Remote Raman detection of chlorine with deep UV excitation wavelengths

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Motivation

- Remote measurements to detect chlorine gas
- Chlorine gas exposure:

➢ **Industrial**

manufacturing
storage
handling

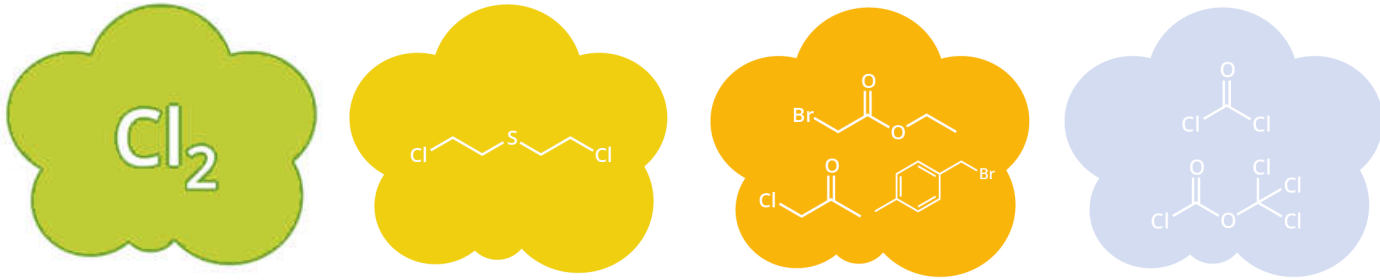
MGPI plant, Kansas, 2016

DPC Enterprises , Missouri, 2002

Motivation

- Chlorine gas exposure:

➢ **Warfare agent -** chlorine, mustard gas, bromine and phosgene



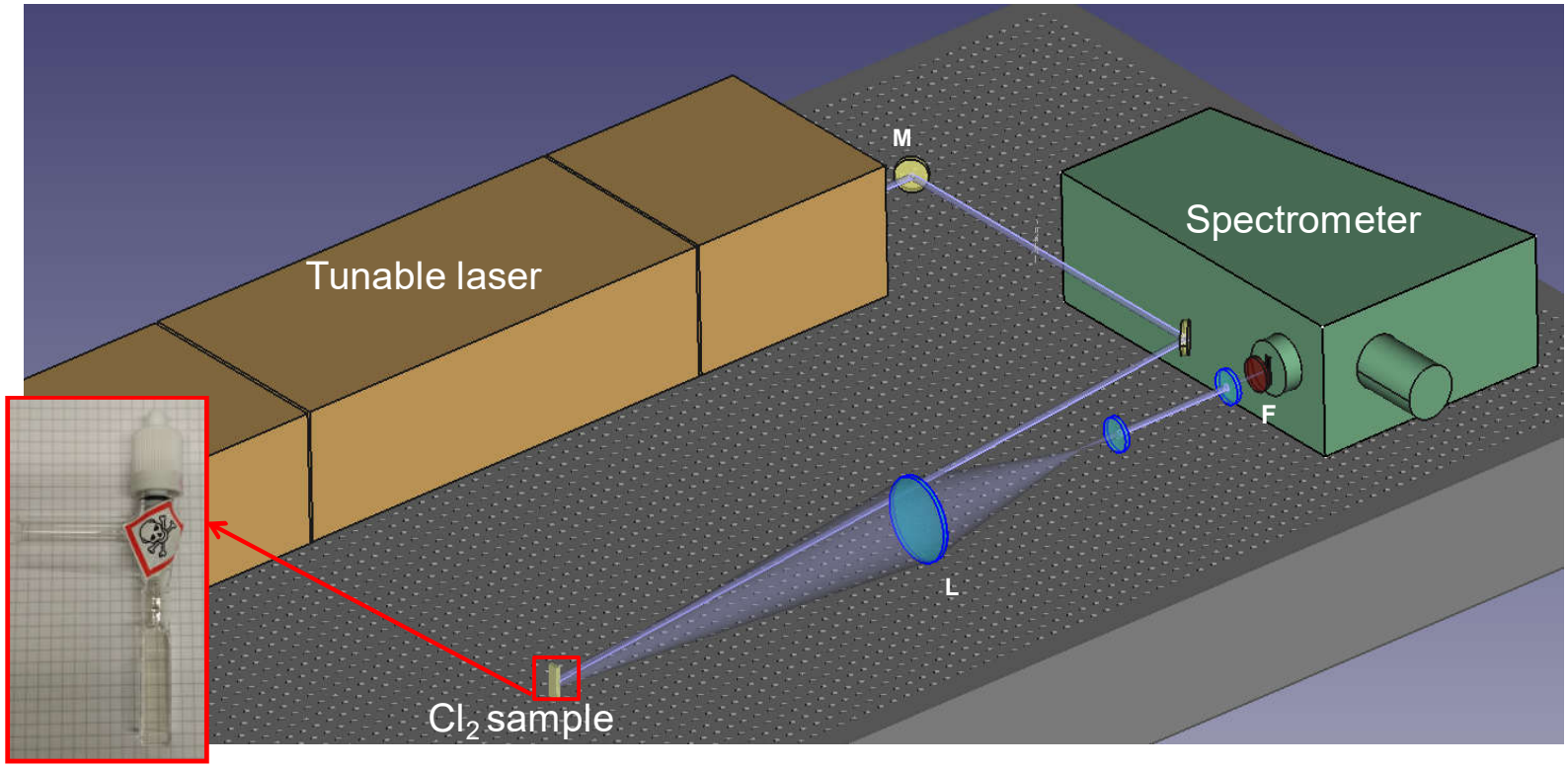
- Lethal doses:

Chlorine	6000 [mg min /m^3] - 2070 ppm min
Mustard gas	900 [mg min /m^3] - 230 ppm min
Tear gasses	30 mins temporary effect
Phosgene	3000 [mg min /m^3] - 740 ppm min

Introduction

- Remote detection set up optimized (distance of 60 cm)
- Change excitation WL in the deep UV => To maximize Cl_2 signal
- Detection limits in acquisition times
- Solution for background interference => Lab test: Cl_2 must be enclosed
- **SYSTEM SETUP**
- **SAMPLE SETUP**
- **RESULTS**
- **CONCLUSION AND FUTURE DEVELOPMENTS**

System setup



- Nd:YAG laser
- dye laser
- mixing unit

- 190-900 nm, 2.5 mJ/pulse, 10Hz

- Liq. N_2 cooled spectr. 2400 grooves/mm

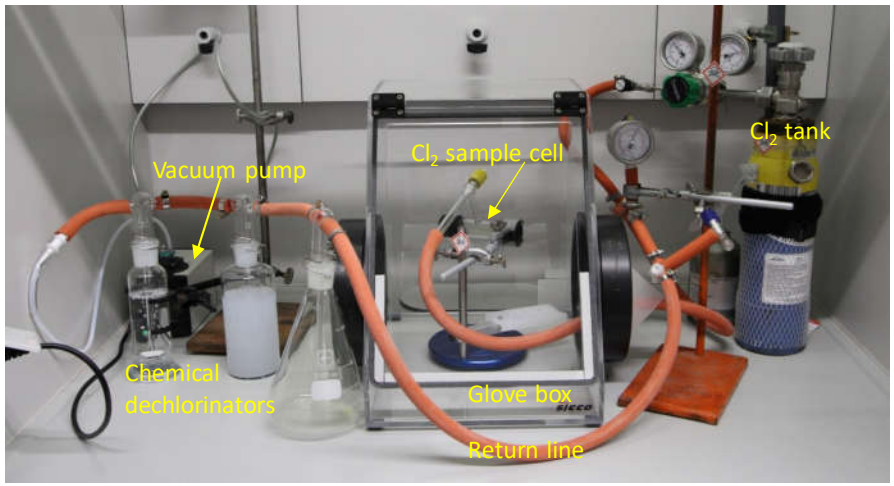
- 60 cm remote distance detection

- Laser filter

- Cl_2 ~ 1 mg/ml

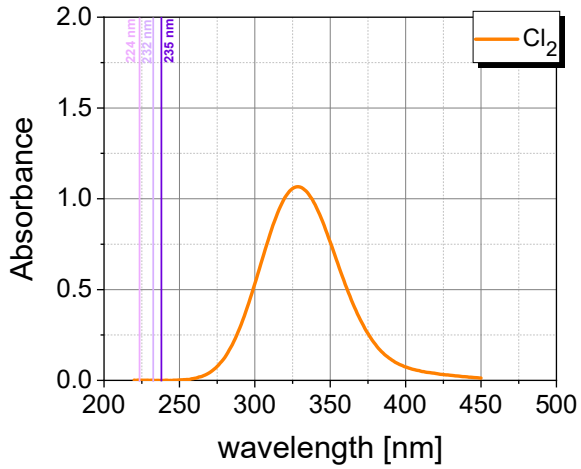
Sample setup

- Self-made system to fill a chlorine gas cell
- chlorine pure gas tank 99.8%
- Vacuum pump below 0.4 bar
- Return line (chemical dechlorinators) sodium thiosulfate, sodium hydroxide, deionized water
- local ΔP < 0.5 bar to avoid window breaking limits
- final sample concentration was 0.36 bar



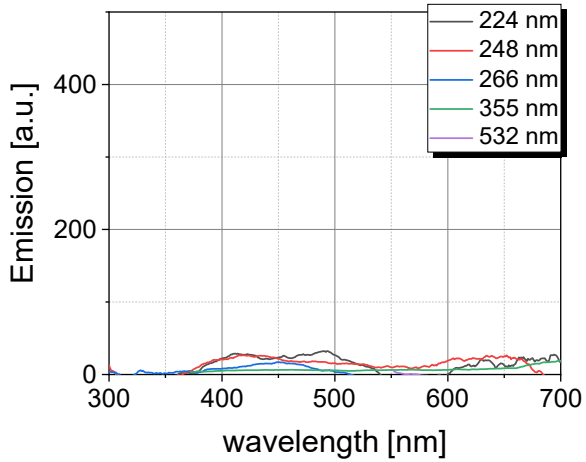
Results

Absorbance vs wavelength



- Edinburgh Instruments FS5 Spectrofluorometer
- 1nm step, 0.5 s sample time per wavelength
- max at 330 nm, FWHM 60 nm
- molar extinction coefficient, path length:
  $[Cl_2]$ = 0.36 bar

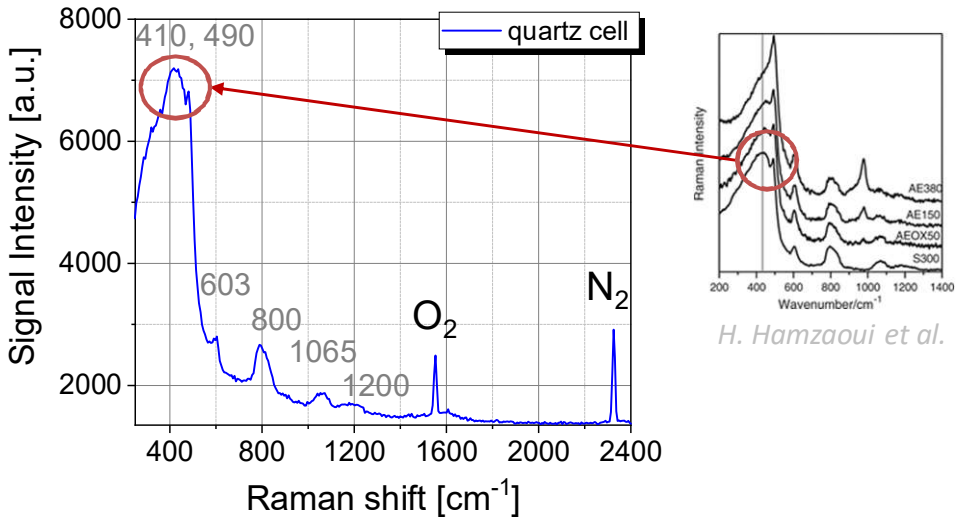
Fluorescence vs wavelength



- standard UV laser sources
- negligible fluorescence

Results

Background signal



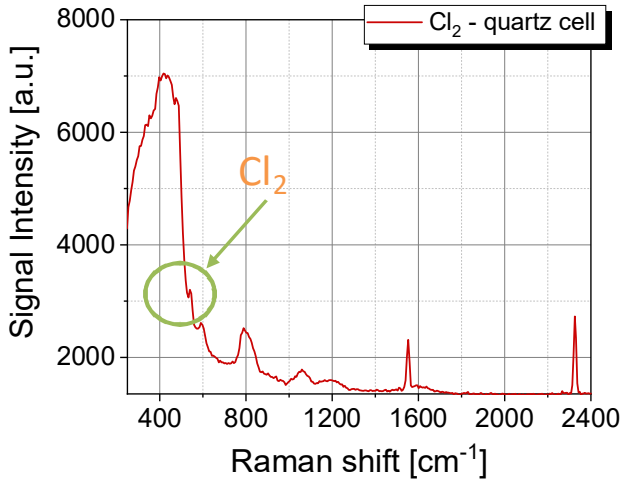
H. Hamzaoui et al.

empty quartz glass cell
as ref. background

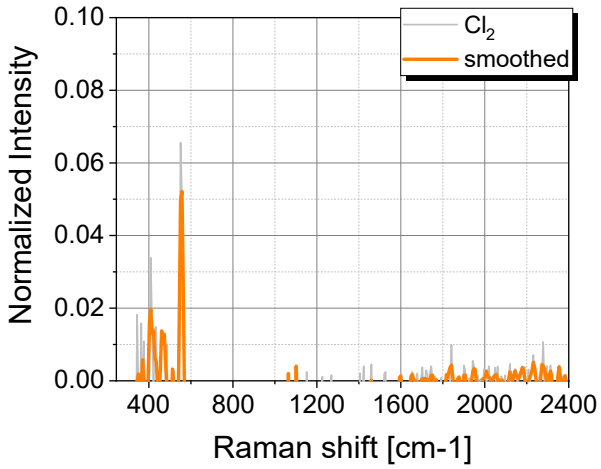
- laser energy density below 20 mJ/cm^2
- 224, 232, 235 nm tested to maximize signal
- broad peak 410 cm^{-1} + sharp one 490 cm^{-1} , in agreement with literature

Results

background & Cl_2 signal



Cl_2 signal

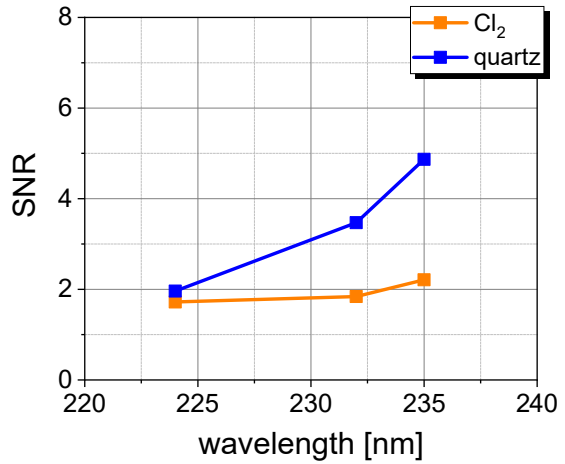


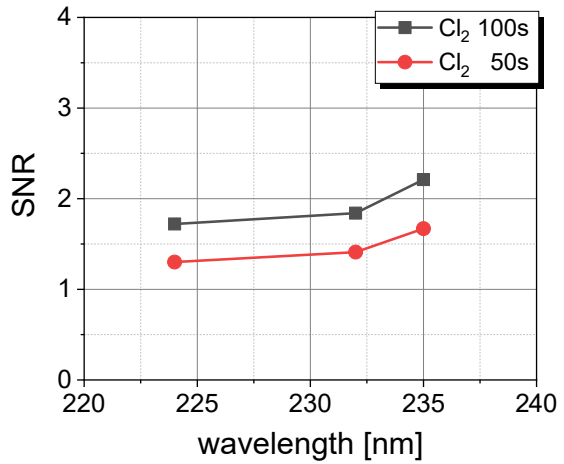
- quartz cell material overlapping with chlorine Raman signal
- Cl_2 sharp peak at 554 cm^{-1} (15 cm^{-1} FWHM)
- expected for Cl_2 at 554, 547, and 539 cm^{-1}

- broad peak quartz residual, in agreement with literature
- hard to separate the two
- remove cell not possible => change material

Results

- Avoid cell material interference around region of interest => Raman grade CaF_2, diamond





- Signal increases at higher excitation wavelengths for both cell material and Cl_2
- strong overlapping of the unwanted quartz material with chlorine at higher wavelengths

- Cl_2 growing increasing the incoming laser wavelength
- Increasing time increases signal by 24%
- 50 s detection limit (peak interference, not intensified camera)

Conclusions & Future Developments

- Chlorine gas was detected in a remote Raman configuration: not standard setup
- Collimated configuration, 60 cm detection distance,
  Total cell 1 mg/ml, probed volume (125 µg)
  laser energy density < 20 mJ/cm^2, acquisition time 50 s
- Reduce acquisition time using an ICCD detector
- Avoid strong quartz interference around region of interest (peaks overlapping) => Raman grade CaF_2, diamond
  New windows material required
- excitation wavelengths, concentration limits

Thank you!

Questions

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