On-line and in situ gas (tar) measurements

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Outline

Introduction to Optical Absorption Spectroscopy/DOAS

- Choice of spectral range
- Choice of medium
- Before real measurements:
 - Gas cell and setup
 - Temperature-dependent Absorption Cross-Sections Database

• Real measurements:

- What can we expect?
- Viking (high-T gasification)
- LT-CFB (low-T gasification)
- "Bad" grade wood fired burner (uncomplete combustion)

• Conclusions

Choice of spectral range



UV (200nm<λ):

- superb sensitivity for organics;
- (very) strong light absorption;
- in situ or on-line measurements.

Special for gasification: no O₂

- possibility to go further down (120nm<λ): far UV;
- superb sensitivity for major/minor gas components;
- compact system;
- in situ or on-line measurements.
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Choice of spectral range



- Larger cross-sections (cs) → stronger absorption → easy to measure
- More (benzene) rings (+substitutes) \rightarrow absorption at longer λ
 - Tar has strong UV absorption at 200nm < λ
 - cs for 1x to 5x about the same magnitude (5x = number of benzene rings)
- BTX and light PAH's have strong UV absorption in 170-200nm
- 120-170nm is tar-"free" region: major/trace gas analysis (H₂O, CO₂, CO, saturated unsaturated (double/triple C-C and C=O) hydrocarbons)
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1Mb=1x10⁻¹⁸ cm²

Choice of medium

Example: 1,2,4,5-tetrazine



- Gas phase, room temperature
- In isopentane-methylcyclohexane matrix, 77K
- III In cyclohexane, room temperature
- IV In water, room temperature

- Molecules have their own "fingerprints"
- Vibrational fine structure disappears in solutions but not in the gas phase
- Fine structure degrades with temperature

Introduction to Optical Absorption Spectroscopy/DOAS





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Set Up for UV Absorption Cross-Sections Measurements with Reactive Gases



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A new design is presented for a gas flow cell for reactive gases at high temperatures. The design features three heated sections that are separated by flow windows. This design avoids the contact of reactive gases with the material of the exchangeable optical windows. A gas cell with this design was validated for high resolution measurements at a component of our to ROM (CAT 2012) to the sub-activation at the scale of the context of the scale of the scale of the context of the scale of the context of the scale of the scale

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CrossMark

Set Up's validation: Absorption Cross-Sections at 22C

Phenol



this experiment 296 K 1.6x10⁻¹⁷ Etzkorn 99 293 K Breho Lesclaux 298 K Trost 97 298K (corrected) cross-section (cm²/molecule) 1.2x10⁻¹⁷ 8.0x10⁻¹ 4.0x10 0.0 264 265 266 267 268 269 270 271 Wavelength (nm)

MeCI



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Ethylene (23C vs 289C)





T-dependent Absorption Cross-Sections





Phenol

With T-raise:

- "coarse" structure widens
- "fine" structure" disappears
- \rightarrow Keep T as low as possible





Set Ups for real measurements: how do they look?





NTII











Setup: on-line gas extraction vs in situ

Extraction



What can we expect?



Gas extrtaction above 2 m (wood fired grade unit) vs in situ cross-stack (wood stove)



- After gas cooler (5C): no water but still some tar/PAH's: easy to identify
- Measurements after filter at **150C**: condensable (= water soluble) vs rest
- NO clear signature
- Tar/soot/NO/... can be measured with time resolution

Clean (from tar) gas: Viking gasifier



Producer gas at 70C, 0.39 cm





nm

Viking	Air ***	O ₂ -CO ₂ 1st run ***	O ₂ -CO ₂ 2nd run***
CH ₄	0.433%	0.866%	1.028%
CO ₂	12.2%	31.08%	24.42%
H ₂ O	2.74%	2.82%	2.8%
0 ₂	0.354%	0.885%	0.955%
CO	8%	14%	14%
N ₂	77%	0%**	0%**
NH ₃	33ppm	0ppm**	0ppm**
C ₆ H ₆	0ppm**	22ppm	22ppm
CH ₃ CHO*	0pmm**	100ppm	100ppm
OCS, CH ₃ CI, HCI	0ppm**	0ppm**	0ppm**

*) Aldehydes in CH₃CHO equivalent

**) below detection limit

***) concentrations calculated from spectra measured over 10 min measurement time

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Dirty gas: LT-CFB gasifier: gas extraction at 150C









Wave	length	(nm)
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Method	Time	Temperature	Phenol	Naphthalene
GC-MS	30 min	15°C	215 ppm	16 ppm
Extraction	3 min	150°C	360 ppm	31 ppm
In-situ	6 min	400°C	500 ppm	N/A

285

Dirty gas: LT-CFB gasifier: in situ



Producer gas at 286C(LT-CFB) vs 70C(Viking) 10 LT-CFB measured spectrum at 286C Viking measured spectrum at 70C 9 CO2 reference H2O reference [I/0]]u 170 120 130 140 150 160 180 190 200 nm

- LT-CFB relatively stable operation in respect to tar/BTX
- "high-tar" operation mode: more BTX/tar (190nm < λ), more NH₃
- In 120-190 nm additional tar absorption gives a base-line like "shift" because nearly flat absorption structures for tar/BTX in 120-170 nm.
- no HCI, CH₃CI(120ppm)





161 nm 171

181

191

201

2

121

131

141

151

Dirty gas: LT-CFB gasifier: in situ



Typical residual spectrum after $H_2O+CO_2+CO+C_2H_4$ subtraction

Tar contribution to the total absorption:

- high: (most absorption (=concentration) due to BTX (170-190nm)
- medium: "light tar" (naphthalene+) (190-220nm)
- low: "heavy tar" (anthracene⁺) (220nm $<\lambda$)

"Bad" grade wood fired burner: incomplete combustion





- "normal" (=optimized) combustion: BTX
- "bad" (=high OGC/PM) combustion: BTX + naphthalene+ + PM
- PM concentration and effective size can be obtained from extinction measurements (absorption + scattering)

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Conclusions

- UV/far UV absorption spectroscopy is a powerful tool for tar and major/minor gas components in situ and on-line measurements
- UV absorption T-dependent cross section databases for various organic molecules are either available or can be generated on request
- Successful demonstration of UV/far UV/DOAS approaches in measurements in various environments (low/high temperature gasification and combustion)
- Tar have about the same absorption cross sections as BTX-family so their contribution into total absorption signal will be proportional to their concentrations
- This can be used for their in situ measurements (absolute or relative) by simple weighting of the 195-230 nm and 170-200 nm areas under an absorption spectrum
- Spectral resolution of the spectrometer does not play any role for this approach and use an ordinary N_2 for purge of the optics would be enough
- Ability unexpansive far UV small spectrometers opens possibility for a new in situ tar/BTX sensor development when a complex tar/BTX sampling can be avoided.

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Thank You

Questions? Comments?