Mass spectrometry of reactive low-pressure and atmospheric plasmas

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Motivation: Analysis of unknown analyte

Analyte

- Transfer to analyzer
- Preparation for analysis

→ Separation of components according to their properties

→ Identification
→ Quantification
Motivation: Analysis of unknown analyte

Analyte

Transfer to analyzer
Preparation for analysis

Separation of components according to their properties

Identification
Quantification

Mass spectrometry of plasmas

Ion transfer

Ions
Sampling:
Plasma ≤ 1 bar

Particles

Ion optics or Ion source

Energy analyzer

m/z analyzer

Detector

Particles – material synthesis, or etching/treatment of substrates
Ions – physical or chemical sputtering, surface modification

Vacuum < 10^{-5} mbar
Outline

1. Basics of MS
2. Ion measurements
3. Detecting neutral particles
4. MS of atmospheric plasmas
wrong self-assessment has already thrown some atoms from their trajectory…
TOPICAL REVIEW

Quadrupole mass spectrometry of reactive plasmas

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Mass spectrometry of atmospheric pressure plasmas

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**MS components: Quadrupole Mass Filter**

Combined RF and DC electric fields for mass analysis

\[
U + V \cos(\omega t)
\]

Ion trajectories

Mathieu equations

\[
\frac{d^2 x}{dt^2} + (a_x + 2q_x \cos 2\tau) x = 0
\]

\[
\frac{d^2 y}{dt^2} + (a_y + 2q_y \cos 2\tau) y = 0
\]

\[
a_x = -a_y = \frac{4eU}{m_1 r_0^2 \omega^2}, \quad q_x = -q_y = \frac{2eV}{m_1 r_0^2 \omega^2}, \quad \tau = \frac{\omega t}{2}
\]
MS components: Energy analysers

Electrostatic fields for energy analysis

**Sector field analyser**

**Bessel box**

100% transition probability

transition probability > 10%, but not 100%

Figure 2: Schematic diagram of the Bessel Box analyzer.
**MS components: Detectors**

**Secondary electron multipliers (SEM)**

With discrete dynodes

![Figure 3.2](image)

_Schematic diagram of electron multiplier. The first dynode is a conversion dynode to convert ions into electrons._

**Faraday cup**

![Electrometer](image)

**Figure 3.3**

Continuous dynode electron multiplier, also known as the channeltron. ⓞ, incident ions; □, secondary particles. Reproduced (modified) from Finnigan MAT documentation, with permission.
**MS components: Detectors**

A typical operating curve for the detector is shown in Figure 3.1.

![Detector operating curve image]

- **Recommended operating voltage** (approximately 2400 V)
- **Never measure here**
- **The curve shifts during the „life“ of a detector**
  - Measure and adjust the operating voltage regularly!!!

**Figure 3.1 Typical detector operating curve**

Detector is a „consumable“ – has a limited lifetime depending on overall number of counts measured!!!

Typical lifetime ~ 1-5 years
Remark: The Use of Channeltron® Detectors
The Channeltron® Electron Multiplier has a history of dependability in mass spectrometer applications. The following instructions and precautions are presented here in order that the user can achieve the maximum useful lifetime of a Channeltron detector.

1. Mounting work should be done in clean vacuum fashion, i.e., the detector should be handled with talc free finger cots or lint free gloves. Care should be taken to avoid dust, lint, or other particulate matter. Nothing should touch the active areas of the detector.

2. Channeltrons are normally operated at pressures of $10^{-5}$ or lower. Higher pressure operation is observed to increase the background current and can result in shortened life. Do not apply high voltage at pressures greater than $10^{-4}$ torr as arcing can occur and permanent destruction of the Channeltron surface is possible.

3. Channeltrons are customarily operated at 1500 to 3000 volts. The maximum rated voltage difference between input and output leads is 3000 volts. Care should be taken to operate at a voltage which gives sufficient gain to achieve acceptable results. Higher gains will shorten Channeltron lifetimes in inverse proportion, i.e. 2x the gain results in 1/2 the potential lifetime.

4. During the first few days of operation of a new detector, it is recommended that high output currents be avoided (i.e. inputs above $10^{-9}$ amps while operating at gains in excess of $10^7$). Taking this initial burn-in precaution can prevent premature failure.

5. Backstreaming from oil diffusion pumps or roughing pumps should not be permitted. It is recommended that cold traps and molecular sieve traps be operated and maintained to manufacturers specifications.

Warranty - All multipliers come with a **one year prorated warranty starting at the date of shipment**. Multipliers with insufficient gain or excessive noise should be returned to S.I.S. for evaluation and testing. If the multiplier proves to be defective due to manufacturing defects it will be replaced at no charge during the first three months of use and prorated thereafter based on a one year life and a gain of $1 \times 10^5$ at 3 KV. Multipliers which test properly or which were damaged due to operator fault or carelessness will not be replaced, and user will be billed --- for testing. Channeltron® is a registered trademark of Burle Electro Optics Corp.
MS components: single ion lens

$E_i \sim 600 \text{ eV}$
MS components: combination of ion lenses

Simulation: Simion 8.1 SW
**MS components: electron impact ionizer**

Electron source: heated filament

- **heating circuit**
- Filament: thermionic electron emission
- Accelerating voltage ($\sim E_{\text{electrons}}$)

[Diagram showing electron flow and ionization process]

HIDEN Analytical
All components together: for example HIDEN PSM
All components together: for example HIDEN EQP

- Ion counting detector: SEM, Faraday and to TOF-card
- 45° Sector field energy analyzer
- Internal ionizer
- Sampling orifice
- Differentially pumped vacuum stage
- Triple filter quadrupole mass analyzer
- Turbo molecular pump port
Outline

1. Basics of MS
2. Ion measurements
3. Detecting neutral particles
4. MS of atmospheric plasmas

- large signals → species already ionized
- every measured m/z ratio is at least one ionic species
**Ion sampling**

Ion sampling through small orifice

- Diameter < mean free path and sheath thickness

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**Ion flux**, not ion density, **is measured!**

$\rightarrow$ mass dependent:

Signal $\sim I \sim n_{\text{ion}} \cdot v_{\text{ion}}(m)$

**Angular distribution important:**

Acceptance angle limited and dependent on:
- ion energy $\rightarrow$ large for small energies
- MS tuning $\rightarrow$ large for large extractor $V$

MS tuning influences in general the shape of the ion velocity distribution function (aberration error), see:


Absolute calibration almost impossible
Ion sampling without ion lenses (all grounded)

Ions travel to the energy filter through space at constant potential

- only the initial angular distribution and the space charge result in repulsion in radial direction
- stronger for low energy ions

as measured

voorbeeld

Tsankov et al., Plasma Sources Sci. Technol. 26 (2017) 055003
HIDEN EQP Mass spectrometer on RF plasma in Ar

M. Zeuner et al., Ion energy distributions in a dc biased rf discharge, JAP 81 (1997) 2985

FIG. 1. Schematic diagram of the discharge arrangement.
Examples: Measurements of ion velocity distribution functions

(≠ ion energy distribution function!)

M. Zeuner et al., Ion energy distributions in a dc biased rf discharge, JAP 81 (1997) 2985
Measurements in pulsed plasmas


Time resolution down to 1 microsecond
Example: Positive Ion Mass Spectra

Energy scan at mass 40 amu

Mass scan for an Argon plasma

mass scan at fixed ion energy (Which one?!)
Positive Ion Mass Spectra

But mass 28 can also be CO$^+$ or mass 30 can be C$_2$H$_6^+$!
Examples: Negative Ion Mass Spectra

→ plasma must be typically pulsed, so the negative ions can leave the positive plasma potential

Hollenstein et al.: Anionic clusters in dusty hydrocarbon and silane plasmas

polymerization of negative ions → cluster formation
Outline

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- smaller signals → low ionization probability \( \sim 10^{-6} \)
- more (fragment) ions from one neutral
- signal \( \sim \) density (effect of higher flux for neutrals with higher velocity cancels due to shorter time in the ionizer)

Plasma \( \leq 1 \) bar

Ion optics or ion source

Energy analyzer

m/z analyzer

Detector

Vacuum < \( 10^{-5} \) mbar
Electron Impact Ionization

I’m hit! I’m hit! I’ve lost an electron!!

Are you sure??

I’m positive!!

Another casualty in the War of the Atoms
Total Electron Impact Ionization Cross Section

Probability of any ionization (direkt + dissociative)

Typical shape

Highest sensitivity at electron energy around 70 eV
Electron Impact Ionization Cross Section

However: at high $E_{el}$ also dissociation or multiple ionization

ions appear at many masses

fragment ions
However: at high $E_{el}$ also dissociation or multiple ionization possible

Fragmentation patterns
+ stable calibration species
→ calibrated measurements of stable species densities

Measured spectrum is a result of a linear combination of fragmentation patterns of all species in the gas mixture

Threshold Ionisation Mass Spectrometry (TIMS)

Dissociative ionization has higher threshold – the bond has to be additionally broken

→ formation of fragment ions limited or avoided

What if we have the same ion from more species?

CH₄ + e⁻ → ion + 2e⁻

CH₂⁺ + H₂

measure here, close to the ionization threshold
C$_2$H$^+$: ion can originate from two sources:

**Dissociative ionization** of C$_2$H$_2$:  
C$_2$H$_2$ + e$^-$ → C$_2$H$^+$ + H + 2e$^-$  
17.22 eV

**Direct ionization** of C$_2$H:  
C$_2$H + e$^-$ → C$_2$H$^+$ + 2e$^-$  
11.62 eV

Quantification of neutral species not available in pure form as reference

$$S_i = T(m_i) \cdot \theta(m_i) \cdot \beta \cdot L_{\text{ionizer}} \cdot I_e \cdot \sigma_i(E_{el}) \cdot n_{i,\text{ionizer}}$$

Signal calibration: measurement of species with known density

$$S_{cal} = T(m_{cal}) \cdot \theta(m_{cal}) \cdot \beta \cdot L_{\text{ionizer}} \cdot I_e \cdot \sigma_{cal}(E_{el}) \cdot n_{cal,\text{ionizer}}$$

$$n_{i,\text{ionizer}} = F(m_i, m_{cal}) \cdot \frac{\sigma_{cal}(E_{el})}{\sigma_i(E_{el})} \cdot \frac{n_{cal,\text{ionizer}}}{S_{cal}} \cdot S_i$$
Mass dependent MS transmission function

The mass-to-charge \((m/q)\) dependent MS response can be calibrated by stable gases of known densities:

\[
n_{i, \text{ionizer}} = F(m_i, m_{cal}) \cdot \frac{\sigma_{cal}(E_{el})}{\sigma_i(E_{el})} \cdot \frac{n_{cal, \text{ionizer}}}{S_{cal}} \cdot S_i
\]

typically \(\sim (m/q)^r\), where \(r \sim 0.5 - 1\)
**Stable species measurement**

Pressure in MS must be $< 10^{-5}$ mbar – **differential pumping necessary:**

Residual Gas Analysis (RGA)

- **Gas mixture (Plasma)**
  - $n_i$

$$A = \pi r^2$$

- $n_{i\_ionizer} = \frac{\text{Flux}_i}{P} = \frac{n_i \cdot C(A,T,m_i,...)}{P} = f(\text{geom}, T, m, ...).n_i$

- $\frac{n_{i\_ionizer}}{n_{cal\_ionizer}} \sim \frac{n_i}{n_{cal}}$

Density calibration for stable species:

$$n_i = F(m_i, m_{cal}) \cdot \frac{\sigma_{cal}(E_{el})}{\sigma_i(E_{el})} \cdot \frac{n_{cal}}{S_{cal}} \cdot S_i$$

However: When species reactive at the surface ($\beta \rightarrow 1$) → lost at the surface → $n_{i\_ionizer}$ much smaller → RGA does not work for the reactive species!
Molecular Beam Sampling

Multiple differential pumping stages + formation of molecular beam

→ Reactive species measurement possible (beam particles don’t collide with the walls)

Ionizer density:
\[ n_{i_{\text{ionizer}}} = n_{i_{\text{ionizer BG}}} + n_{i_{\text{ionizer Beam}}} \]

(1) measured without chopper blocking the beam

Background density:
\[ n_{i_{\text{ionizer BG}}} = n_i \cdot C_1 \cdot C_2 / P_1 P_2 \]

(2) measured with chopper blocking the beam

Density in the beam:
\[ n_{i_{\text{ionizer Beam}}} = f(\text{geom}) \cdot n_i \]

measured as difference (1) – (2)
Molecular Beam Sampling

Formation of molecular beam depends on Knudsen number \( K_n = \frac{\lambda}{d} \)

\( K_n > 1 \)
Free molecular flow without collisions

Density in the beam easy to determine:

\[
n_{i,beam}(x) = \frac{1}{4} \left( \frac{d}{x} \right)^2 n_i
\]

\( n_{i,ionizer\_Beam} = f(geom) \cdot n_i \)

Density calibration for reactive species:

\[
n_i = F(m_i, m_{cal}) \cdot \frac{\sigma_{cal(E_{el})}}{\sigma_i(E_{el})} \cdot \frac{n_{cal}}{S_{cal,beam}} \cdot S_{i,beam}
\]
**Molecular Beam Sampling**

Formation of molecular beam depends on Knudsen number $K_n = \frac{\lambda}{d}$

Kn > 1

Free molecular flow without collision

Density in the beam easy to determine:

$$n_{i,\text{beam}}(x) = \frac{1}{4} \left( \frac{d}{x} \right)^2 n_i$$

$$n_{i,\text{ionizer}\_\text{Beam}} = f(\text{geom}) \cdot n_i$$

More stages provide better beam-to-background ratio

Example: Singh et al.: $\text{CF}_x$ species measurement

Beam signal with triple stage much bigger, because bigger sampling orifice can be used.

Electron impact ionizer: problems by closed ionizers

Beam particles a source of additional background → error in calibration


Outline

1. Basics of MS
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Formation of a free jet

Kn << 1
Collisional „continuum“ sampling

Formation of a free jet

Plasma ≤ 1 bar

Ions or Ion source

Ion optics

Energy analyzer

m/z analyzer

Detector

vacuum < 10^{-5} mbar
Molecular Beam Sampling free jet

Supersonic "free jet" expansion \((\lambda \ll d)\)

\[
\frac{P_o}{P_b} > \left(\frac{\gamma + 1}{\gamma - 1}\frac{\gamma}{2}\right)
\]

Max 2.1

\(P_0, T_0, M \ll 1\)

BACKGROUND PRESSURE \(P_b\)

COMPRESSION WAVES

EXPANSION FAN

ZONE OF SILENCE

MACH DISK SHOCK

REFLECTED SHOCK

SLIP LINE

BARREL SHOCK

JET BOUNDARY

FLOW

\(M > 1\)

\(M \gg 1\)

\(M < 1\)
Molecular Beam Sampling free jet to “vacuum”

Supersonic „free jet“ expansion  

\[ \frac{P_o}{P_b} > \left( \frac{\gamma + 1}{2} \right)^{\frac{\gamma}{\gamma - 1}} \]

Max 2.1

Preferred case for the MB sampling from high pressure
MB composition differs from gas composition → composition distortions
Molecular Beam Sampling composition distortions

- Acceleration into probe orifice
- Radial diffusion in free-jet
- Mach-number focusing

![Diagram of molecular beam sampling](image-url)
Molecular Beam Sampling composition distortions

- Acceleration into probe orifice
- Radial diffusion in free-jet
- Mach-number focusing


87.8% CO$_2$
21.2% H$_2$

Ratio of [CO$_2$/H$_2$]

$Re_0 = 130$
$Re_0 = 380$
$Re_0 = 2180$
Molecular Beam Sampling from atm. pressure

calibration measurements has to be performed with the same carrier gas mixture (the same main collisional partners) to have the same/similar composition distortion for both measured and calibrated species.

Figure 4. Measurement of the Ne and N₂O signal of different He/air mixtures with constant addition of Ne (1%) and N₂O (0.5%).
Molecular Beam Sampling from atm. pressure

- Collisional sampling both for neutrals and ions
  - Ions thermalized with the gas
  - Low ion energies (< 2 eV)

- In seeded gases (for example He with just small impurity of other gas) are “impurities” accelerated in the expansion to the terminal velocity of the main gas → kinetic energy of ions growth linearly with ion mass.

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Ion detection from atmospheric pressure plasmas

He plasma, 1.4 slm He, 2 mm distance from the orifice

Impurities dominant, spectra “stable“ after 60 min

Ion reactions at 1 atm very fast – manly secondary ions detected, not a primary “plasma ions”
Conclusions

Mass spectrometry is a powerful plasma diagnostic
- absolutely calibrated densities of reactive neutral species
- energy resolved ion fluxes
- almost all species detectable (no optical transitions needed)
- measurement at the surface – place of interest in plasma treatments
- suitable for atmospheric plasma analysis

Careful device design and understanding needed
- MBMS → background subtraction critical
  → composition distortion at 1 atm
- ion measurements: ion-energy dependent sensitivity → relative signal calibration difficult
- detection limit usually worse than for laser based diagnostics
**MBMS with special chopper design**

Rotating chopper (14 Hz) with an imbedded skimmer

Chopper separates 1\textsuperscript{st} and 2\textsuperscript{nd} stage – it closes effectively the connection to atmosphere

→ Very low pressures are achieved

Allows formation of MB for a short time (0.5% duty cycle), which expands to a god vacuum region

→ Very high beam-to-BG ratio can be achieved

The signal in MB can be measured with time resolved measurements synchronized with the chopper revolutions:
MBMS with special chopper design

Beam-to-BG ratio > 15!

N$_2$ from air

D. Ellerweg et al. PSST 21 (2012) 034019