8th Harsh-Environment Mass Spectrometry Workshop
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Magnet portable mass spectrometer for direct control of gases in sea water

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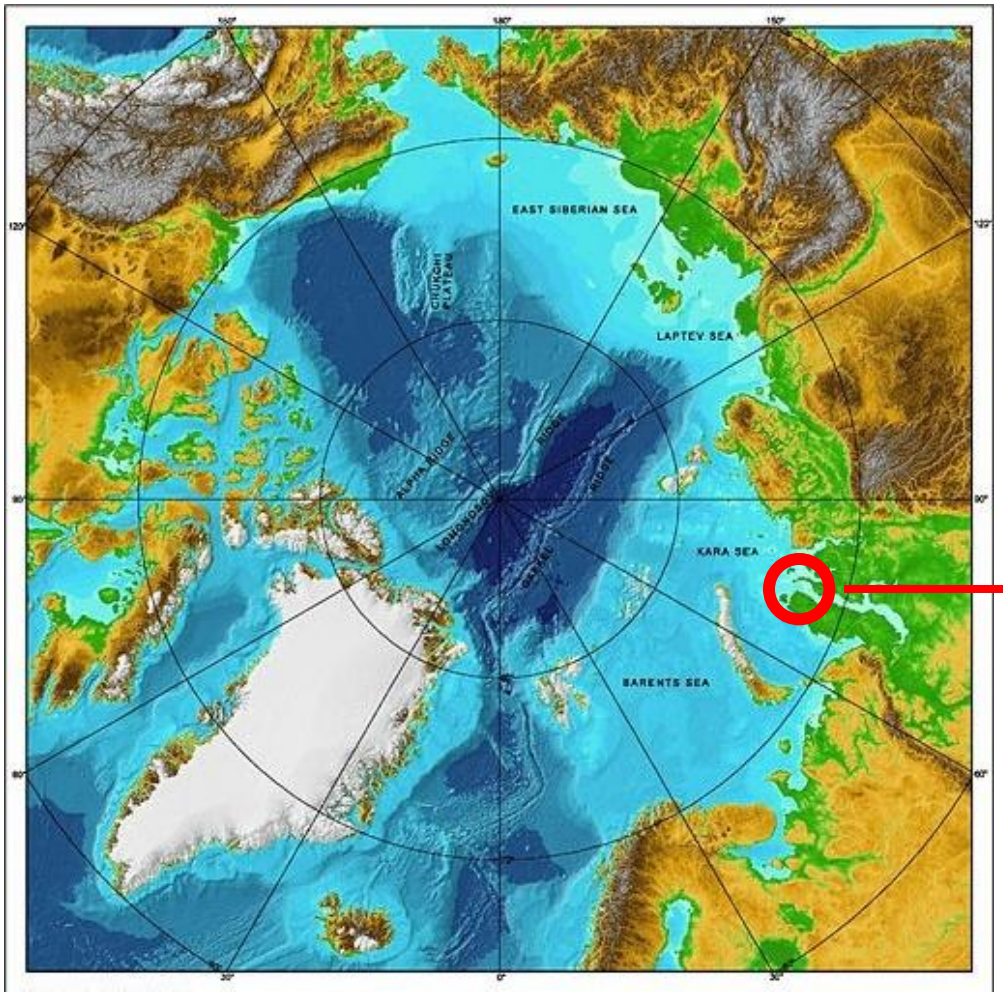
The main purpose of this study is design system for in situ on-line monitoring for oil and gas prospecting and environmental control

Overview:

- Motivations
- Instrument description
- Compound identification
- Conclusions and prospects

Motivations

Investigation of gas concentration in shelf sea water for prospecting

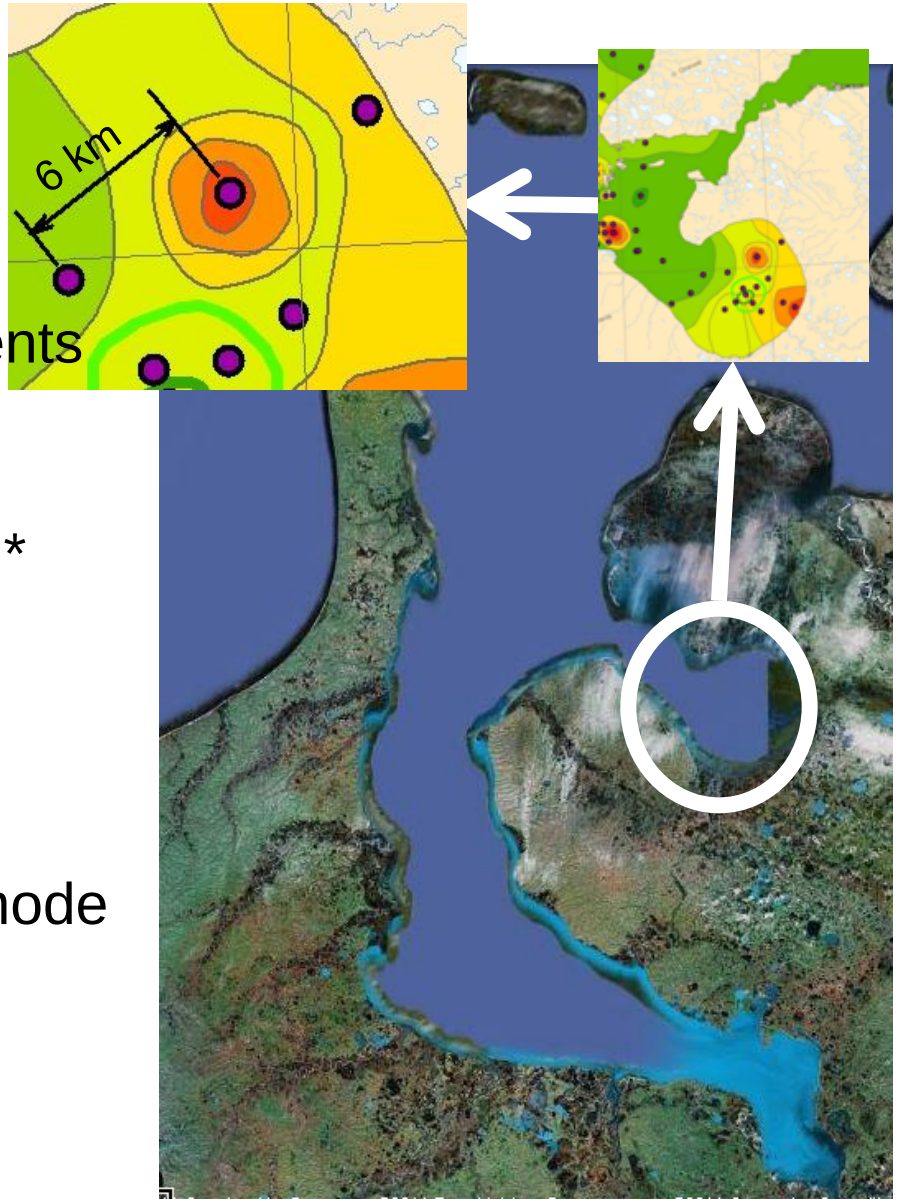


Measurement modes

previously:
- Extraction of bottom sediments
- Discrete sampling:
  sample size ~10 cm,
  sampling distance >3 km*
- Laboratory studies

In this study we assume:
- Direct analysis of seawater
- Continuous measurement mode (spatial averaging ~50 m)
- on-line research

(*) – compare with the size of the sources >100м



mapping of gas saturation

Target compounds

For prospecting:

- Methane – 1-40 ppm*
- Ethane – 1-160 ppb*
- Propane – 1-80 ppb*
- Butane – 1-500 ppb*
- Pentane – no information

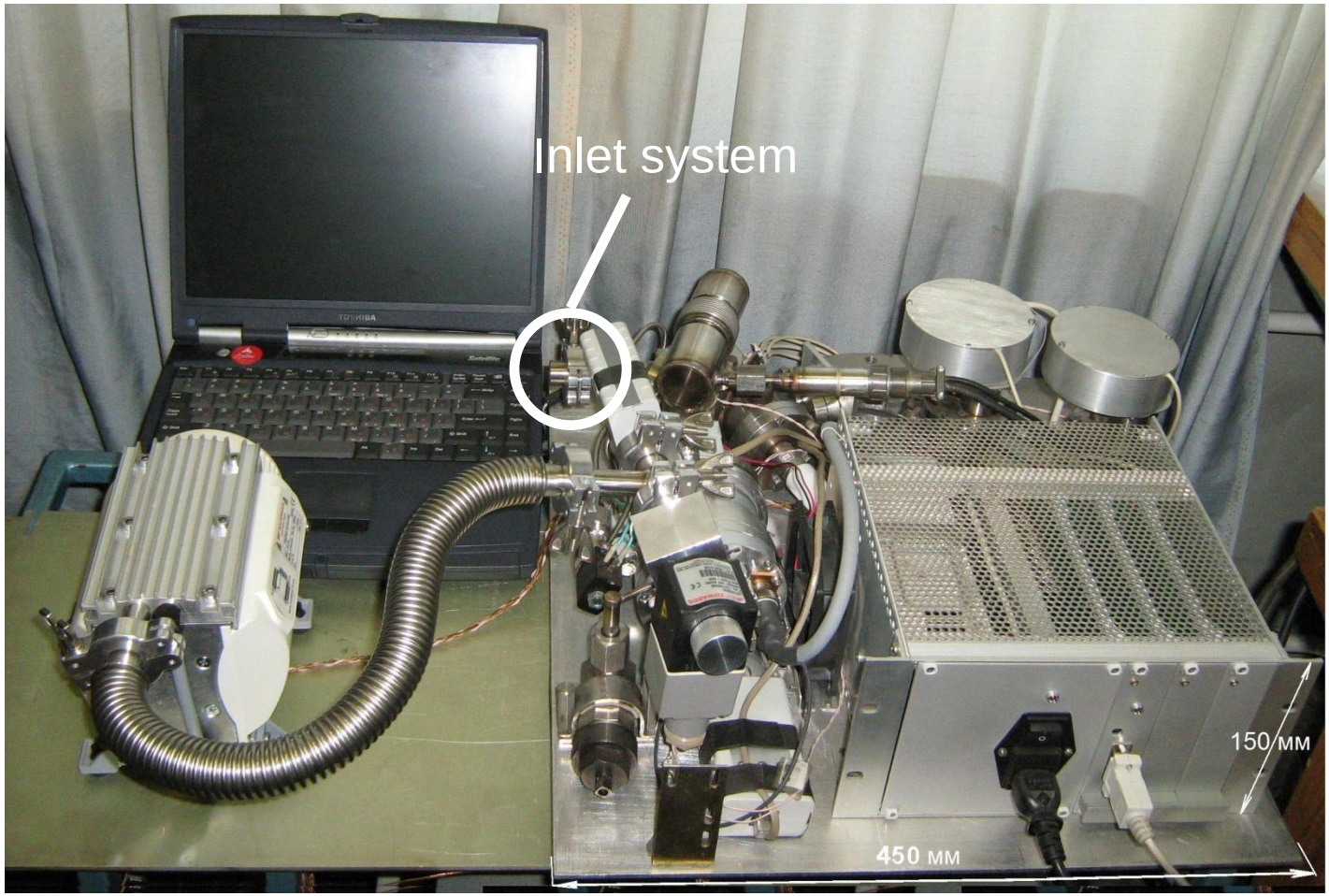
- Isobutane – <8 ppb*
- Ethylene – <1.6 ppb*

(*) – concentration in bottom sediment (Chromatographic technique)

For environmental control:

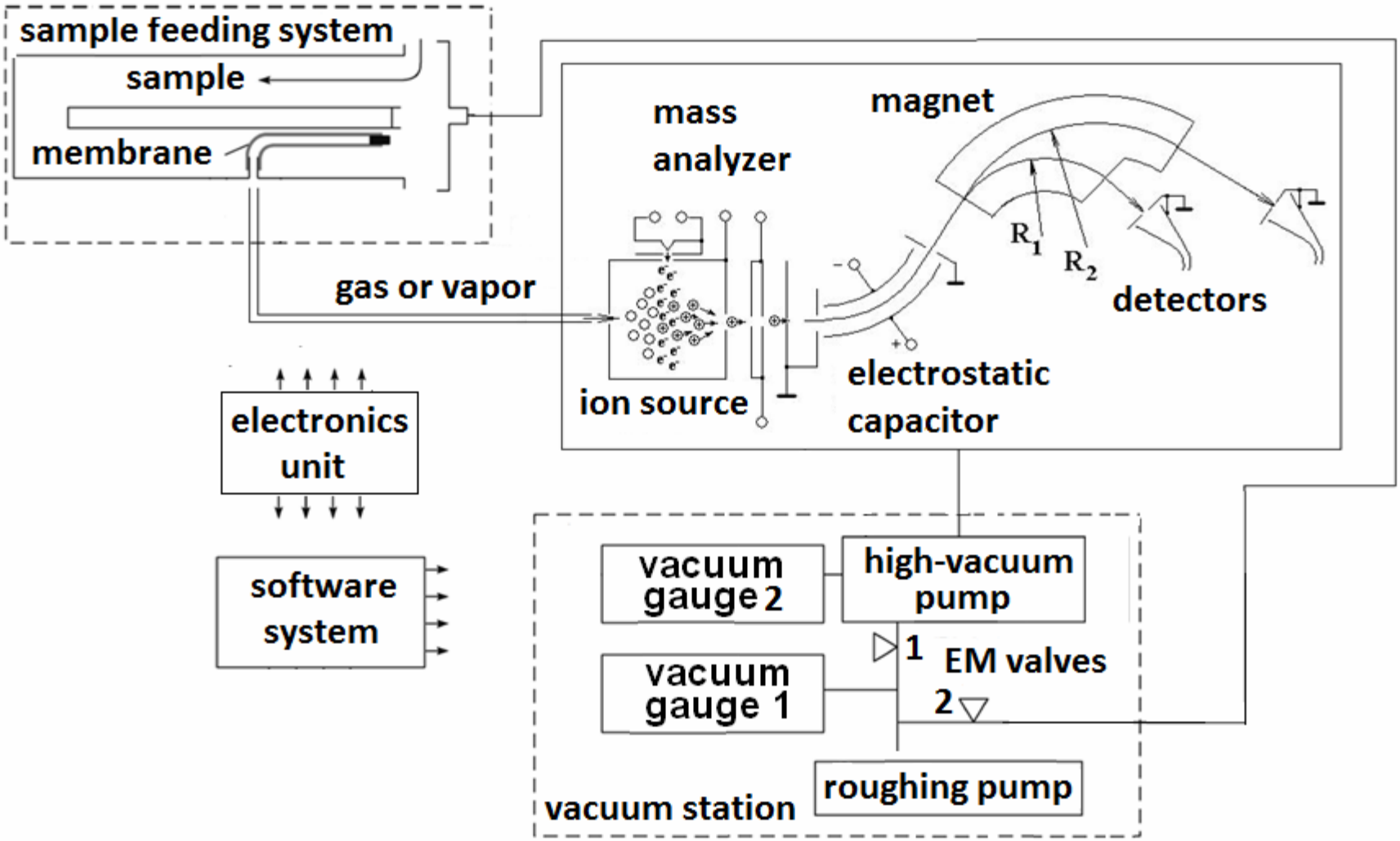
- Air constituents
- Benzene
- Toluene
- and others

Instrument description

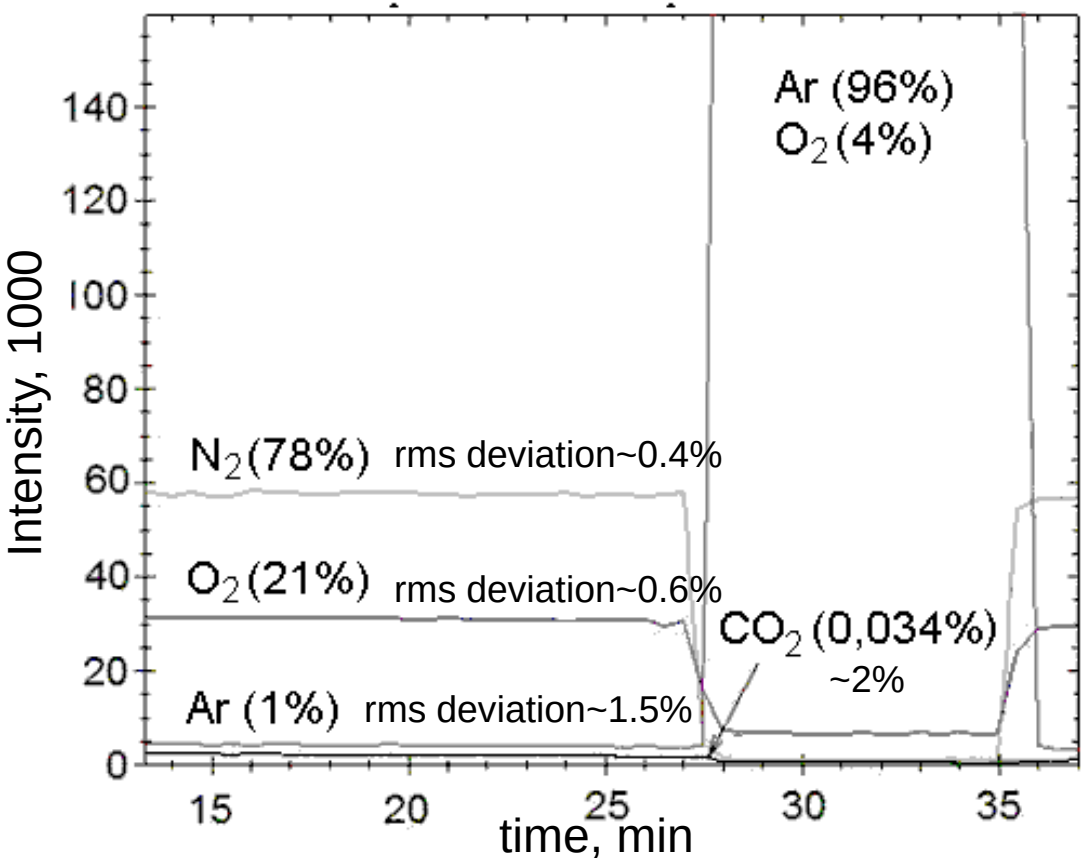


Appearance of mass spectrometer

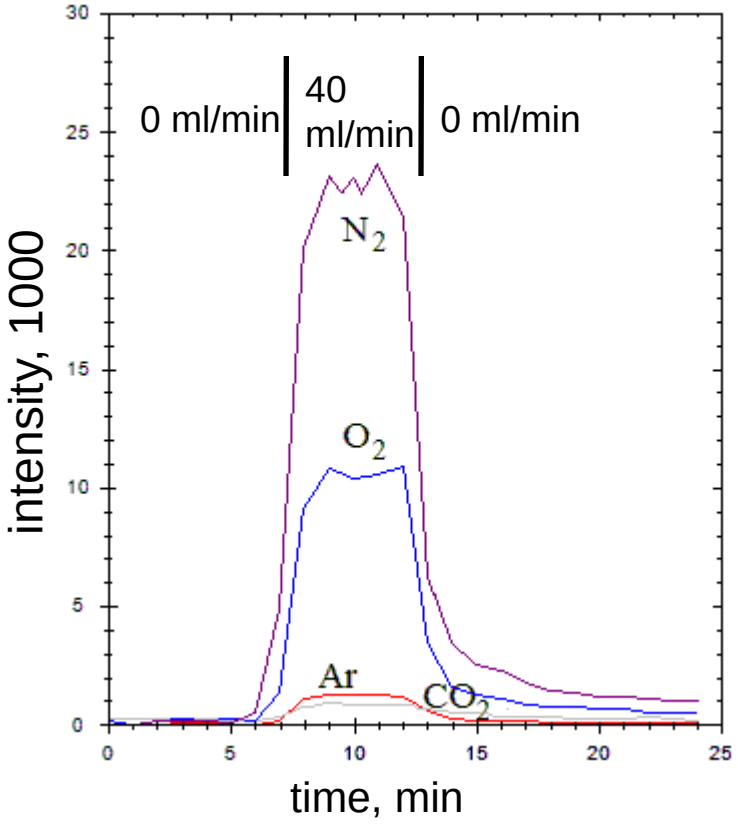
Instrument scheme



Test of the system



The results of monitoring of samples of atmospheric air and argon with an oxygen impurity



Peak intensity variations of the mass spectra of air constituent in the not degassed water sample

Characteristics

- Type of mass analyzer - static
- Dimensions - 17 cm × 40 cm × 45 cm
- Weight – 20 kg
- Average power consumption – 50 W
- Mass range – 100 a.m.u.
- Measurement cycle – 30 sec
- Inlet System - Membrane introduction system
- Multi-compounds analysis (5-7)

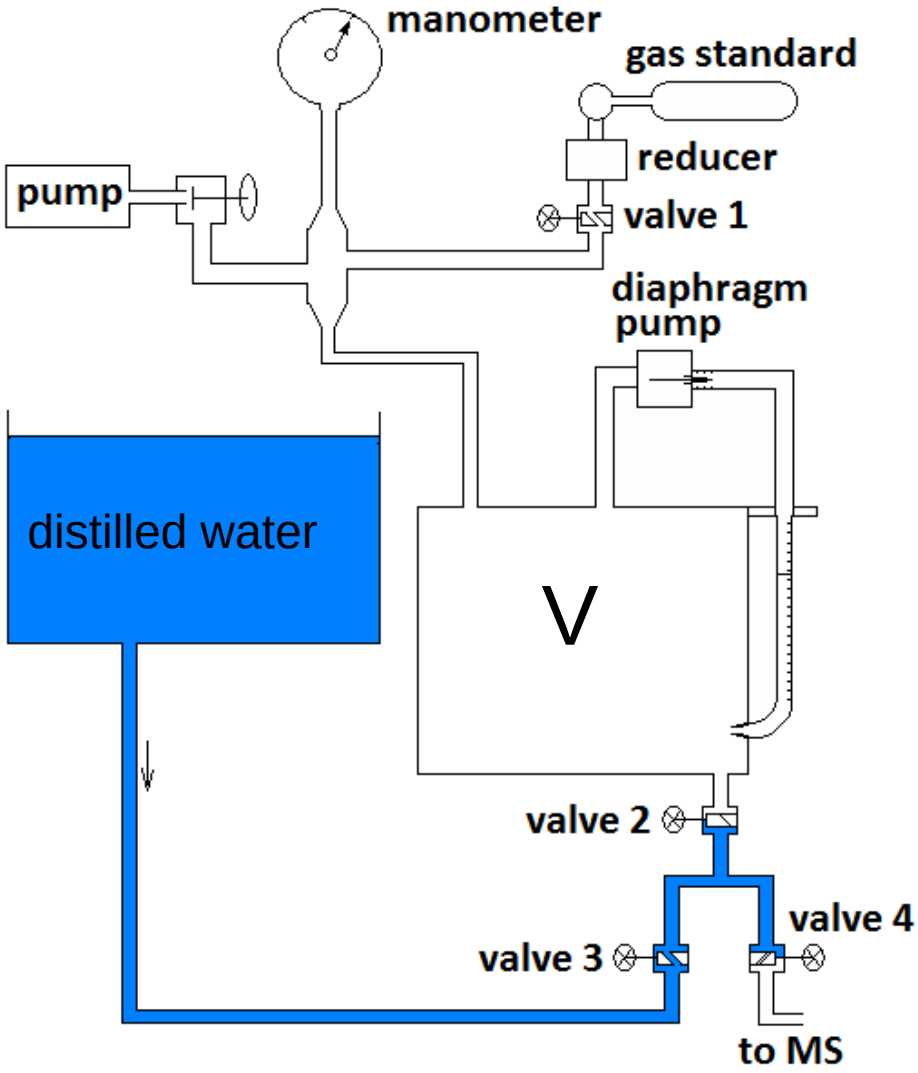
Identification and quantification

of compounds with mass spectrum interference require:

- Calibration to obtain characteristic matrix
- Accounting for the qualitative composition of the sample to simplify the matrix
- 2 analysis modes

  - precise analysis (at the fixed point, higher accuracy)
  - express analysis (when ship is moving, accounting for transient processes in the membrane)

Instrument calibration



Calibration system

The sequence of actions :

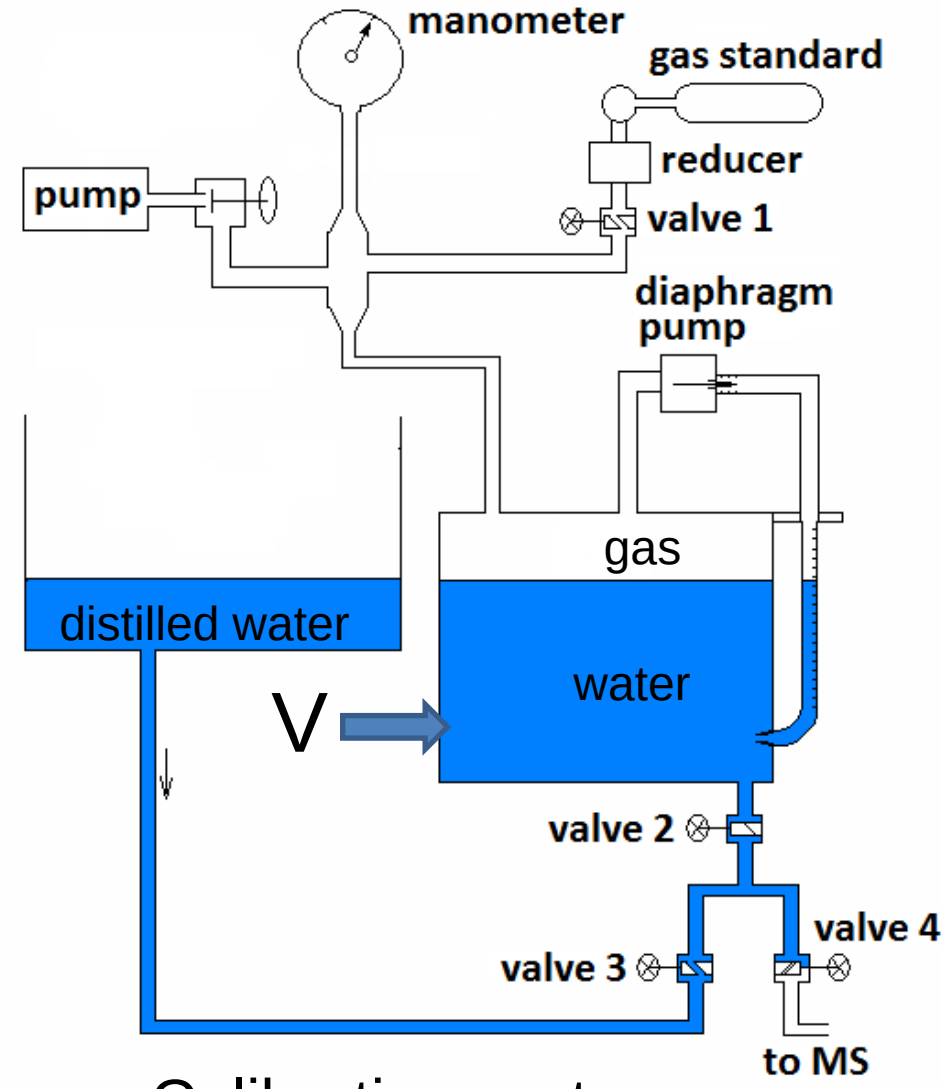
- V is evacuated by pump
- V is occupied with gas to provide its needed concentration in water
- V is occupied with water
- Sparging with diaphragm pump (1 hour)
- Sample is fed to MS

gas volume / water volume = 0.5

Distribution coefficients:

- nitrogen – 93
- oxygen – 55
- argon – 64
- CO2 – 2,8
- methane – 26
- ethane – 22
- propane- 26
- butane – 32
- pentane - 72

Instrument calibration



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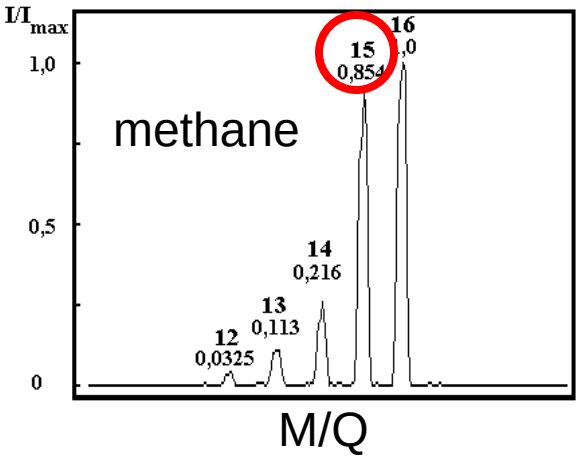
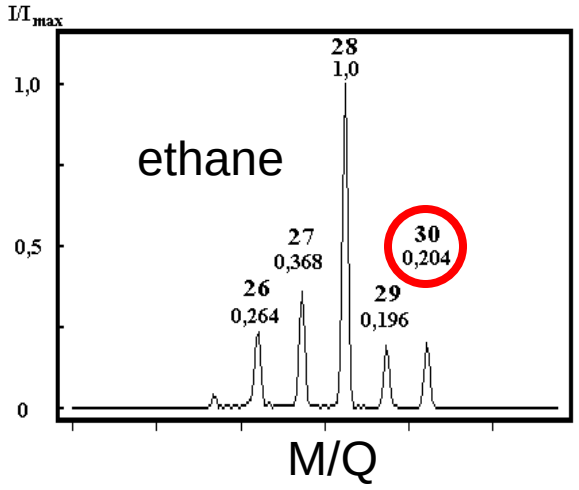
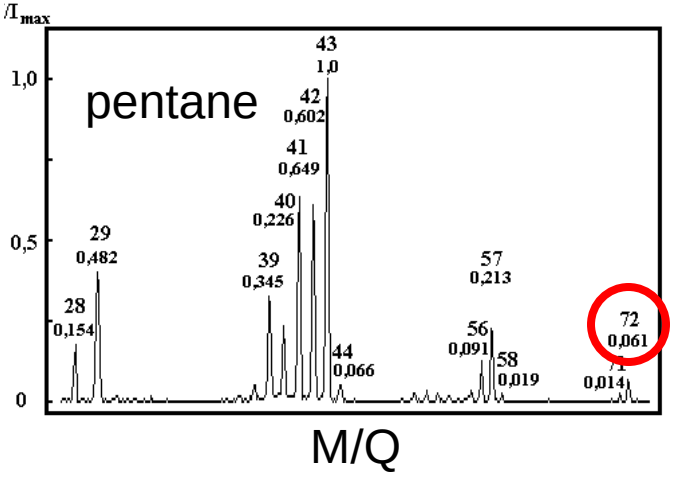
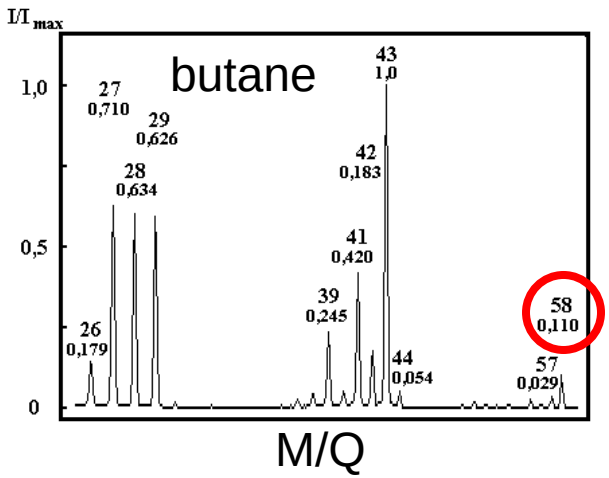
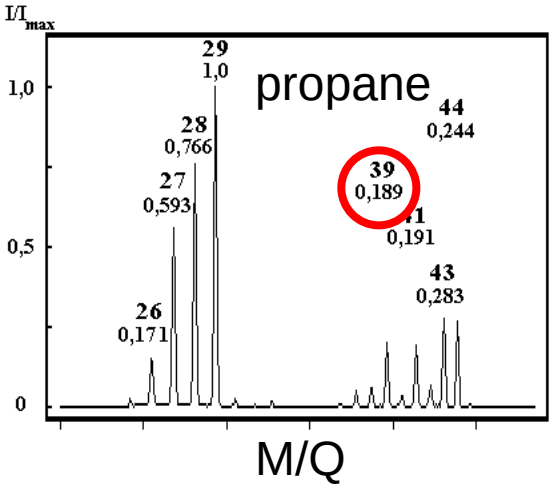
peculiar peaks of target compounds

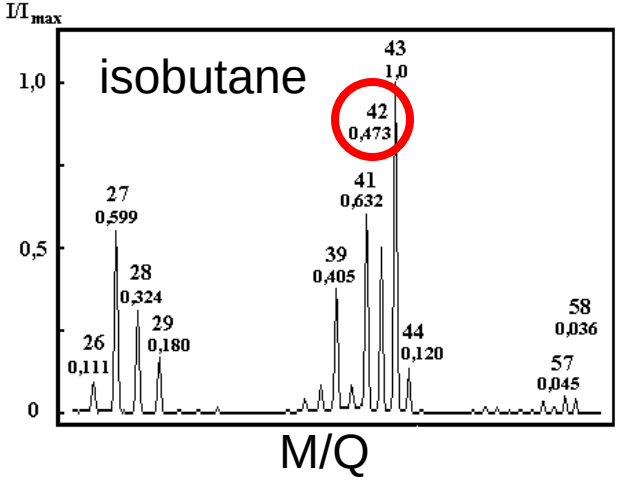




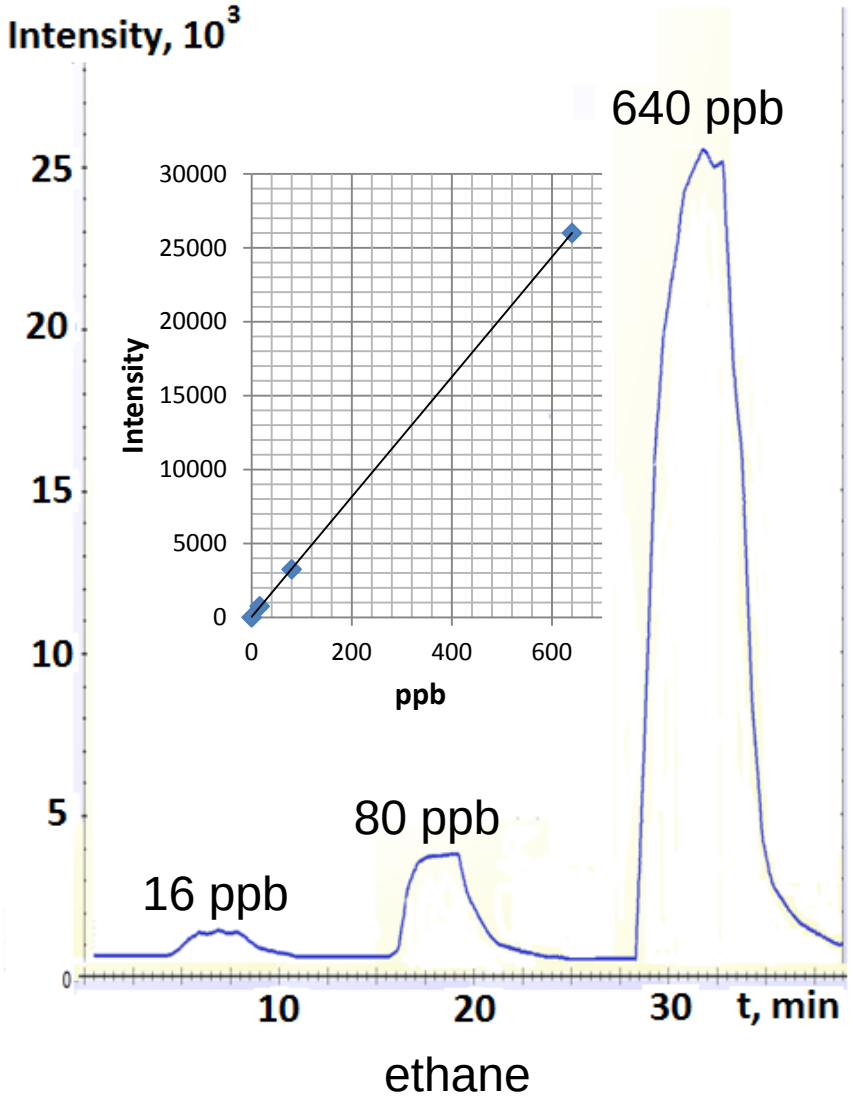


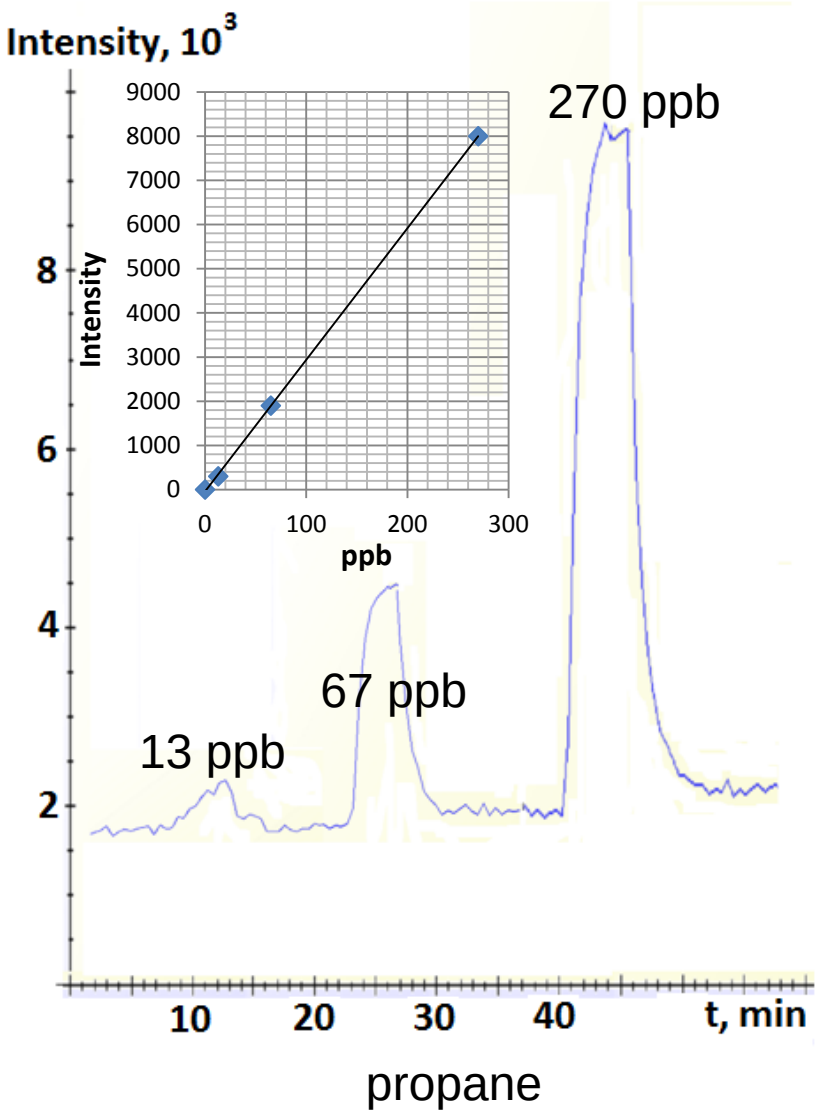




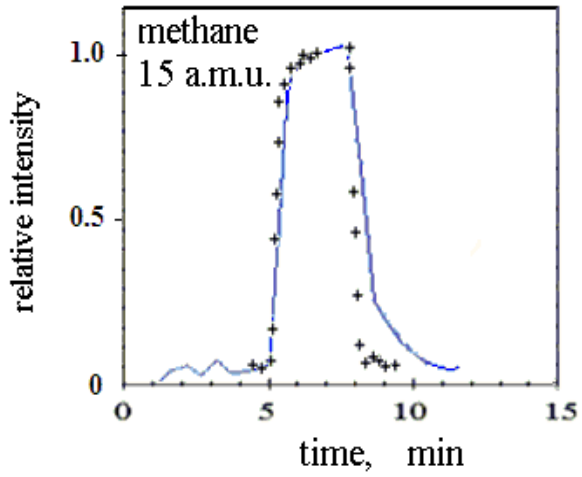


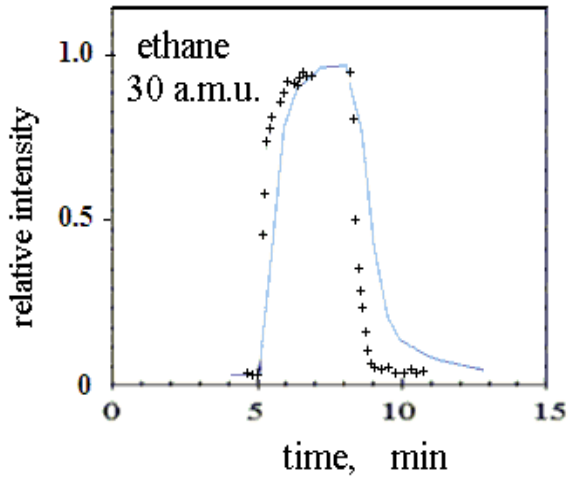
Instrument response

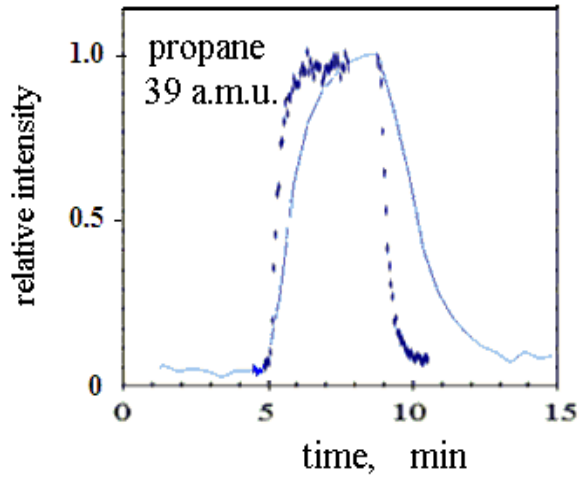


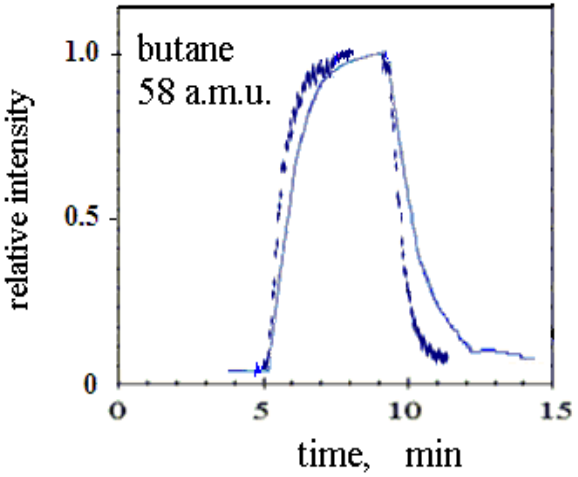


Times of transition to steady state









\+ - gas
▬ - gas dissolved in water

in water:
methane – 30 sec
ethane – 1 min
propane - 2 min
butane – 2 min

Polydimethilsiloxane membrane
o. d. – 1.2 mm
i. d. – 0.6 mm

Detection limit estimation for prospecting

	Concentrations of interest	*Detection limits*
• Methane –	1 - 40 ppm	4 ppb
• Ethane –	1 - 160 ppb	1.6 ppb
• Propane –	1 - 80 ppb	3.5 ppb
• Butane –	1 - 500 ppb	1.2 ppb
• Pentane		3 ppb

On-line analysis of measurement results

- System of equations should be solved.

I(i)=a(i,j)k(j); i,j=1…m

Where: **a(I,j)** - coefficients of the calibration matrix for the characteristic peaks,

m - number of target compounds in the sample,

k(i) – concentrations of the compounds,

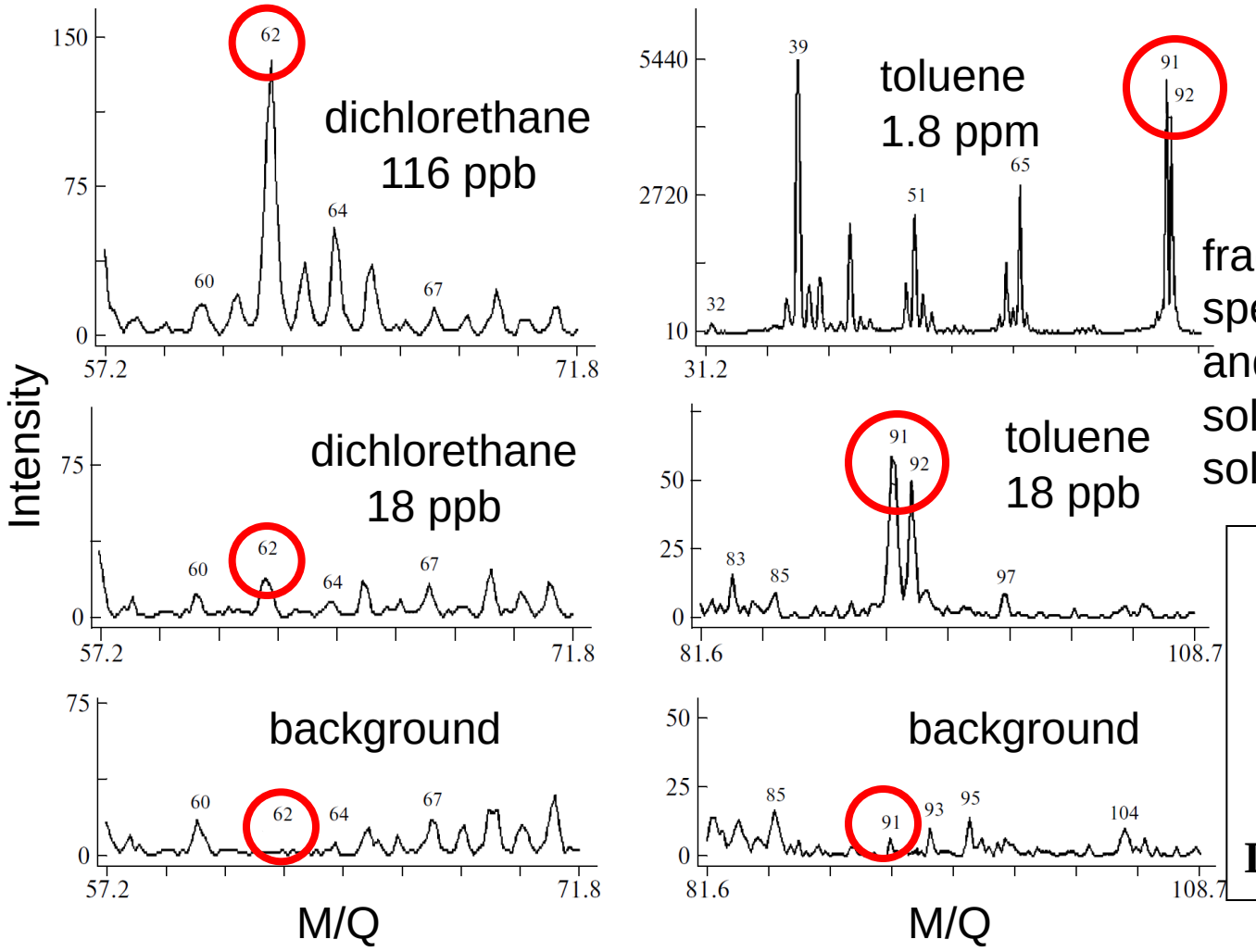
I(i) – intensities of peculiar mass peaks

In the case of express analysis:

- the desired accuracy achieves with the cycling measurement mode:
  - almost simultaneous measurement of a group of 5-7compounds with a scanning cycle ~3 sec
  - averaging over 10 cycles (~30 sec)
- matrix a(i,j) takes the form

	methane	ethane	propane	butane
15	a	0	0	0
30	0	b	0	0
39	0	0	c	e
58	0	0	0	d

The possibility of environmental monitoring of volatile compounds in water



fragments of the mass spectra of dichlorethane and toluene aqueous solutions at different solution concentrations

Detection limit

Benzene - 0.1 ppb

Toluene - 0.1 ppb

Dichlorethane -0.5 ppb

Conclusions

• The static mass spectrometric system for direct control of gases in sea water was designed,

• Parameters of cycling measurement mode was chosen to provide the accuracy desired and the identification procedure was determined

• The system is able to determine the regions promising for prospecting

Prospects

• Completion of data processing software for on-line measurements of interference compounds,

• Increase in sensitivity,

• Underwater measurements

Acknowledgements

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Thank you for attention!