

Investigating the Halo-FAPA for Molecular Emission Spectrometry of Heteroatom-Containing Organic Compounds

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Abstract: In gas chromatography, spectrometric methods are employed for multi-channel detection (i.e. atomic emission and mass spectrometry). Detection of heteroatom-containing organic compounds by atomic emission can be challenging. A potential alternative to the detection of heteroatom-containing compounds via elemental emission could be the use of molecular bands of heteroatom containing molecular fragments. In previous studies, the general suitability of the halo-FAPA [1] as a universal detector for organic substances in gas chromatography was already demonstrated on the basis of the emission of the C₂ radical [2]. The presented study focuses on the suitability of halo-FAPA-OES for the determination of heteroatomic compounds, based on the emission of corresponding heteroatomic molecular fragments, employing exponential dilution for calibration and method simplification [3]. Considerations for the design of the halo-FAPA-OES system will be given and analytical figures of merit for acetonitrile, acetone and chloroform based on the detection of the emission bands of biatomic molecules such as CN, CO⁺ and CCl will be documented and critically discussed. Suggestions for future design modifications will also be given.

Experimental setup

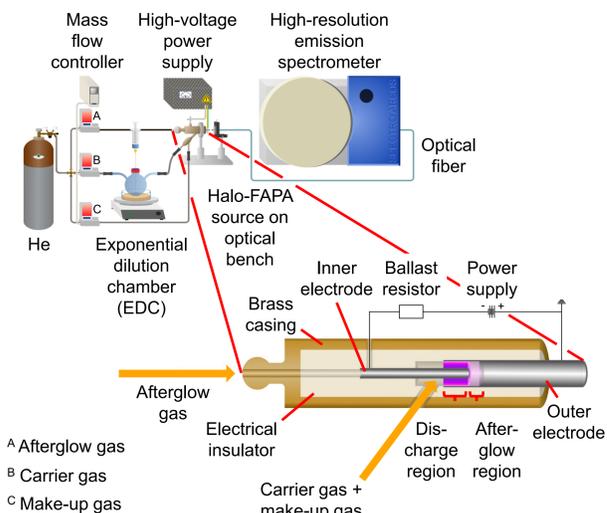
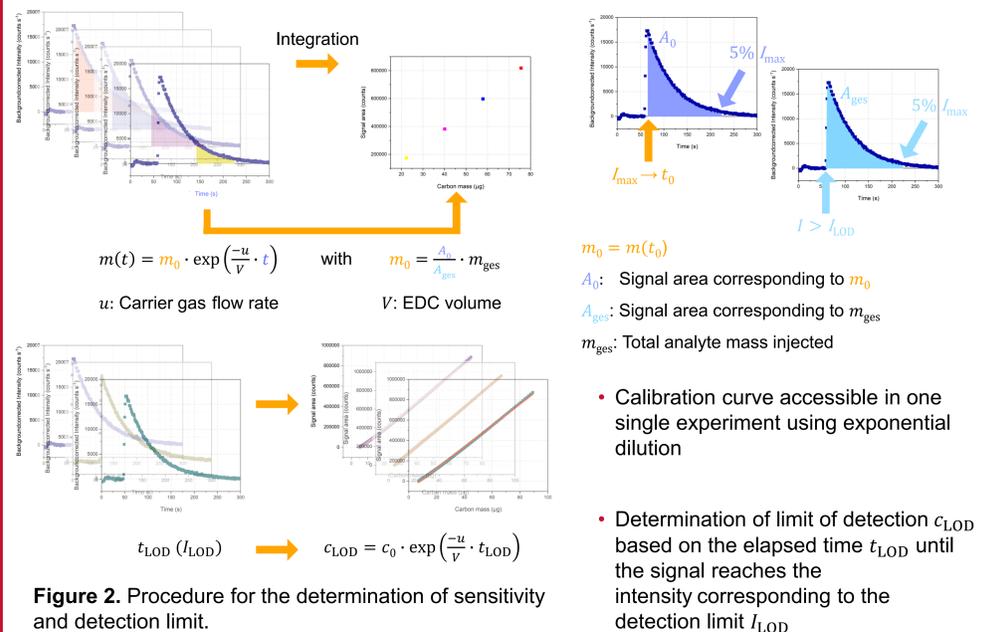


Figure 1. Experimental setup and a side-on view of the halo-FAPA source.

- Identification of emission bands observable under continuous sample introduction
- Observation of band heads associated with heteroatom containing biatomic molecules employing exponential dilution (ED) for sample introduction
- Optimization of the operating conditions of the halo-FAPA source (i.e. discharge current, make-up gas flow rate, length of discharge region)
- Determination of analytical figures of merit

Determination of analytical figures of merit



Identification of observed band heads

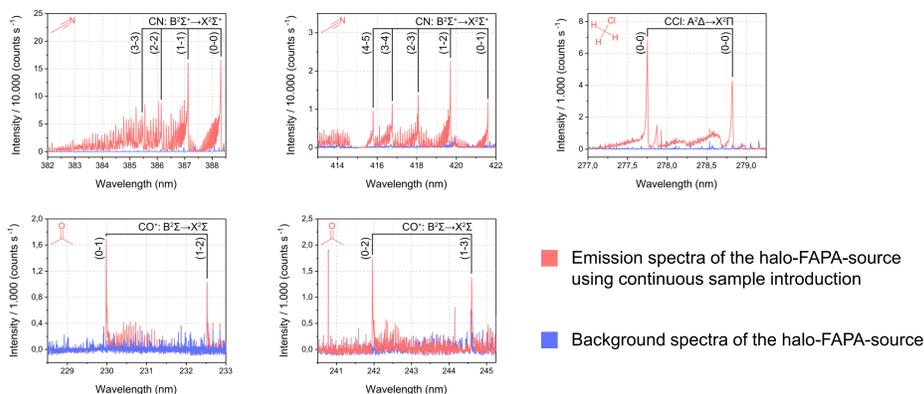


Figure 3. Exemplary emission spectra of the halo-FAPA source in different wavelength ranges. Blue: Background spectrum. Red: Emission spectrum, continuous introduction of selected organic solvents.

Table 1. Band head positions and degradation of the emission bands as well as the corresponding emitting species.

Experimentally determined		Literature data [4, 5]		Corresponding transition
Band head positions / nm	Degradation ^{1,2}	Band head positions / nm	Degradation ^{1,2}	
B ² Σ ⁺ (v') → X ² Σ ⁺ (v'') of the CN radical				
385.447 ^{3,4,5}	v	385.47	v	v' = 3 v'' = 3
386.158 ^{3,4,5}	v	386.19	v	v' = 2 v'' = 2
387.136 ^{3,4,5}	v	387.14	v	v' = 1 v'' = 1
388.331 ^{3,4,5}	v	388.34	v	v' = 0 v'' = 0
415.796 ^{3,4,5}	v	415.81	v	v' = 4 v'' = 5
416.761 ^{3,4,5}	v	416.78	v	v' = 3 v'' = 4
418.077 ^{3,4,5}	v	418.10	v	v' = 2 v'' = 3
419.697 ^{3,4,5}	v	419.72	v	v' = 1 v'' = 2
421.584 ^{3,4,5}	v	421.60	v	v' = 0 v'' = 1
B ² Σ ⁺ (v') → X ² Σ ⁺ (v'') of the CO radical				
229.980 ⁴	r	229.96	r	v' = 0 v'' = 1
232.525 ⁴	r	232.52	r	v' = 1 v'' = 2
241.956 ⁴	r	241.94	r	v' = 0 v'' = 2
244.597 ⁴	r	244.58	r	v' = 1 v'' = 3
A ² Δ(v') → X ² Π(v'') of the CCl radical				
277.752 ⁵	v	277.76	v	v' = 0 v'' = 0
278.822 ⁵	v	278.83	v	v' = 0 v'' = 0

- Identification of observable emission bands was based on:
 - Position of the band heads
 - Degradation of the emission bands
 - Presence of multiple emission bands of the same band system
 - Good agreement of the experimentally determined band head positions and degradation with literature data
 - Emission bands of CN non-specific for nitrogen containing compounds
- ¹ v: Band degraded to violet
² r: Band degraded to red
³ Observable by introduction of acetonitrile
⁴ Observable by introduction of acetone
⁵ Observable by introduction of chloroform

Method optimization

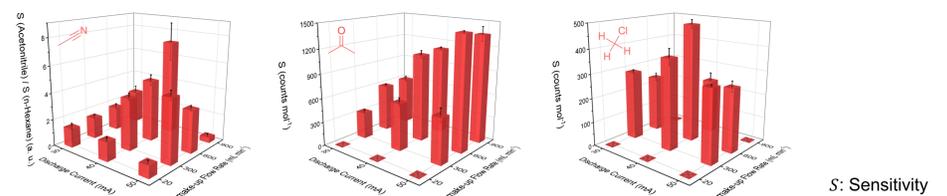


Figure 4. Sensitivity of the ED-halo-FAPA-OES method for the determination of acetonitrile, acetone and chloroform (length of the discharge region 5.0 mm, 1.0 mm and 5.0 mm, respectively).

- Method optimization with respect to maximum sensitivity
- Emission bands of CN non-specific for nitrogen-containing compounds → Optimization of the FAPA-OES method for determination of acetonitrile with respect to maximum sensitivity ratio (with/without N-containing compound)
- 2 different discharge region lengths, 3 discharge currents and 4 make-up gas flow rates investigated

Table 2. Achievable detection limits through ED-halo-FAPA-OES.

Analyte	Limit of detection / mg L ⁻¹	Wavelength / nm	Operating conditions considered optimal		
			Discharge region length / mm	Discharge current / mA	Make-up flow rate / mL min ⁻¹
Acetonitrile	0.41 ± 0.06	388.331	5.0	40	900
Acetone	0.34 ± 0.06	241.956	1.0	50	600
Chloroform	2.8 ± 0.8	277.752	5.0	40	600

- No emission bands of CCl radical visible using a 1.0 mm discharge region → Connection with a lower dissociation energy (compared to that of CN and CO⁺) possible

Summary and Outlook

- Proof of principle for determination of heteroatom-containing compounds by means of ED-halo-FAPA-OES employing the emission of non-metal containing biatomic molecules
 - Emission on molecular bands of CN non-specific for nitrogen-containing molecules
 - Upper trace concentration detection limits for acetonitrile, acetone and chloroform
- Possible future design modifications:
- Enlargement of the inner electrodes contact surface (coaxial alignment of the electrodes proved to be challenging with discharge region lengths exceeding 5.0 mm)
 - Reversing the discharge polarities or establishing a floating ground → Preventing discharges in the region of the inner electrodes contact pin (Occasionally occurred with the current setup)

References

- [1] K. P. Pfeuffer, J. N. Schaper, J. T. Shelley, S. J. Ray, G. C.-Y. Chan, N. H. Bings, G. M. Hieftje, *Anal. Chem.* **2013**, *85*, 7512-7518.
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 [3] T. R. Booher, R. C. Elser, J. D. Winefordner, *Appl. Spectrosc.*, **1982**, *36*, 99-102. [5] M. Larsson, M. R. A. Blomberg, P. E. M. Siegbahn, *Mol. Phys.* **1982**, *46*, 365-382.