Production of NH_3 in N_2-Corona Discharges and ^{63}Ni-Sources: Unequivocal Identification and Quantification

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Introduction

Challenge:

- Find a rational for $[nM+NH_4]^+$-signals frequently observed with plasma source driven API methods (e.g. APCI) *without taking into account* "contamination" of the bulk gases with ammonia.
  - Different mechanisms conceivable
    - → Electrolysis of water and nitrogen
    - → Surface reaction of H- and N-atoms formed by dissociation of water and nitrogen
- Hypothesis: *in-situ* ammonia generation in the presence of nitrogen and water; required energy supply and subsequent surface catalysis.

Experimental approach:

- Replacement of nitrogen by argon
  - → search for N-source
  - and water by deuterated water
  - → exchange of H-atoms by deuterium atoms in the ammonia molecules
- Unequivocal ammonia detection and quantification with a selective ammonia-measuring device ("NH_3-LOPAP")

Methods

Detection

Mass spectrometer

- micrOTOF mass spectrometer (TOF-MS), Bruker Daltonics
- amaZon speed ETD (QIT-MS), Bruker Daltonics
- Esquire3000 (QIT-MS), Bruker Daltonics
- LOng Path Absorption Photometer (LOPAP), Quma Elektronik & Analytik GmbH

Ionization Methods

- Atmospheric pressure chemical ionization source (APCI)
- VUV Kr discharge RF lamp (APPI) - emitting 10.0 eV and 10.6 eV photons (Syagen)
- Custom ^{63}Ni β-radiation source
- Custom capillary atmospheric pressure chemical ionization (cAPCI) source [2,3]

Analyte treatment

- **RF-activation:** Custom RF stage ("ion tunnel")
- **GC:** 7890A, Agilent Technologies Inc.
- **Transferline:** Custom temperature-controlled GC-transferline
- **Analyte:** C_4 - C_{24} Even carbon saturated fatty acid methanol esters ("FAME-Mix"), Supelco Analytical

Data Analysis

- Data Analysis, (version) Bruker Daltonics
- mMass (version 5.5.0; open source software)

Experimental Setup

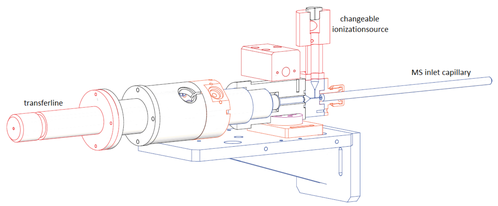
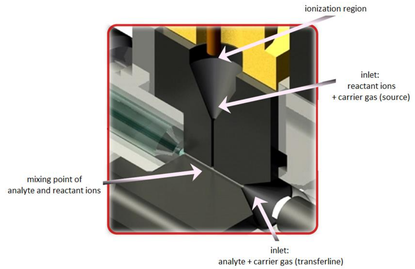


Fig. 1: Schematic drawing of the transfer line/ionization source [1].

- Different mechanisms conceivable
- Dissociation, electrolysis and ionization with corona discharge in the same region possible
- Adsorption of N- and H- atoms on surrounding metal surfaces may promote catalyzed ammonia generation via heterogeneous reactions

Fig. 2: Schematic of the ionization region. This arrangement was used for all ionization methods investigated. Generated ions are in close vicinity to metal surfaces [2,3].



Ammonia Measurements

- Measurements were performed with a NH_3-**Lo**ng **P**ath **A**bsorption **P**hotometer (LOPAP) recently developed by our group.
- NH_3 is sampled from the gas phase in a stripping coil by an acid solution. The coil is directly situated at the sampling site, which avoids the use of any longer sampling lines.

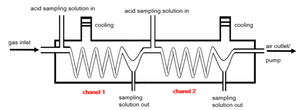


Fig. 3: LOPAP reaction of detection [3].

- NH_3 is quantified by a selective chemical reaction (Berthelot) as a highly absorbing dye. The dye is detected using long path absorption with a liquid core waveguide.

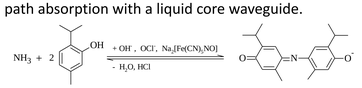


Fig. 4: NH_3-LOPAP.

Performance Characteristics	Parameters
Absorption wavelength Length of absorption tube	560 – 690 nm 0.95 m
Precision	1%
Measurement range Limit of detection	0.07 - 900 ppbV 70 pptV

Table. 1: LOPAP setup parameters.

Mass spectrometric results

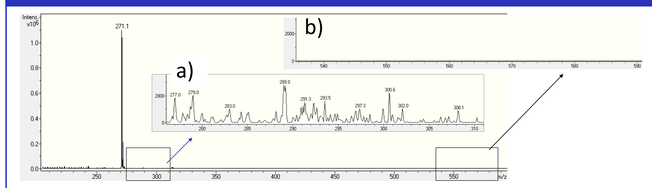


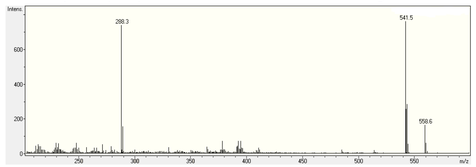
Fig. 5: Mass spectrum of methyl palmitate using cAPCI/QIT-MS showing $[M+H]^+$ as base peak
Insert a: Expanded mass range 277 - 311 ($[2M+H+NH_3]^+$; $[2M+H_3O]^+$)
Insert b: Expanded mass range 539 - 590 ($[2M+H]^+$; $[2M+H+NH_3]^+$; $[2M+H_3O]^+$).

Mass spectrometers with different ion transfer stages and settings treat equilibrated ion populations differently. For QIT MS this is also true for the ion detection phase

- TOF-MS employed: Softest transfer and detection conditions, with many cluster signals
- QIT: Significantly harsher conditions. Depending on settings the dimers (Esquire QIT) or the entire cluster distribution are "lost" (amaZon QIT)

- Ammonia production is indirectly observed with corona discharge and β-radiation excitation by $[M+H+NH_3]^+$
- APCI, cAPCI and ^{63}Ni are principally providing sufficient energy to drive N_2 and H_2O dissociation as well as ionization processes [4]
- APPI provides max. 10.6 eV to the reacting system → no ammonia production route feasible

Fig. 6: Mass spectrum of methyl palmitate using cAPCI/TOF-MS showing $[2M+H]^+$ as base peak (41%) and $[M+H+NH_3]^+$ as second largest species (36%) - the entire distribution is shown in figure 7.



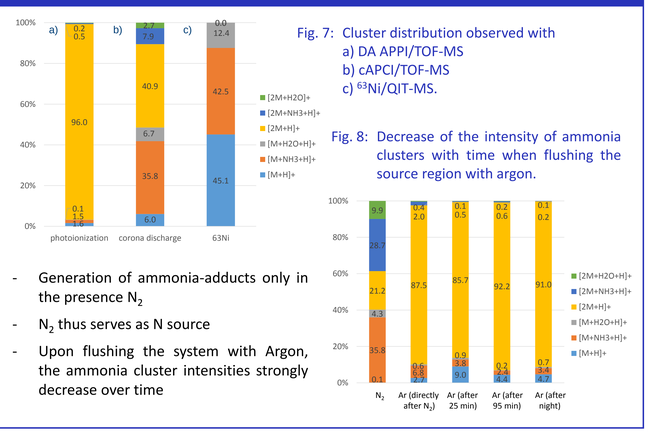


Fig. 7: Cluster distribution observed with
a) DA APPI/TOF-MS
b) cAPCI/TOF-MS
c) ^{63}Ni/QIT-MS.

- Generation of ammonia-adducts only in the presence N_2
- N_2 thus serves as N source
- Upon flushing the system with Argon, the ammonia cluster intensities strongly decrease over time

Fig. 8: Decrease of the intensity of ammonia clusters with time when flushing the source region with argon.

LOPAP results

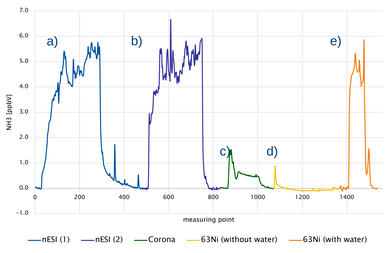


Fig. 9: Ammonia mixing ratios measured with
a/b) cAPCI with same conditions on different days
c) APCI with addition of water
d) ^{63}Ni β- ion source without and
e) with addition of water.

LOPAP

- Corona discharge ionization (cAPCI, APCI) and ^{63}Ni β-radiation generate ammonia. This finding is supports the notion of sufficient energy supply as prerequisite for NH_3 generation
- Measurements with cAPCI show good reproducibility
- The extent of ammonia generation using ^{63}Ni β-radiation excitation clearly shows a strong humidity dependence
  - Ammonia is only generated in the presence of water
  - Water is most probably the hydrogen-source (as H_{ad} and or H_2) for NH_3 generation
  - Ammonia molecules can be adsorbed on the source surface and may disguise as higher ammonia mixing ratios when washed out with water satiated gas phase
  - Temporal evolution of the signals suggest a heterogeneous production route

D_2O experiments

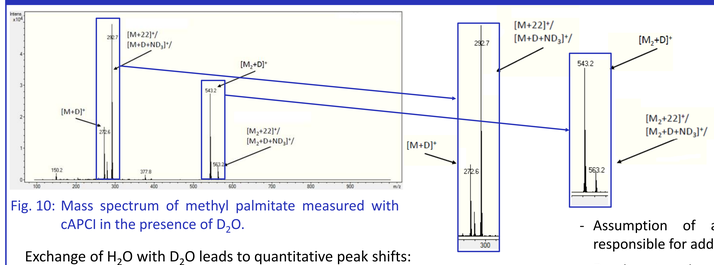


Fig. 10: Mass spectrum of methyl palmitate measured with cAPCI in the presence of D_2O.

Exchange of H_2O with D_2O leads to quantitative peak shifts:

- m/z: 271 $[M+H]^+$ → 272 $[M+D]^+$
- m/z: 288 $[M+H+NH_3]^+$ → 292 $[M+D+ND_3]^+$
- m/z: 542 $[2M+H]^+$ → 543 $[2M+D]^+$
- m/z: 559 $[2M+H+NH_3]^+$ → 563 $[2M+D+ND_3]^+$

Stretched sections of the mass spectrum showing the absence of a hydrogen/deuterium distribution.

- Assumption of ammonia impurities being responsible for adduct formation is discouraged
- Results strongly support the assumption of water as hydrogen source, since H_2O leads quantitatively to $[M+H+NH_3]^+$ and D_2O to $[M+D+ND_3]^+$ clusters, respectively
- Missing H/D distribution renders a simple exchange reaction implausible

Conclusions

Mechanism:

- Several NH_3 sources in API are conceivable
  - NH_3 contamination of nitrogen gas supply
    - → inconsistent with absence of $[(NH_3)_n+H]^+$cluster distributions, which are well established in literature [5]
    - → inconsistent with absence of NH_3/ND_3 distributions in D_2O experiments
    - → inconsistent with unequivocal NH_3 detection in the LOPAP measurements
  - NH_3 production via an electrolysis based mechanism
    - → inconsistent with ammonia detection using the ^{63}Ni-source
  - NH_3 production via gas phase initiated dissociation/ionization mechanism, followed by surface catalyzed heterogeneous reactions
    - → currently consistent with all results presented in this contribution

Outlook:

- Systematic measurements on the water dependency of the extent of NH_3 generation each with LOPAP and mass spectrometry
- Further experiments with photoionization using LOPAP and mass spectrometry
- Experiments using different ion source surface materials

Literature

[1] M. Thinius "Studies on the ion transmission and ion activation," Master Thesis, Department of Chemistry, University of Wuppertal, 2015.

[2] Y. Brachthäuser et al. "GC-MS Performance of a Novel Capillary Atmospheric Pressure Chemical Ionization (cAPCI) Source," in Proceedings of the 61th ASMS Conference of Mass Spectrometry and Allied Topics, Minneapolis, Minnesota, USA, 2013.

[3] S. Klee et al., "Capillary atmospheric pressure chemical ionization using liquid point electrodes", RCM **28**, 1591 – 1600, 2014.

[4] S. Peters "Entwicklung eines Messgerätes zur selektiven und sensitiven Messung von Ammoniak (NH_3) und Ammonium (NH_4^+) in der Atmosphäre", 1. Year progress report, 2014.

[5] M.M. Shahin, "Mass-Spectrometric Studies of Corona Discharges in Air at Atmosperic Pressure", J. Phys. Chem. 45 (7), New York, 1966

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