Mass spectrometry as analytical tool in catalysis research

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Contents

- Fundamentals of mass spectrometry
- Instrument set up
  - Ionization
  - Mass separation
  - Ion detection
- Signal evaluation
- Application example in catalysis
Mass spectrometry

Introduction

• Diagnostic aid in
  – Process engineering
  – Technology and product development
  – Medicine and basic scientific research

• Gas mixture separation
  – Mass/charge ratio of the ions
  – Generation of vacuum

No separation
★ Total pressure

Separation in **time** or **space**
★ Individual partial pressures
Mass spectrometry

General application

• Analytical technique used to measure the mass-to-charge ratio of ions
  – Analysis of catalytic reactions on the surface of solids
• Composition of a physical sample
  – Generation a mass spectrum representing the masses of sample components
• Identification of compounds by the mass of molecules or their fragments
• Determination of the isotopic composition of elements in a compound or its structure by observing its fragmentation
• Quantification using carefully designed methods
  – Composition and purity of process gases
    • mass spectrometry is not inherently quantitative
• Studying the fundamentals of gas phase ion chemistry
  (the chemistry of ions and neutrals in vacuum)
• Determining physical, chemical or biological properties of compounds with a variety of other approaches
  – Biochemical substance transformations
Mass spectrometry

Background

• Substance is bombarded (with an electron beam having) sufficient energy to fragment a molecule
• Positive fragments (cations and radical cations) are accelerated in a vacuum through a magnetic field and are sorted on the basis of mass-to-charge ratio
• Ions carry a unit positive charge
• m/e value is equivalent to the molecular weight of the fragment
  – \(-1 \text{ e} = -1,602 \, 176 \, 53(14) \cdot 10^{-19} \text{ C}\)
• Analysis: re-assembling of fragments backward to generate the original molecule
Mass spectrometry

Composition

- All mass spectrometers consist of three distinct regions:
  1) Ionizer  2) Ion Analyzer  3) Detector
- Charged particles are formed by ionization
  - Impart of enough energy to remove an electron from molecules
    \[ \text{CH}_3\text{OH} + 1 \text{ e}^- \rightarrow \text{CH}_3\text{OH}^+ + 2 \text{ e}^- \]
- Ionization produces singly charged ions containing one unpaired electron
- A charged molecule which remains intact is called the molecular ion
- Energy imparted by the electron impact and instability in a molecular ion can cause that ion to break into smaller pieces (fragments)
  - \[ \text{CH}_3\text{OH}^+ \text{ (molecular ion)} \rightarrow \text{CH}_2\text{OH}^+ \text{ (fragment ion)} + \text{H}^- \]
  - \[ \text{CH}_3\text{OH}^+ \text{ (molecular ion)} \rightarrow \text{CH}_3^+ \text{ (fragment ion)} + \cdot\text{OH} \]
**Mass spectrometer**

**Instrumental set up**

Ionization of a low concentration of sample molecules

Acceleration through a charged array

Ions having follow the path of the analyzer, exit through the slit and collide with the Collector

Generation of an electric current, amplification and detection.

Varying the strength of the magnetic field, varies the mass-to-charge ratio
Ionization methods

- **Gas-Phase Ionization**
  - Electron Impact Ionization = EI
  - Chemical Ionization = CI
  - Desorption Chemical Ionization = DCI
  - Negative-ion chemical ionization = NCI

- **Atmospheric Pressure Ionization**
  - Electrospray Ionization = ESI
  - Atmospheric Pressure Chemical Ionization = APCI

- **Particle Bombardment**
  - Fast Atom Bombardment = FAB

- **Thermal Ion sources**
  - Inductively Coupled Plasma = ICP
  - Spark Source = SS

- **Field Desorption and Ionization**
  - Field Desorption = FD
  - Field Ionization = FI

- **Laser Desorption**
  - Matrix-Assisted Laser Desorption Ionization = MALDI
## Ionization methods

<table>
<thead>
<tr>
<th>Ionization method</th>
<th>Typical Analytes</th>
<th>Method Highlights</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Impact (EI)</td>
<td>Relatively small volatile</td>
<td>• Impact of accelerated electrons with sample form ions by collision</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Hard method versatile provides structure info</td>
</tr>
<tr>
<td>Chemical Ionization (CI)</td>
<td>Relatively small volatile</td>
<td>• Ion formation by H⁺ transfer to sample</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MH + C₂H₅⁺ → MH₂⁺ + C₂H₄ no fragmentation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Soft method, molecular ion peak [M+H]⁺</td>
</tr>
<tr>
<td>Electrospray (ESI)</td>
<td>Peptides</td>
<td>• Formation of charged liquid droplets from which ions are desolvated or desorbed</td>
</tr>
<tr>
<td></td>
<td>Proteins</td>
<td>• Soft method ions often multiply charged</td>
</tr>
<tr>
<td></td>
<td>nonvolatile</td>
<td></td>
</tr>
<tr>
<td>Fast Atom Bombardment (FAB)</td>
<td>Carbohydrates</td>
<td>• Impact of high velocity atoms on a sample dissolved in a liquid matrix</td>
</tr>
<tr>
<td></td>
<td>Organometallics</td>
<td>• Soft method but harder than ESI or MALDI</td>
</tr>
<tr>
<td></td>
<td>Peptides</td>
<td></td>
</tr>
<tr>
<td></td>
<td>nonvolatile</td>
<td></td>
</tr>
<tr>
<td>Matrix Assisted Laser Desorption (MALDI)</td>
<td>Peptides</td>
<td>• Impact of high energy photons on a sample embedded in a solid organic matrix</td>
</tr>
<tr>
<td></td>
<td>Proteins</td>
<td>• Soft method very high mass</td>
</tr>
<tr>
<td></td>
<td>Nucleotides</td>
<td></td>
</tr>
</tbody>
</table>
Ion Sources

Electron Impact Ionization

- Axial ion source
  - High sensitivity
  - Good injection conditions
  - Residual gas analysis
  - W, Re filaments

- Grid ion source
  - Open construction: low desorption rates
  - Easy degassing by electron bombardment
  - Partial pressure determination in UHV
  - Desorption measurements
  - W filament
Ion Sources

Electron Impact Ionization

• Cross-beam ion source
  – Directed gas jet without wall interaction
  – Prevention of vapor condensation
  – Two filaments W, Re, Y₂O₃
  – Outside to suppress surface reactions

• Applications:
  – Residual gas analysis
  – Molecular beam measurements
  – Isotope ratios
  – Material flows

• Prisma ion source
  – Dual filament: W, Y₂O₃
  – Two cathodes available
  – Similar grid ion source
Operation of Cross beam Ion Source

Electrode configuration and potential characteristics

- Filament emits electrons thermally: W, Re, Y$_2$O$_3$ coated Ir cathodes
  - Focused by electrical extraction fields to reach ionization area
- Crucial process: Neutral particles are ionized by electrons
- Positive ions are accelerated (short dwell time)
  - Reduces undesired ion-neutrals-reactions
  - Faster penetration of transition fields
**Ion Sources**

**Contaminants**

- Adsorbents on the ion source surface: EID ions
  - UHV conditions
  - $16 (O^+)$, $19 (F^+)$, $23 (Na^+)$, $35/37 (Cl^+)$, $39/41 (K^+)$
  - Reduced by degassing

- Strongly reduced field axis voltage
  - EID ions less affected, formed on the highest potential
  - Detection of normal ions: higher “Field Axis”
Mass spectrometry

Ionization process

- Small fraction of sample is converted in ionized state
  - Singly and multiply charged positive ions
- Collision energy influences the number and type of ions
  - 50-150 eV

Ionic current:

\[ i_k^+ = i^- \cdot l \cdot s \cdot p_k \ [A] \]

- \( i^- \) = Electron (emission) current \([A]\)
- \( l \) = Mean free path of the electrons \([\text{cm}]\)
- \( s \) = Differential ionization of \( k \) \([\text{cm} \cdot \text{mbar}]\)
- \( p_k \) = Partial pressure of \( k \) \([\text{mbar}]\)

60-100 eV
Ionizations process

Cracking pattern of $\text{CO}_2$

- Fragment distribution at 70 eV

- Library for compound of frequent interest
  - E.g. Quad-Star

- Distribution depends on ionization energy, temperature, transmission characteristics of the mass analyzer

$$\text{ABC} + e^- \rightarrow \text{ABC}^+ + 2e^-$$
$$\text{ABC}^{++} + 3e^-$$
$$\text{AB}^+ + \text{C} + 2e^-$$
$$\text{BC}^+ + \text{A} + 2e^-$$
$$\text{A}^+ + \text{BC} + 2e^-$$
$$\text{C}^+ + \text{AB} + 2e^-$$
$$\text{B}^+ + \text{A} + \text{C} + 2e^-$$
Ionizations process

Multiply charged ions

- Production suppressed by lower electron energies

- < 43 eV for Ar/Ne mixtures
  - Minimize $^{40}\text{Ar}^{++}$ at 20 amu for $^{20}\text{Ne}$
**Ionizations process**

**Overlapping of ion currents**

- Encountered frequently with gas mixtures
- Total intensity made by superimposition
  - Less suitable for quantitative determination (e.g. oxygen, CO)
  - Requires calibration factors and matrix calculations
### Mass Analyzers

<table>
<thead>
<tr>
<th>Analyzer</th>
<th>System Highlights</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quadrupole</td>
<td>Unit mass resolution, fast scan, low cost</td>
</tr>
<tr>
<td>Sector (Magnetic and/or Electrostatic)</td>
<td>High resolution, exact mass</td>
</tr>
<tr>
<td>Time-of-Flight (TOF)</td>
<td>Theoretically, no limitation for m/z maximum, high throughput</td>
</tr>
<tr>
<td>Ion Cyclotron Resonance (ICR)</td>
<td>Very high resolution, exact mass, perform ion chemistry</td>
</tr>
</tbody>
</table>
Time-of-flight mass analyzers

- Ion separation by virtue of their different flight times over a known distance
- Ions of like charge have equal kinetic energy and then are directed into a flight tube
  - \( E_{\text{kin}} = \frac{1}{2} mv^2 \), \( m = \) mass; \( v = \) velocity
- The travel time measured in microseconds, transformed to the m/z value
- TOF mass spectrometers offer high sensitivity, rapid scanning, data for very high-mass biomolecules
- The transit time (t) through the drift tube is \( \frac{L}{V} \) where \( L \) is the length of the drift tube
  - \( \frac{1}{2} mv^2 = eV \)
  - \( V = \left( \frac{2eV}{m} \right)^{1/2} \)
  - \( t = \frac{L}{\left( \frac{2V}{m/e} \right)^{1/2}} \)
Magnetic Sectors

- Trajectories of ions bend into circular paths depending on m/z
- Ion trajectories changed through variations of the magnetic field strength \( E_{\text{kin}} = \frac{1}{2} mv^2 = eV \)
- The ions are deflected by the magnetic field \( H \)
  - Only ions of mass-to-charge ratio that have equal centrifugal and centripetal forces pass through the flight tube:
    - \( \frac{mv^2}{r} = HeV \)
- Radius of the ion path: \( r = \frac{mv}{eH} \)
Ions are trapped electrostatically in a constant magnetic field.
A covalent orbital ("cyclotron") motion is induced by a radio-frequency pulse: orbiting ions generate a faint signal.
The frequency = orbital frequency \( \Rightarrow \) inversely related to its m/z value.
Signal intensity \( \sim \) number of ions having that m/z value.
At low pressure the ion orbital motion can be maintained over many cycles and the frequency can be measured with very high precision.
Generate very high resolution spectra.
Mass spectrometry

Quadrupole mass filter

- Molecular ions and fragment ions are accelerated by manipulation of the charged particles through the mass spectrometer.
- Uncharged molecules and fragments are pumped away.
- The quadrupole mass analyzer uses positive (+) and negative (-) voltages to control the path of the ions.
- Ions travel down the path based on their mass to charge ratio (m/z).
- Ionization produces singly charged particles, so the charge (z) is one: an ion's path will depend on its mass.
- Voltages are not fixed, but are scanned so that ever increasing masses can find a successful path through the rods to the detector.
Quadrupole mass spectrometer

- Ion generation by electron collision ionization in the ion source
- Ion separation according to the m/e ratio in the rod system
- Ion detection in the ion detector

Diagram:
- Ion optics
- Filament
- Formation space

Symbol: $(U + V \cos \theta)$
Quadrupole mass spectrometer

- Separation of ions according to their mass/charge ratio
- High frequency quadrupole field
  - Four cylindrical rod electrodes with \( r = 1.1444 \times \text{field radius } r_0 \)
- Motion of ions: Mathieu differential equation
  1. Direct voltage \( U \) applied to the rod electrodes \( U \):
     - \( \text{xz plane: ions are repelled, reach the detector} \)
     - \( \text{transmission: full} \)
     - \( + \)
     - \( - \)

     + U

     \( \text{yz plane: ions are attracted and neutralized, cannot reach the detector} \)
     - \( \text{transmission: none} \)
     - \( - U \)
2. High frequency voltage of amplitude $V$ is superimposed on the direct voltage potential

- $xz$ plane: with increasing voltage ion execute unstable oscillations with increasing amplitude, are neutralized

- $yz$ plane: with increasing amplitude $V$ ions execute stable oscillations with decreasing amplitude, reach the detector
3. Fixed mass/charge ratio $M$ resulting ion current $i^+$:
   - $xz$ plane: for $V < V_1$ ions reach the detector, for $V > V_1$ no transmission
   - $yz$ plane: for $V < V_1$ no transmission, for $V > V_1$ ions reach the detector
4. Fixed U/V ratio resulting ion current $i^+$:

- xz plane: for ions with $M < M_1$ no transmission, ions with $M > M_1$ reach the detector.

- yz plane: ions with $M < M_1$ reach the detector, for ions with $M > M_1$ transmission suppressed.
4. Combination of both planes the resulting ion current \( i^+ \) with fixed U/V ratio:

- Region I (xz plane): ions cannot pass
- Region III (yz plane): ions cannot pass
- Region II: The transmission factor for a mass number \( M \) is determined by ratio \( U/V \)

- Compromise between sensitivity and resolution
Resolution

\[ V = 14.438 \cdot M \cdot f^2 \cdot r_0^2 \]

\[ f = \text{HF frequency} \]

- Resolution varies with changing U/V ratio
- Low HF amplitudes: stable ions reach detector (255)
  - For total pressure measurements
- Increasing HF amplitudes: light masses ions with increasing mass number M become unstable, are rejected

Variation of resolution for H$_2$O group
Quadrupole mass filter

Quality increase

- With increasing rod diameter $r$ and length $L$
  - Maximum injection angle: $\tan \psi < 11.85 \times r_0^2/L^2$
  - Injection diameter: $D = \frac{1}{2} r_0 \times (m/\Delta m)$
- With increasing frequency $f$ of the high frequency field
- BUT: larger space and lower operating pressure required
Ion Detector

- Electric detection by
  - Faraday cup
  - Continuous dynode secondary electron multiplier (C-SEM)
  - Discrete secondary electron multiplier (SEM)
- Choice depends on required sensitivity, detection speed, stability and space available
- Producing an electronic signal when struck by an ion
- Timing mechanisms which integrate those signals with the scanning voltages allow the instrument to report which m/z strikes the detector
- The mass analyzer sorts the ions according to m/z and the detector records the abundance of each m/z
- Calibration is performed by introducing a well known compound into the instrument and "tweaking" the circuits so that the compound's molecular ion and fragment ions are reported accurately.
Ion detection

Faraday cup

- Named after Michael Faraday who first theorized ions (1830)
- Conducting metal cup measures the current in a beam of charged particles
- Ions hit the metal which will be charged while the ions are neutralized
- Discharging of the metal: current equivalent to the number of discharged ions (voltmeter)
- A magnetic field is usually used to prevent secondary emission
- Not known for sensitivity but are highly regarded for accuracy because of the one-to-one relation between the two parts of the circuit and our ability to measure current accurately
Ion detection

SEM

- Device multiplies current in an electron beam by incidence of accelerated electrons upon the surface of an electrode which in turn emits further secondary electrons so that the process can be repeated
- Detector-surface collision energy of the ions into emitted ions, electrons, or photons is detected
- Light or charge detectors

A series of dynodes at increasing potentials produce a cascade of electrons.

10^6 electrons out
Output of the MS

Background - Spectrum

- Plot of relative intensity vs the mass-to-charge ratio (m/e)
- Peaks are very sharp (vertical lines)
- **Base peak**: most intense peak in the spectrum
- **Molecular ion** (M+): parent molecule, minus an electron
- Process of fragmentation: chemical pathways
- Ions: most stable cations and radical cations
- Small peaks are due to the natural isotopic abundance (^{13}\text{C}, ^{2}\text{H})
- Molecules with especially labile protons do not display molecular ions: e.g. alcohols, where the highest molecular weight peak occurs at m/e one less than the molecular ion (m-1)
- Identification by mass-to-charge ratio or the mass which has been lost
  - methyl group: m-15; ethyl gourp: m-29, etc.
Interpreting spectra

EI ionization

- **Molecular ion (M⁺):** highest mass in an EI spectrum, represent the molecular weight of the compound
  - Appearance depends on the stability of the compound
  - Double bonds, cyclic structures and aromatic rings stabilize the molecular ion and increase the probability of its appearance

- **Reference Spectra:** reproducible
  - Mass spectra of many compounds published
  - Used to identify unknown compounds by spectral libraries

- **Fragmentation:** general rules exist
  - Functional groups and overall structure determine how molecules resist fragmenting, while other fragment easily

- **Isotopes:** occur in the same abundances that they occur in nature
Commonly Lost Fragments

- m-15: $\cdot \text{CH}_3$
- m-17: $\cdot \text{OH}$
- m-26: $\cdot \text{CN}$
- m-28: $\text{H}_2\text{C}==\text{CH}_2$
- m-29: $\cdot \text{CH}_2\text{CH}_3$, $\cdot \text{CHO}$
- m-31: $\cdot \text{OCH}_3$
- m-35: $\cdot \text{Cl}$
- m-43: $\text{CH}_3\cdot \text{C}==\text{O}$
- m-45: $\cdot \text{OCH}_2\text{CH}_3$
- m-91: $\text{CH}_2$ benzene

Common Stable Ions

- m/e = 43: $\cdot \text{CH}_3 - \text{C}==\text{O}$
- m/e = 91: benzene cation
- m/e = m-1: $\text{R} - \text{C}==\text{O}$
Mass spectrum of toluene (methyl benzene)
- m/e = 92, small m+1 and m+2 peaks, a base peak at m/e = 91 and minor peaks m/e = 65
- Molecular ion: loss of an electron
- Peaks above the molecular ion are due to isotopic abundance
- Base peak at \( m/e = 91 \) in toluene is the relatively stable benzyl cation (tropylium cation)
- Peak at \( m/e = 65 \): loss of neutral acetylene
- Minor peaks below this arise from more complex fragmentation
Fragmentation

Aromatic Hydrocarbons

- Fragmentation of the aromatic nucleus is complex:
  - $m/e = 77, 65, 63,$ etc.
- They form a pattern ("aromatic cluster")
- If the molecule contains a benzyl unit, generation of the benzyl carbocation, which rearranges to form the tropylium ion
- Expulsion of acetylene (ethene): $m/e = 65$

\[
\begin{align*}
\text{m}^+ \\
\text{m} - 1 \\
\text{Tropylium Ion} \\
\text{m}/e = 65
\end{align*}
\]
Fragmentation

Alkanes

• Fragmentation by the initial loss of a methyl group to form a \( (m-15) \) species
• Formed carbocation undergoes stepwise cleavage down the alkyl chain, expelling neutral two-carbon units (ethene)
• Branched hydrocarbons form more stable secondary and tertiary carbocations, these peaks will tend to dominate the mass spectrum
Fragmentation

Aldehydes and Ketones

• Loss of one of the side-chains to generate the substituted oxonium ion
• Extremely favorable cleavage and this ion often represents the base peak in the spectrum
• Methyl derivative (CH₃C O⁺) is commonly referred to as the "acylium ion"
• Expulsion of neutral ethene via a process known as the McLafferty rearrangement:

\[
\begin{align*}
\text{R}_1 \text{R}_2 \xrightarrow{\text{McLafferty rearrangement}} & \quad \text{R}_1 \text{C}=\text{O} + \text{R}_2 \text{C}=\text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \xrightarrow{\text{McLafferty rearrangement}} \\
\text{H} & \quad \xrightarrow{\text{McLafferty rearrangement}} \\
\end{align*}
\]
Fragmentation

Esters, Acids and Amides

- Expulsion of the "X" group to form the substituted oxonium ion
- For carboxylic acids and unsubstituted amides, characteristic peaks at m/e = 45 and 44 are also often observed
Fragmentation

Alcohols

- Lose a proton and hydroxy radical and the -alkyl groups (or hydrogens) to form the oxonium ions.
- For primary alcohols, this generates a peak at m/e = 31; secondary alcohols generate peaks with m/e = 45, 59, 73, etc., according to substitution.
Interpreting spectra

Methanol

- x-axis: increasing m/z ratio
- y-axis: relative abundance of each ion
- Molecular ion \( \text{CH}_3\text{OH}^+ \).
- Most abundant ion (100%): \( \text{CH}_2\text{OH}^+ \)
- Other ions are shown as a percentage (64% of the ion \( \text{CHO}^+ \))
- EI ionization: "hard" ionization method
  - producing fragments which generate information about the structure of the compound
  - the molecular ion does not appear or is a smaller peak in the spectrum
  - initial fragments undergo further fragmentation and rearrangements occur

<table>
<thead>
<tr>
<th>ions</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{OH}^+ )</td>
<td>32</td>
</tr>
<tr>
<td>( \text{H}_2\text{C}=\text{OH}^+ )</td>
<td>31</td>
</tr>
<tr>
<td>( \text{HC}=\text{O}^+ )</td>
<td>29</td>
</tr>
<tr>
<td>( \text{H}_3\text{C}^+ )</td>
<td>15</td>
</tr>
</tbody>
</table>
Ethers

- Following the trend of alcohols, ethers will fragment, often by loss of an alkyl radical, to form a substituted oxonium ion.
- Example: diethyl ether

\[
\text{O}^+ \quad \text{CH}_3 \quad \text{O}^+ \quad \text{m}-15
\]
**Fragmentation**

**Halides**

- Simple expulsion of the halogen
- The molecular ions of chlorine and bromine-containing compounds will show multiple peaks due to the fact that each of these exists as two isotopes in relatively high abundance
- Thus for chlorine, the $^{35}\text{Cl}/^{37}\text{Cl}$ ratio is roughly 3:1 and for bromine, the $^{79}\text{Br}/^{81}\text{Br}$ ratio is 1:1
- The molecular ion of a chlorine-containing compound will have two peaks, separated by two mass units, in the ratio 3:1, and a bromine-containing compound will have two peaks, again separated by two mass units, having approximately equal intensities.
Relative Isotope Abundance

Common elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>rel. A</th>
<th>Isotope</th>
<th>rel. A</th>
<th>Isotope</th>
<th>rel. A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>$^{12}\text{C}$</td>
<td>100</td>
<td>$^{13}\text{C}$</td>
<td>1.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>$^{1}\text{H}$</td>
<td>100</td>
<td>$^{2}\text{H}$</td>
<td>.016</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>$^{14}\text{N}$</td>
<td>100</td>
<td>$^{15}\text{N}$</td>
<td>.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>$^{16}\text{O}$</td>
<td>100</td>
<td>$^{17}\text{O}$</td>
<td>.04</td>
<td>$^{18}\text{O}$</td>
<td>.20</td>
</tr>
<tr>
<td>Sulfur</td>
<td>$^{32}\text{S}$</td>
<td>100</td>
<td>$^{33}\text{S}$</td>
<td>.78</td>
<td>$^{34}\text{S}$</td>
<td>4.40</td>
</tr>
<tr>
<td>Chlorine</td>
<td>$^{35}\text{Cl}$</td>
<td>100</td>
<td></td>
<td></td>
<td>$^{37}\text{Cl}$</td>
<td>32.5</td>
</tr>
<tr>
<td>Bromine</td>
<td>$^{79}\text{Br}$</td>
<td>100</td>
<td>$^{81}\text{Br}$</td>
<td>98.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Methyl Bromide: The ratio of peaks containing $^{79}\text{Br}$ and its isotope $^{81}\text{Br}$ (100/98) confirms the presence of bromine in the compound.
Ionization Efficiency Curves

- “Number of ions produced as a function of the energy of the electrons used to produce ionization” (IUPAC)

- Electron Impact (EI) Ionization
  - Gas molecules are bombarded by a high-energy electron beam (70 eV)
  - Intensity of an ion as a function of the energy of the ionizing electron
    - \( i = f(V) \)
    - Variation of the electron energy: 4eV-150eV
    - Steps: 0.1eV
  - Electron bombardment ionization
  - Ionization probability \( p: p(E) \sim (E-Ei)^n \)
    - Simple ionization \( n = 1 \), double ionization \( n = 2 \) ... 
  - Linear ascent of the intensity of the mass from the corresponding IP
  - Problem: thermal energy spread of electrons (Maxwell-Boltzmann)

\[
\frac{dN}{N} = \frac{2}{\sqrt{\pi}} \left(\frac{E}{kT}\right)^{3/2} e^{-\frac{E}{kT}} dE
\]
Experimental Approach

Catalytic reaction analysis

- catalytic wall reactor (Pt, \( T_{\text{max}} = 1300 \) °C, atmospheric pressure)
- coupling to a QMS via molecular beam sampling interface
- QMS with electron impact source & threshold ionization capability
- principle \( \Rightarrow \) discrimination of interfering ions (same nominal m/z value) by means of their ionization- and appearance potentials
- Inhomogeneous electrons \( \Rightarrow \) determination of shape and width of the electron energy spread function
Energy Spread and Offset

Energetically inhomogeneous electrons from the source

- Filament contaminations
- Thermal energy spread (Maxwell-Boltzmann)
- Potential drop along the filament
- Potential gradients inside the source

- $\text{N}_2$ at 28 amu
- $IP_{\text{N}_2} = 15.6 \text{ eV}$

**energy offset $\approx 1 \text{ eV}$**

**energy spread: $\sigma = 0.49 \text{ eV}$**

$IP \pm 2\sigma = IP \pm 0.5 \text{ eV} \approx 1 \text{ eV}$

**Gaussian**

$$i(V) = \frac{C}{\sigma \cdot \sqrt{2\pi}} \int_{IP}^{\infty} e^{-\frac{(E-IP)^2}{2\sigma^2}} (E-IP)^{1.127} dE$$
Appearance Potential MS

Discrimination between species with the same mass numbers

- \( \text{e}^- + \text{CH}_3\cdot \rightarrow \text{CH}_3^+ + 2\text{e}^- \)
- \( \text{e}^- + \text{CH}_4 \rightarrow \text{CH}_3^+ + \text{H}\cdot + 2\text{e}^- \)
- \( \text{e}^- + \text{C}_2\text{H}_6 \rightarrow \text{CH}_3^+ + \text{CH}_3\cdot + 2\text{e}^- \)

\( m/z = 15 \text{ amu} \)
\( \text{IP(} \text{CH}_3^+ \text{)} = 9.84\text{eV} \)
\( \text{AP(} \text{CH}_3^+ \text{)} = 14.30\text{eV} \)
\( \text{AP(} \text{CH}_3^+ \text{)} = 13.46\text{eV} \)

- **Ionization potential (IP)** of an atom or molecule is the energy required to remove completely an electron
- Minimum energy that must be imparted to an atom or molecule to produce a specified ion is called **appearance potential (AP)**
- \( X \) can be selectively detected at \( m/z \) (\( X^{z+} \)) if \( \text{IP(} X \text{)} < \) electron energy < \( \text{AP(} X^{z+}/XY \text{)} \)

Identification of the reactive gas phase species by their IP/AP potentials

\( \Rightarrow \) **threshold ionization method**
Why AP-MS?

- to discriminate reactive intermediates from fragments of stable molecules via their ionization- or appearance potential
- sampling and stabilization of reactive species in a molecular beam
- cost-efficient and universal compared to other methods (MIESR, LIFS, CRDS)
- successful prove of the Hiden EPIC MS in literature (plasma physics, CVD e.g. diamond growth)

Why In Situ?

- detection of intermediates in heterogeneously catalyzed reactions
- to clarify the role of gas phase reactions initiated by the catalyst
- to get insight into the reaction mechanism under working conditions
- bridging the gap between macrokinetic and microkinetic
Target Reaction

Catalytic Partial Oxidation (CPO)

\[ \text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2 \text{H}_2 \quad \Delta H_r = -36 \text{ kJ/mol} \quad (\text{Ni, Pt, Rh } \tau \sim 1\text{ms}) \]

Catalytic Wall Reactor

adiabatic expansion ⇒ quenching of all gas phase species

$\text{CH}_4 + \text{O}_2$
He
$\Delta T$

$\text{H}_2 + \text{CO}_2$
$\text{CO}_2 + \text{H}_2\text{O}$
He
$\Delta T$
**Threshold Ionization**

**CO in N₂ as model system for CH₃⋅ radical detection**

**CH₃⋅ in methane CPO on Pt**

Expected radical concentration:

\[10^2 \text{ – } 10^3 \text{ ppm}\]

**CO in N₂**

Measured concentration range:

\[2260 \text{ – } 20960 \text{ ppm}\]

\[{}^{12}\text{C}^1\text{H}_3^+ / {}^{12}\text{C}^1\text{H}_3^\cdot \text{ at m/z } = 15\text{amu}\]

\[\text{CH}_3^\cdot + e^- \rightarrow \text{CH}_3^+ + 2e^-\]

IP = 9.84 eV

\[{}^{12}\text{C}^1\text{H}_3^+ / {}^{12}\text{C}^1\text{H}_4^+ \text{ at m/z } = 15\text{amu}\]

\[\text{CH}_4 + e^- \rightarrow \text{CH}_3^+ + \text{H}^\cdot + 2e^-\]

AP = 14.01 eV

\[{}^{14}\text{N}_2^+ / {}^{14}\text{N}_2 \text{ at m/z } = 28\text{amu}\]

\[\text{N}_2 + e^- \rightarrow \text{N}_2^+ + 2e^-\]

IP = 15.58 eV

\[{}^{12}\text{C}^{16}\text{O}^+ / {}^{12}\text{C}^{16}\text{O} \text{ at m/z } = 28\text{amu}\]

\[\text{CO} + e^- \rightarrow \text{CO} + 2e^-\]

IP = 14.014 eV
Threshold Ionization

CO in N₂ as model system for CH₃ radical detection

- Linear calibration

\[ \text{N}_2 + \text{e}^- \rightarrow \text{N}_2^+ + 2 \text{e}^- \]

\[ IP = 15.58 \text{ eV} \]

\[ \text{CO} + \text{e}^- \rightarrow \text{CO}^+ + 2 \text{e}^- \]

\[ IP = 14.014 \text{ eV} \]

Detection Limit: 230 ppm
Reaction-Zone-Shifting

- Access to different reaction zones by variation of temperature during methane CPO

He: 2000 ml/min
CH₄: 200 ml/min
O₂: 150 ml/min
C/O = 0.7

T_{Zone}: 681 °C

Only educts detectable

T₁
Reaction-Zone-Shifting

$T_{\text{Zone}}$: 925 °C

mainly total oxidation products

$T_2$

Reaction-Zone-Shifting

$T_{\text{Zone}}$: 1103 °C

Partial oxidation products

$T_3$

Compound survey by mass scanning
Threshold Ionization

Discrimination between species with the same mass numbers

Ionization energy: 10 eV
Peak formation at 15 amu
No peak overlap

Ionization energy: 12 eV

CH$_4$$^+$?

Discrimination between species with the same mass numbers

CH$_3$$^+$?

Filament
Focus
to MS
Detection of intermediates

CH₃· in oxidative coupling of methane on Pt

$^{12}$C¹H₃⁺ /$^{12}$C¹H₃· at m/z = 15 amu

$^{12}$C¹H₃⁺ /$^{12}$C¹H₄ at m/z = 15 amu

$\text{CH}_3\cdot + e^- \rightarrow \text{CH}_3^+ + 2 \text{e}^-$

IP = 9.84 eV

$\text{CH}_4 + e^- \rightarrow \text{CH}_3^+ + \text{H}· + 2 \text{e}^-$

AP = 14.01 eV

CH₄: 600 ml/min

O₂: 500 ml/min

He: 200 ml/min

$T_{\text{max}}$: 1520 K
Detection of \( \text{CH}_3^\cdot \)
IE curves: Radical concentrations

CH₃⁺ from CH₄
14.01 eV + 0.6 eV offset

~ 1250°C

~ 1100°C
General Reading