell MIMS and MEPS pre-concentrating

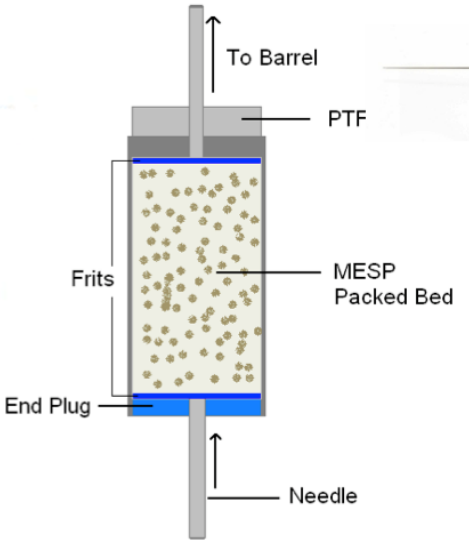
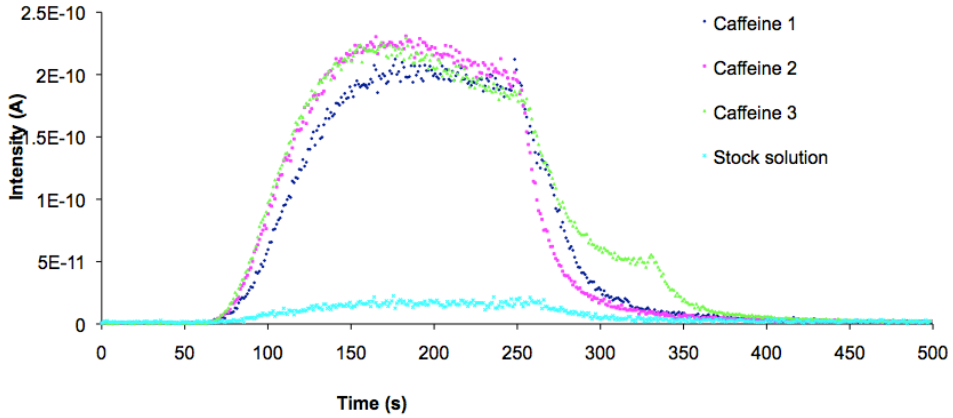


Figure 1. (Above) The MEPS syringe with the packed solid phase placed between the needle and the barrel.
(Left) A magnification of the solid phase, containing 1 mg of packed material, which can have different surface coatings for selective analyte binding and eluting properties.

Reproducibility of MEPS



K. Nielsen; Master thesis, 2011

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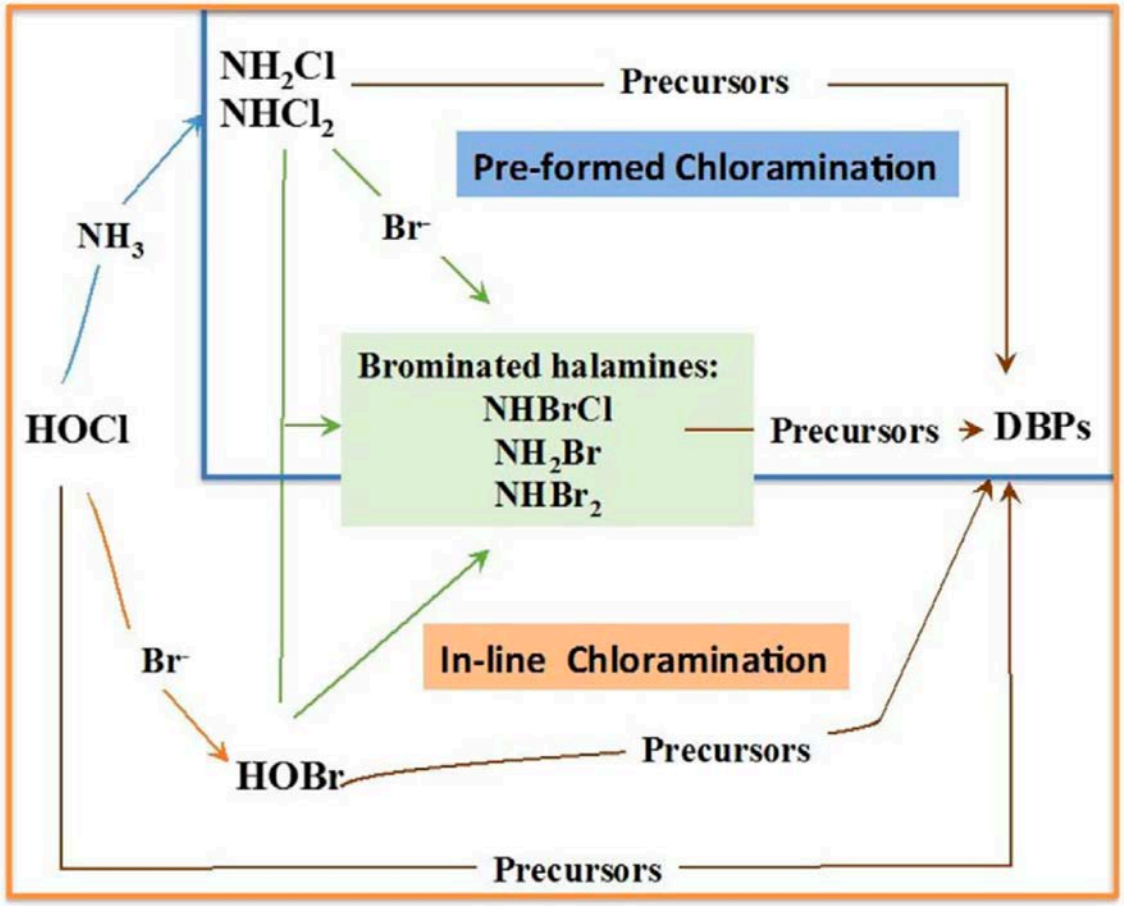
Analysis of Haloamines following disinfection

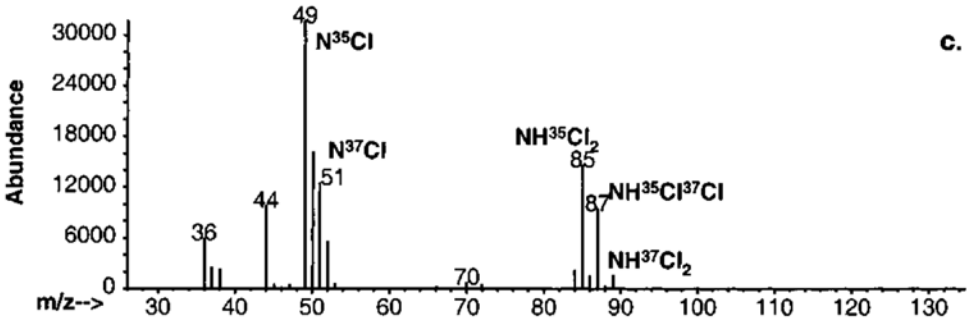
Impact of brominated amines on monochloramine stability during in-line and pre-formed chloramination assessed by kinetic modelling

Problem:
Can MIMS be used for quantitative on-line studies of haloamines?

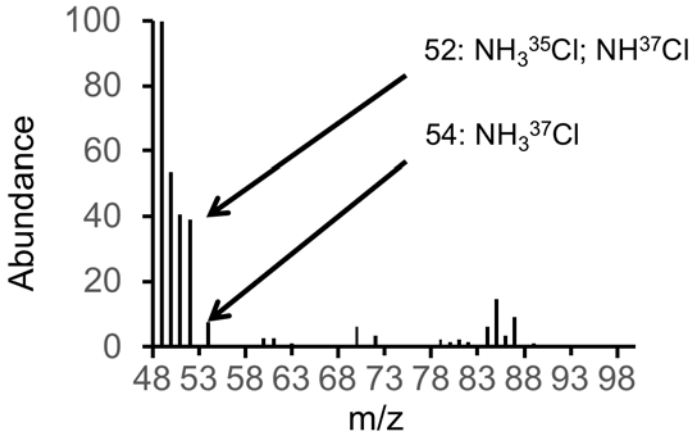


Sébastien Allard ∗, Keith Cadee, Rachel Tung, Jean-Philippe Croué
Science of the Total Environment 618 (2018) 1431–1439

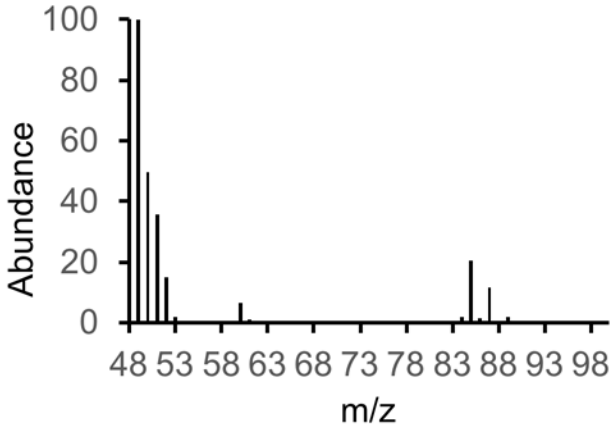
Verification of mass spectra: Dichloroamin



Chang and Blatchley III: Environ. Sci. Technol. 1999, 33, 2218-2223

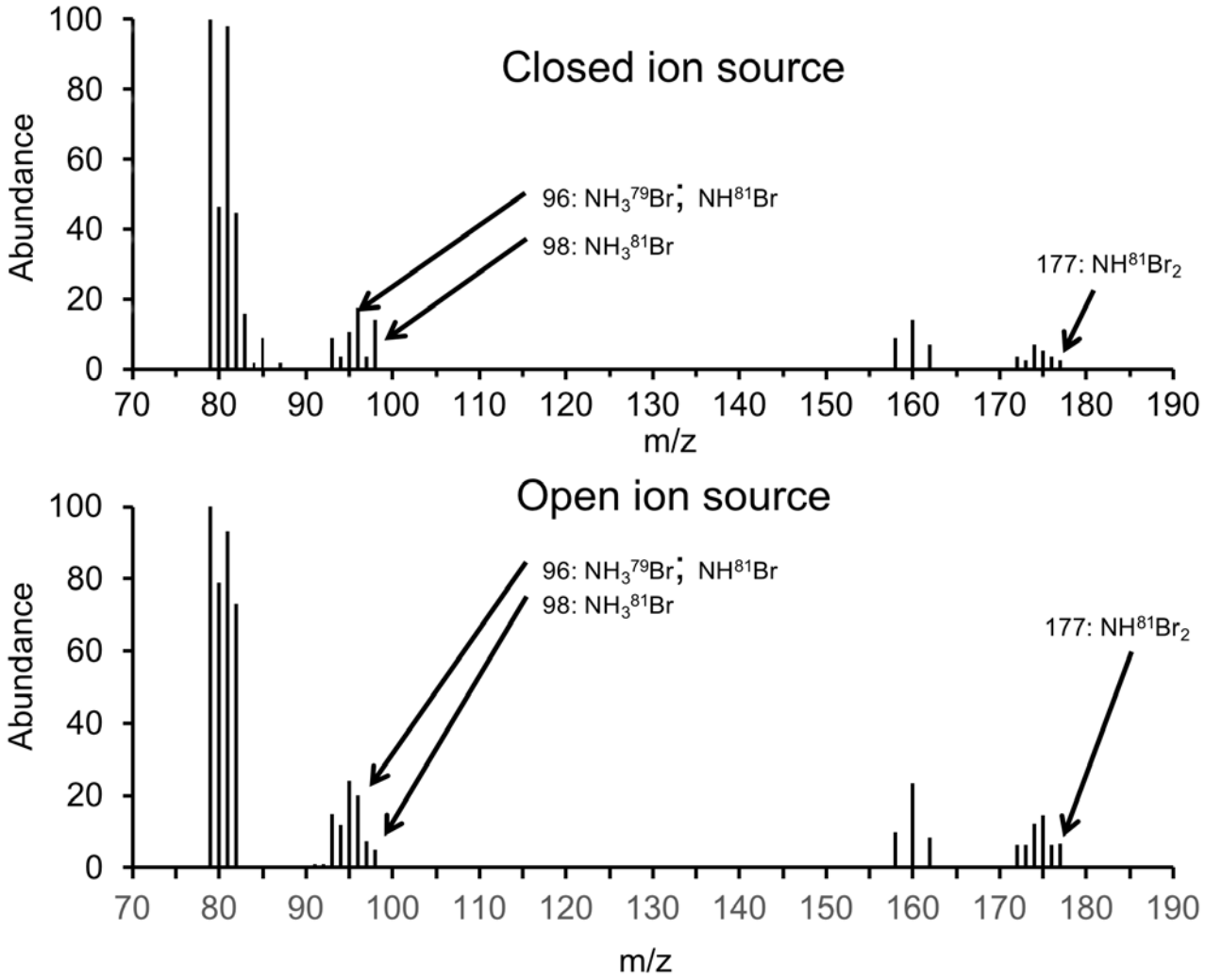


Dichloroamin: Closed ion source without ceramic connection



Dichloroamin: Open ion source

Dibromamine



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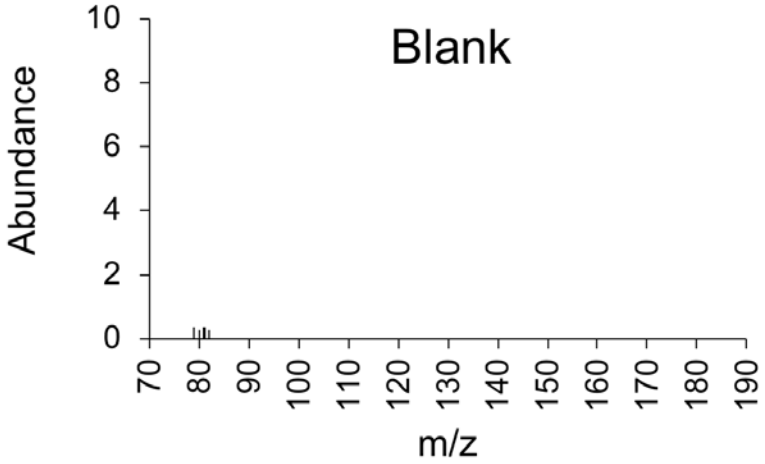
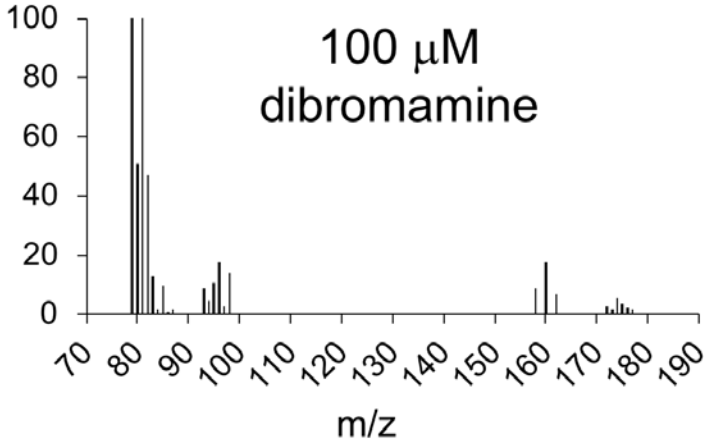
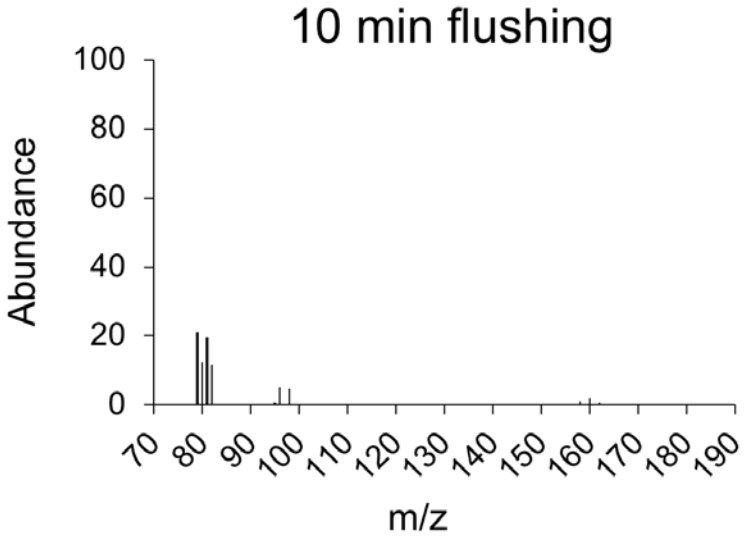
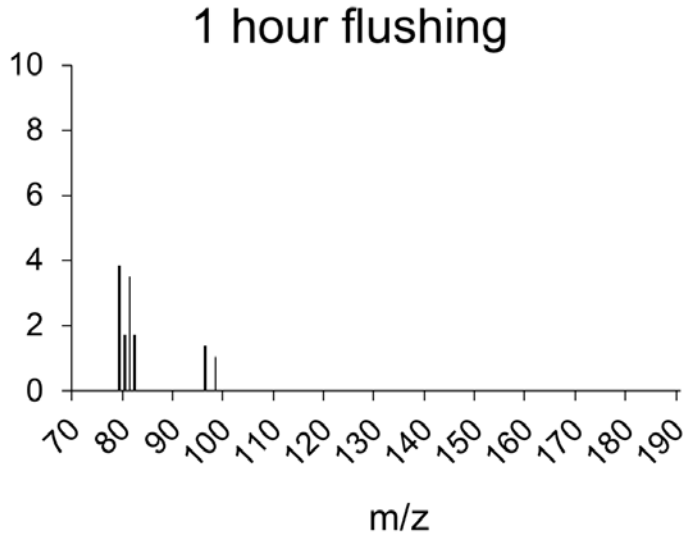
Appearence and disappearence of ions









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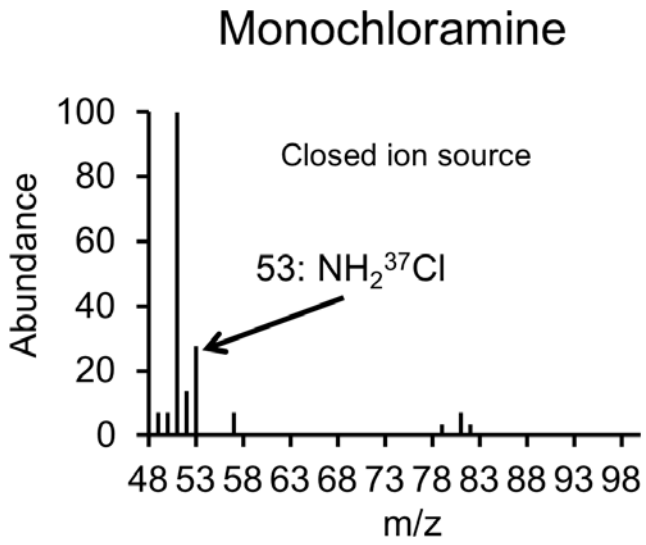
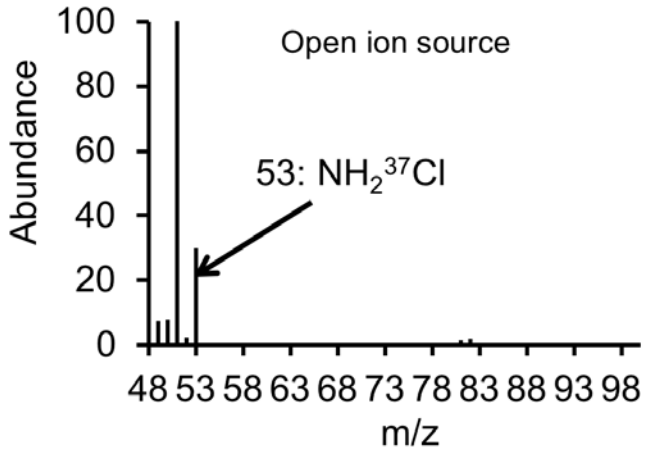
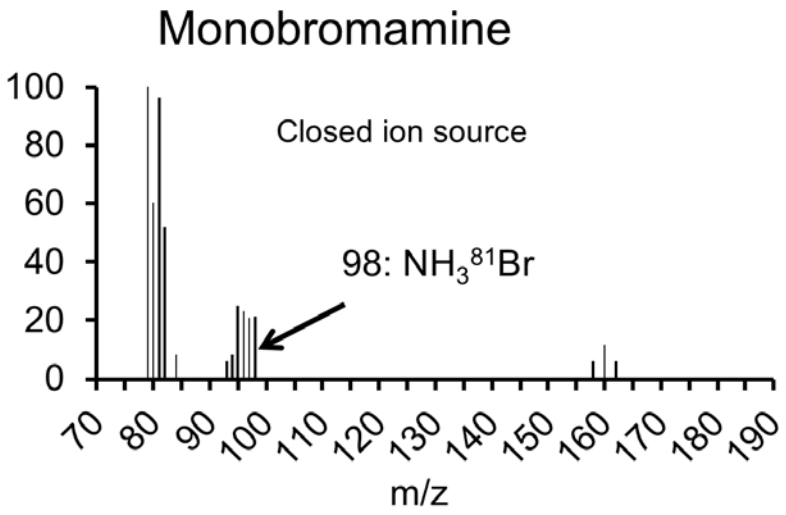
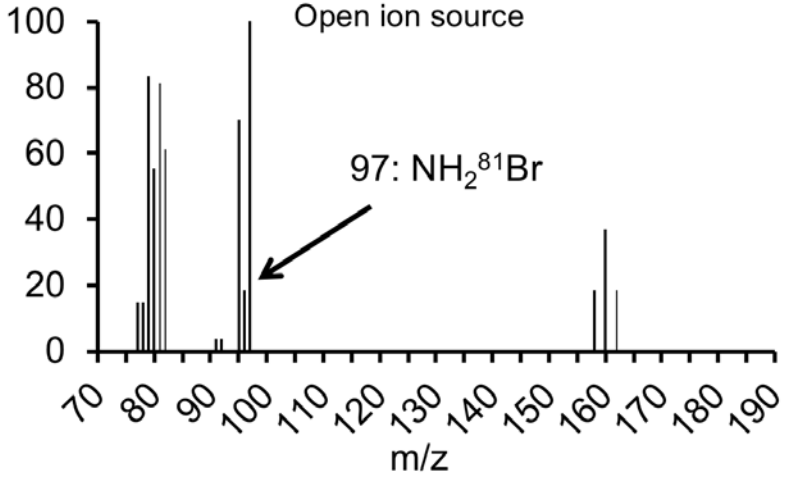
Mono haloamines









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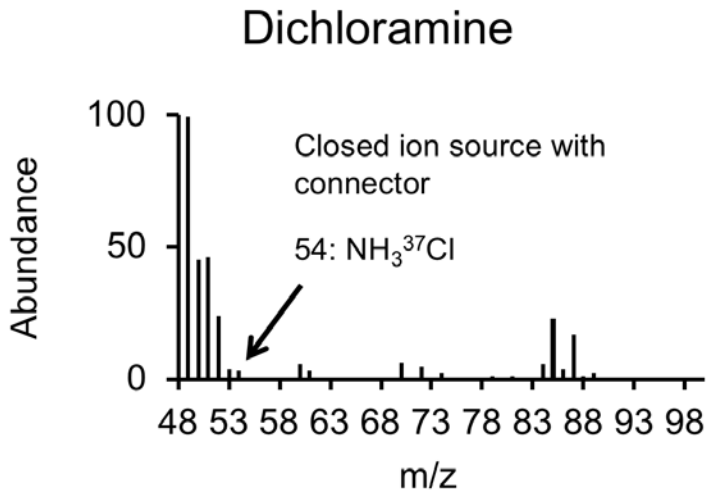
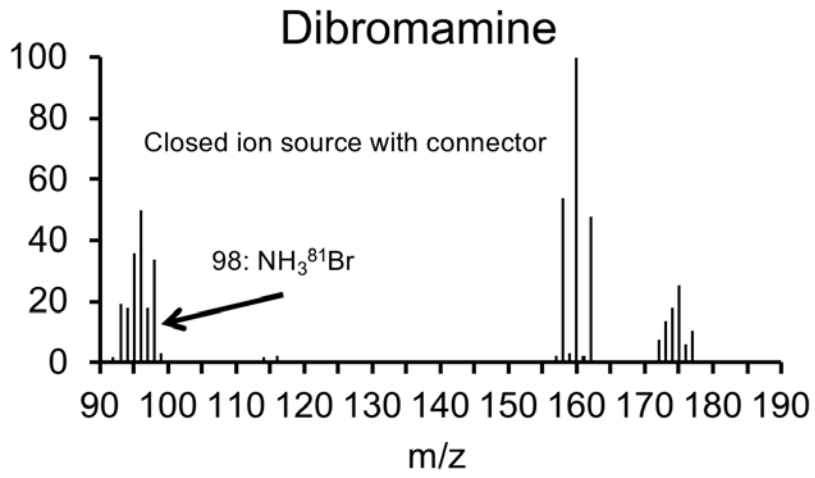
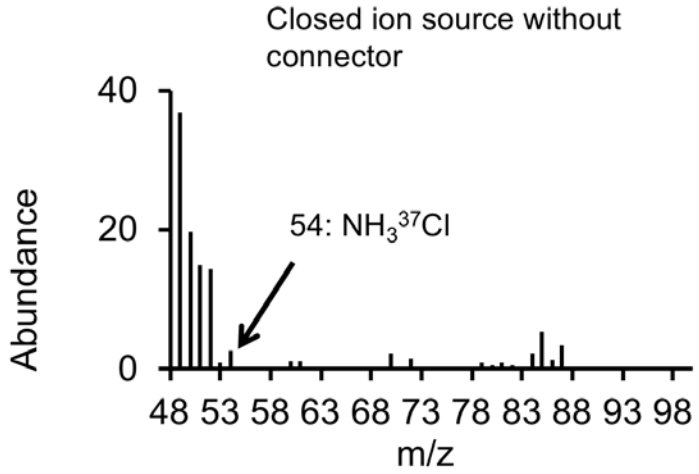
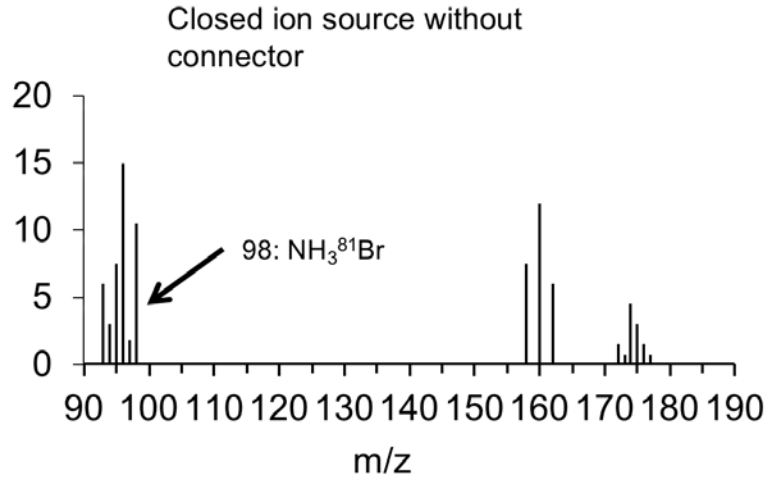
The importance of the ceramic connector









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Conclusions

- The potential applications of MIMS are very diverse covering air, liquid and solid samples from inorganic gases to hydrophobic organic compounds of both volatile and very low volatility.

- For the best individual setup for an application the choice of membrane area, thickness and temperature, distance and type of connection between membrane and ion source as well as choice of ion source must be considered.

- In my experience the best choice of membrane for +95% of the applications is a polydimethylsiloxane (PDMS) membrane. It is just a matter of adjusting the interface parameters.

- Halogenated compounds can decompose on hot metal surfaces and create reactive radicals and new ions in the mass spectrum.

- An open ion source design reduce production of reactive radicals.

Thanks for your attention

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