Determination of pesticides and degradation products by means of Spectroscopic techniques (DOAS – FTIR)

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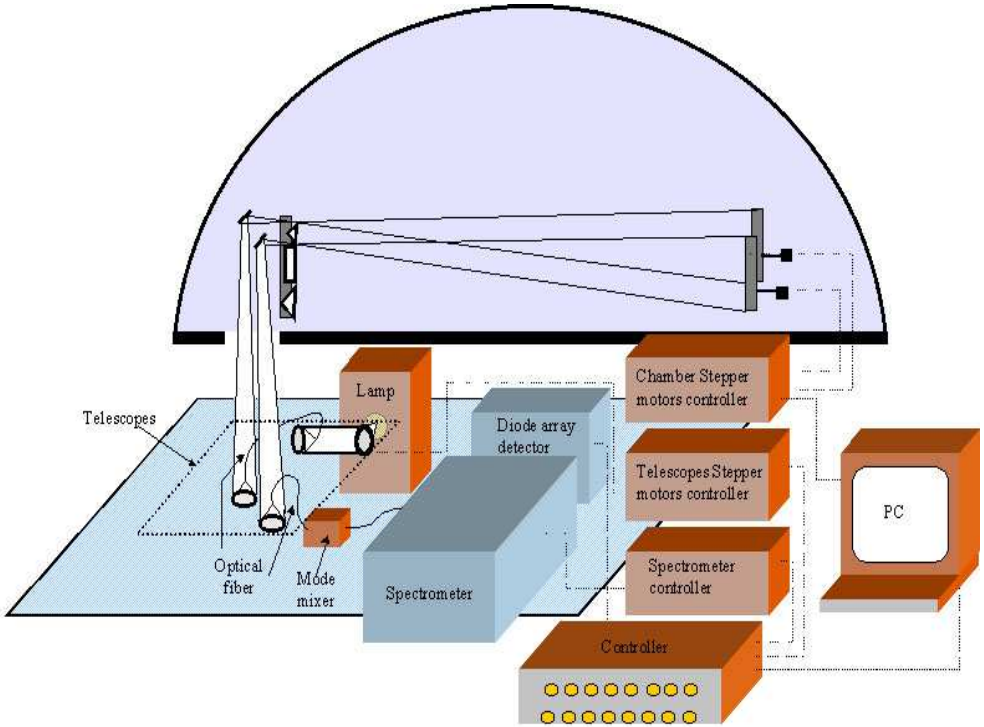
DOAS UV-Vis Spectrometer

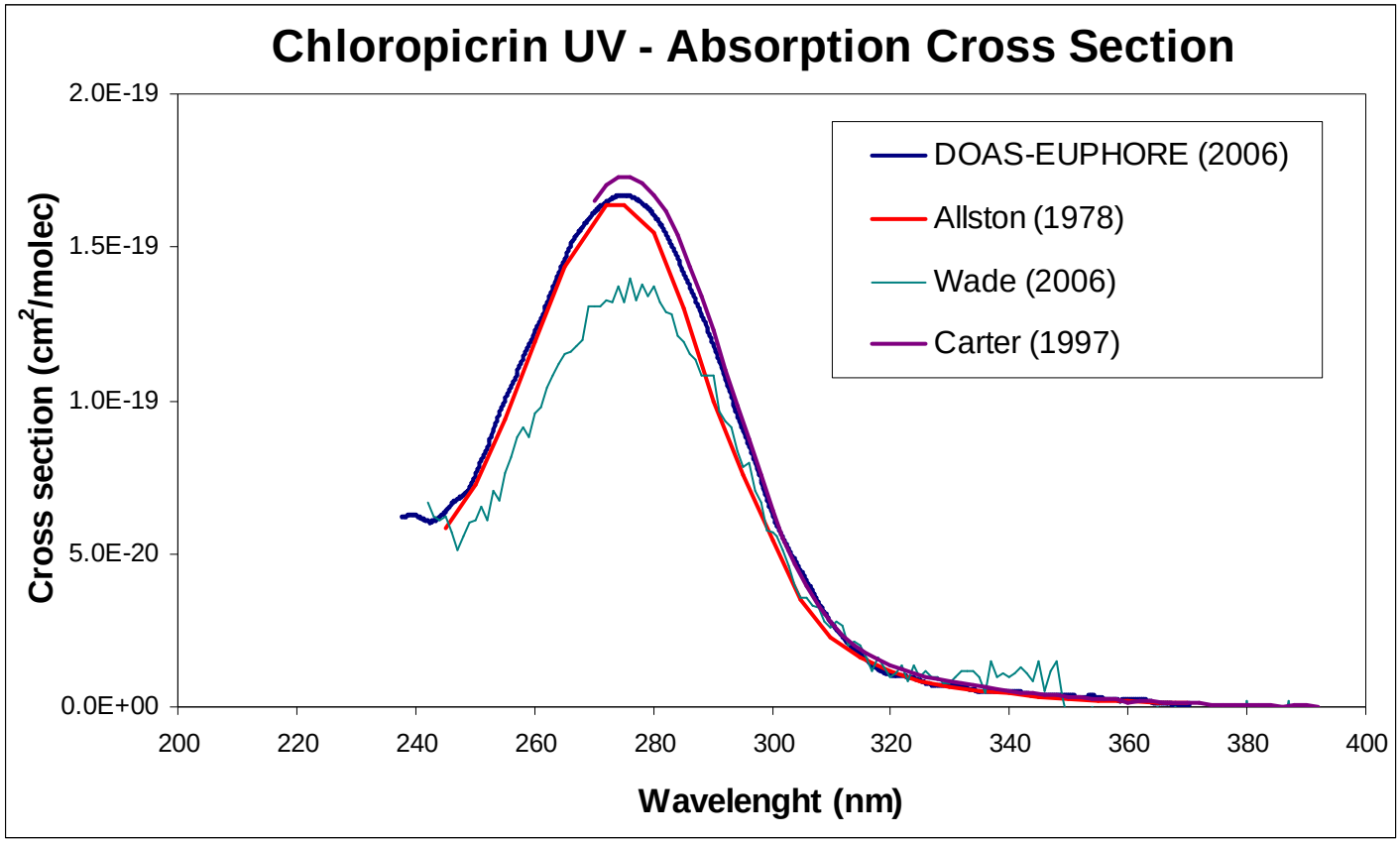


DOAS scheme

DOAS Setup

- White-multireflection cell: 8m base-path (EUPHORE)
- Optical Pathlengths: 128-386-640-896-1154m
- Resolution: 0.04, 0.08, 0.16 nm/pixel (FWHM=0.18, 0.35, 0.72 nm, resp.)
- Several sets of mirrors for detection of different compounds
- Range: UV and Visible (200 – 1000 nm)
- Automatic adjustment of mirrors in the chamber
- Automatic positioning of optical fibers
- Spectrometer (Acton-500 Pro) and detector (PDA-3904 Hamamatsu) are thermostated
- Evaluation of spectra by minimum squares fitting

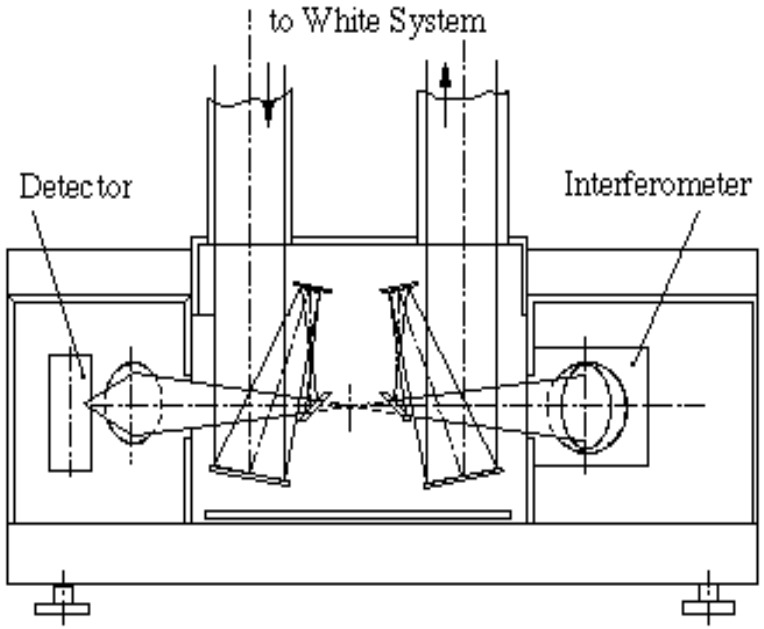
DOAS UV-Vis Spectrometer

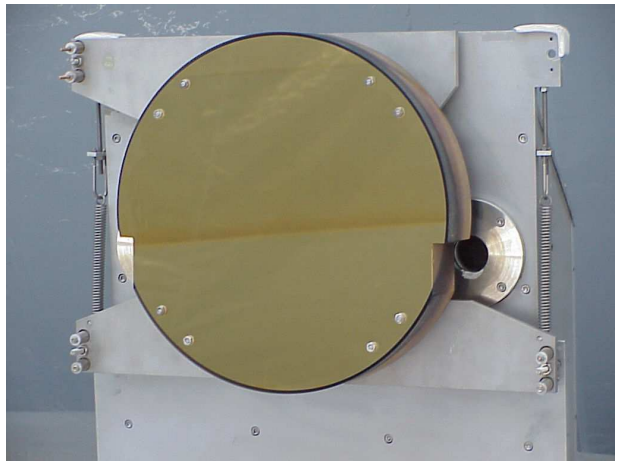


UV cross section of Chloropicrin at high resolution (FWHM=0.7 nm)

Vera et al., 2010

FTIR Spectrometer





Characteristic Data:

Spectrometer: FTIR NICOLET Magna-550

FTIR NICOLET 6700

Detector: MCT

Diam. Mirrors: 0.4 m

Surface Coating: Gold (High Reflectivity in the IR Spectral Range)

Spectral Range: 4000-400 cm^{-1}

Resolution: 1 cm^{-1}

Base Length: 8.170 m

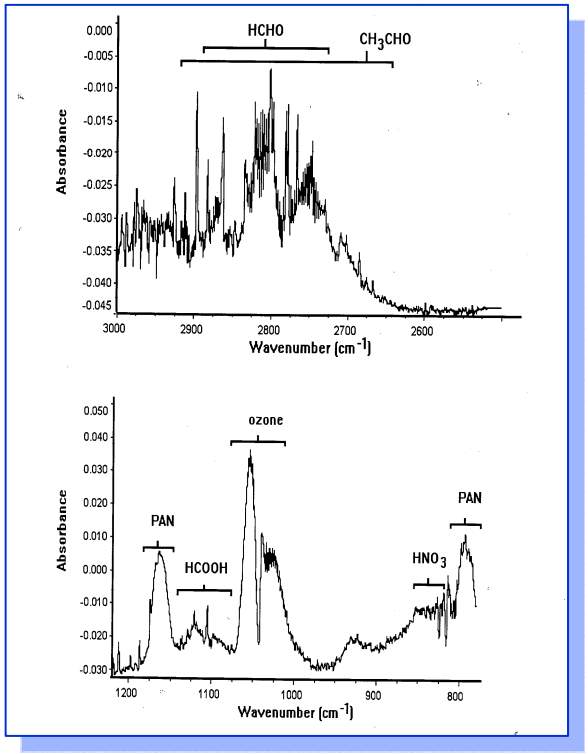
Temporal resolution: 5 minutes

Max. Path-Length of multi-reflection cell:

616.6 m in Chamber A 553.4 m in Chamber B

FTIR Spectrometer

FTIR products identified during a Photooxidation process



Bond	Compound Type	Frequency range, cm^{-1}
C-H	Alkanes CH3 Umbrella Deformation	2960-2850(s) stretch 1470-1350(v) scissoring and bending 1380(m-w) - Doublet - isopropyl, *t*-butyl
C-H	Alkane	3080-3020(m) stretch 1000-675(s) bend
C-H	Aromatic Rings Phenyl Ring Substitution Bands Phenyl Ring Substitution Overtones	3100-3000(m) stretch 870-675(s) bend 2000-1600(w) - fingerprint region
C-H	Alkynes	3333-3267(s) stretch 700-610(b) bend
C=C	Alkenes	1680-1640(m,w)) stretch
C= C	Alkynes	2260-2100(w,sh) stretch
C=C	Aromatic Rings	1600, 1500(w) stretch
C-O	Alcohols, Ethers, Carboxylic acids, Esters	1260-1000(s) stretch
C=O	Aldehydes, Ketones, Carboxylic acids, Esters	1760-1670(s) stretch
O-H	Monomeric - Alcohols, Phenols Hydrogen-bonded - Alcohols, Phenols Carboxylic acids	3640-3160(s,br) stretch 3600-3200(b) stretch 3000-2500(b) stretch
N-H	Amines	3500-3300(m) stretch 1650-1580 (m) bend
C-N	Amines	1340-1020(m) stretch
C= N	Nitriles	2260-2220(v) stretch
NO_2	Nitro Compounds	1660-1500(s) asymmetrical stretch 1390-1260(s) symmetrical stretch

FTIR SPECTRA DATABASE

The EUPHORE FTIR Cross-Sections Database created in IALSI project

Joined to the EUROCHAMP-2 database

Spectra in the database

Mid-IR spectra (4000 – 400 cm^{-1})

Gas-phase

257 spectra

136 different compounds

73 calibration documents

Useful information on spectra

Access free upon registration

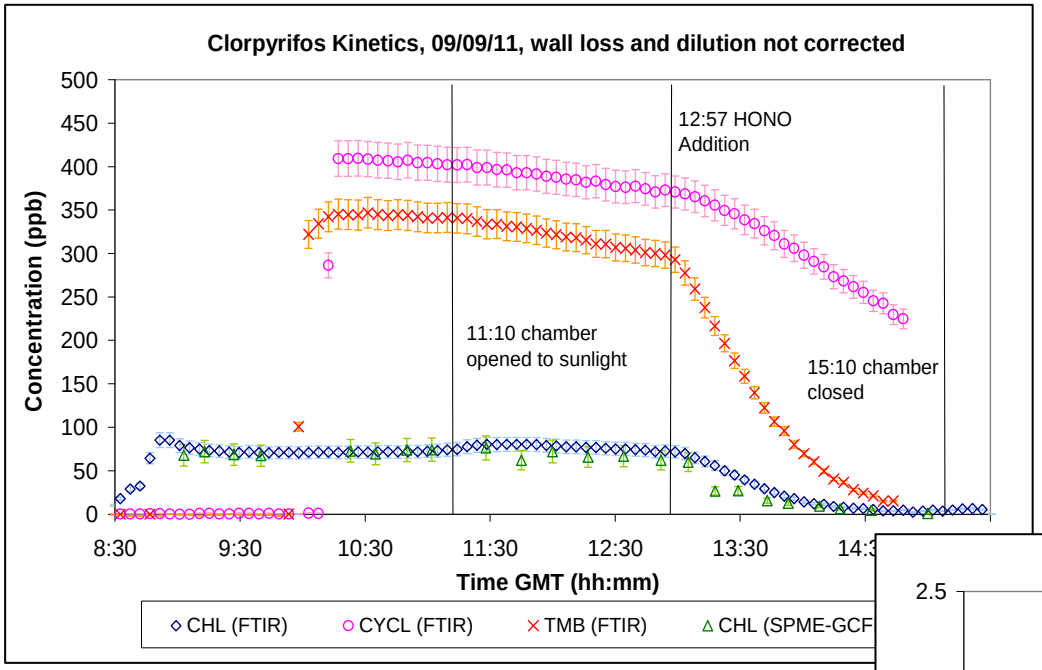
http://euphore.es/FTIRReferences2/login.php

FTIR analysis software

- Developed at CEAM
- Based on classic minimum square fitting
- Allows to filter overlapping broadband curves (aerosols, optical misalignment or broad absorptions of unknown compounds)
- No training needed or high number of concentration varying spectra (PCA, neural network, etc)
- Reduces the required intervention of the analyst
- Eliminates interferences, i.e. decreases the residual noise improving the data quality
- Useful in complex gas mixtures with overlapping compounds (common in real IR samples)

Ródenas, 2008

A case study: Chlorpyrifos - Kinetics



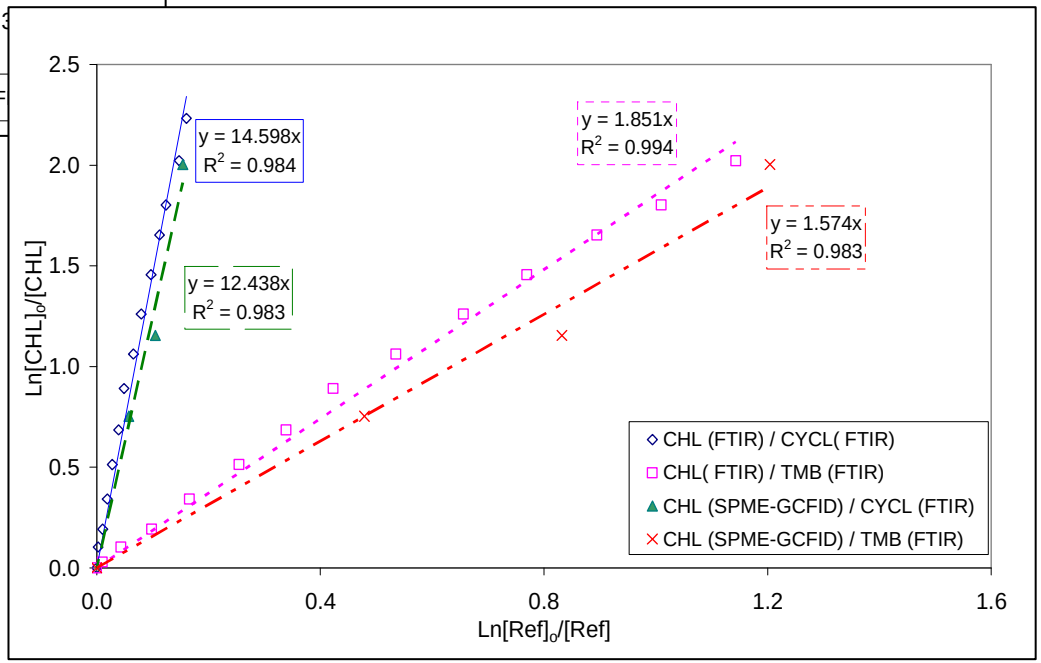
J: Photolysis Rate constant

$K(_{OH})$: Rate constant for the reaction of CHL with OH (relative method)

$K(_{O3})$: Rate constant for the reaction of CHL with Ozone

↓

Life time



Muñoz et al., 2014

A case study: Chlorpyrifos - Products

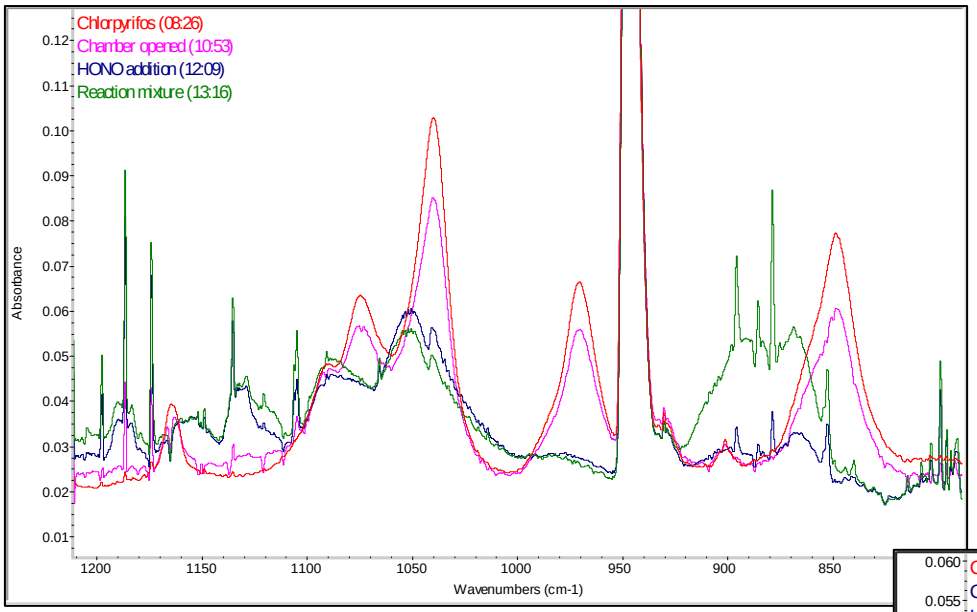


Photo-oxidation of Chlorpyrifos

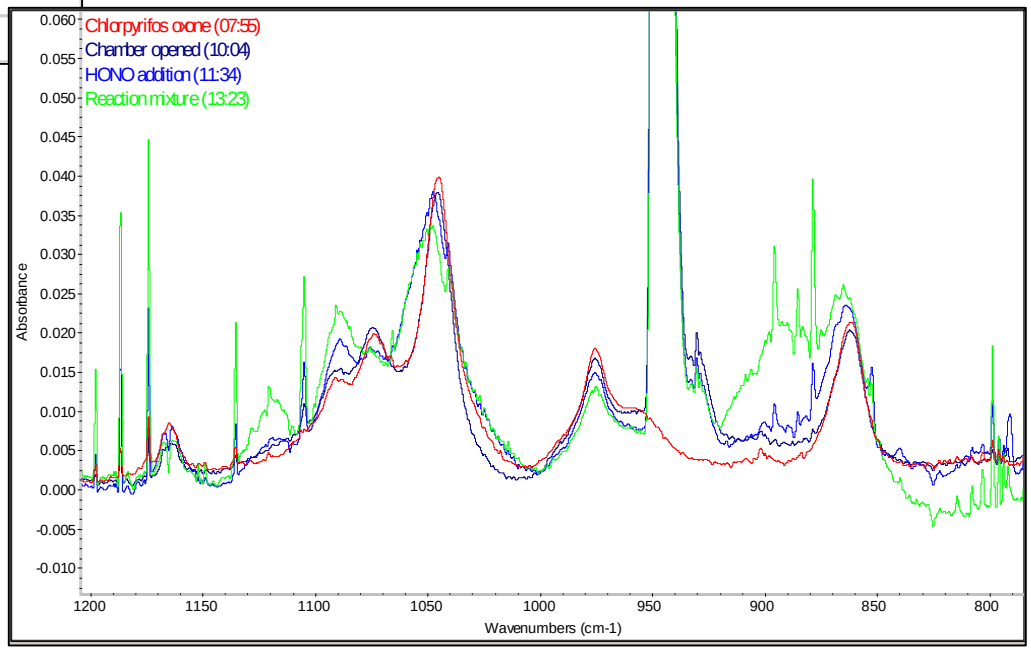
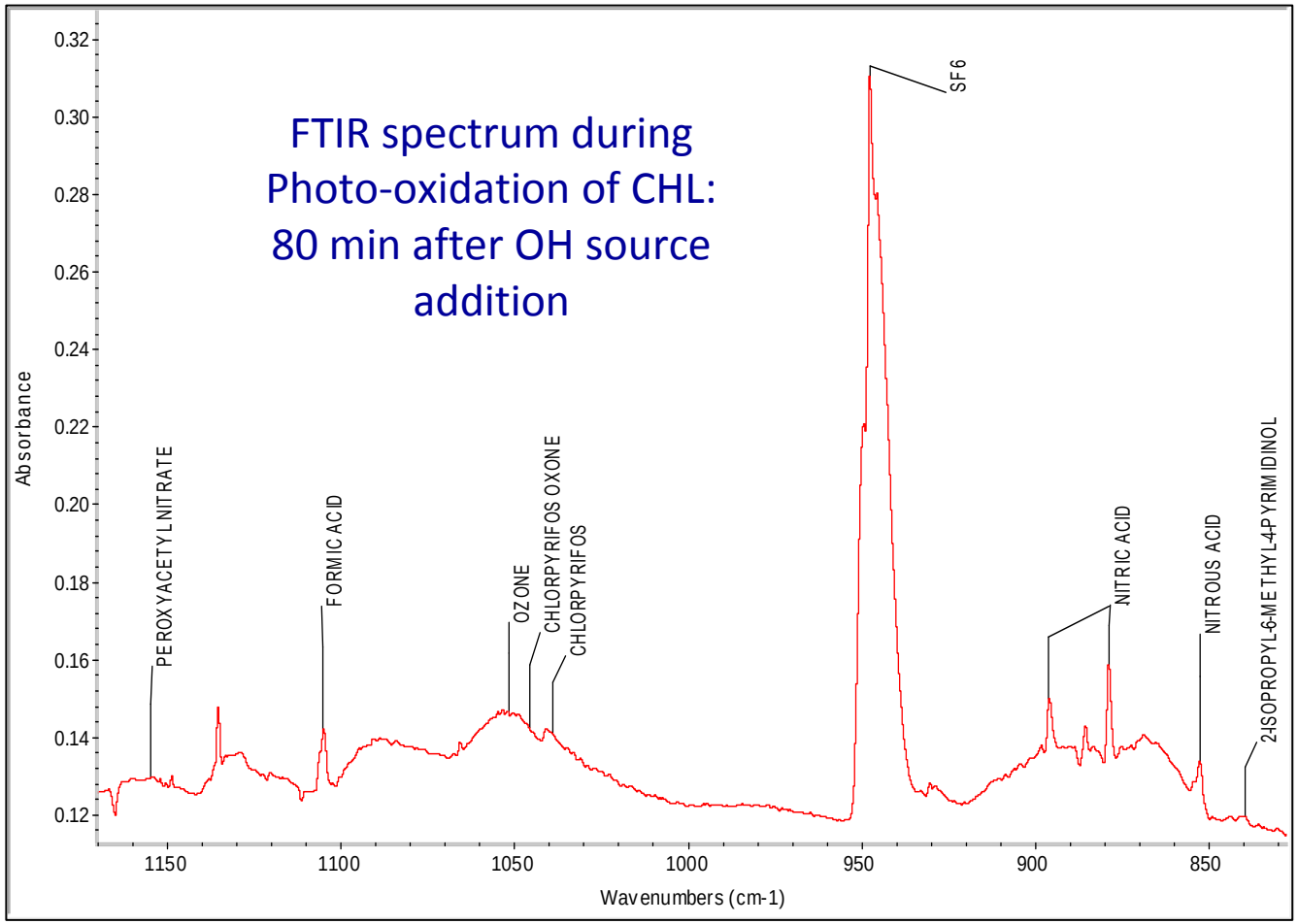


Photo-oxidation of Chlorpyrifos-oxone

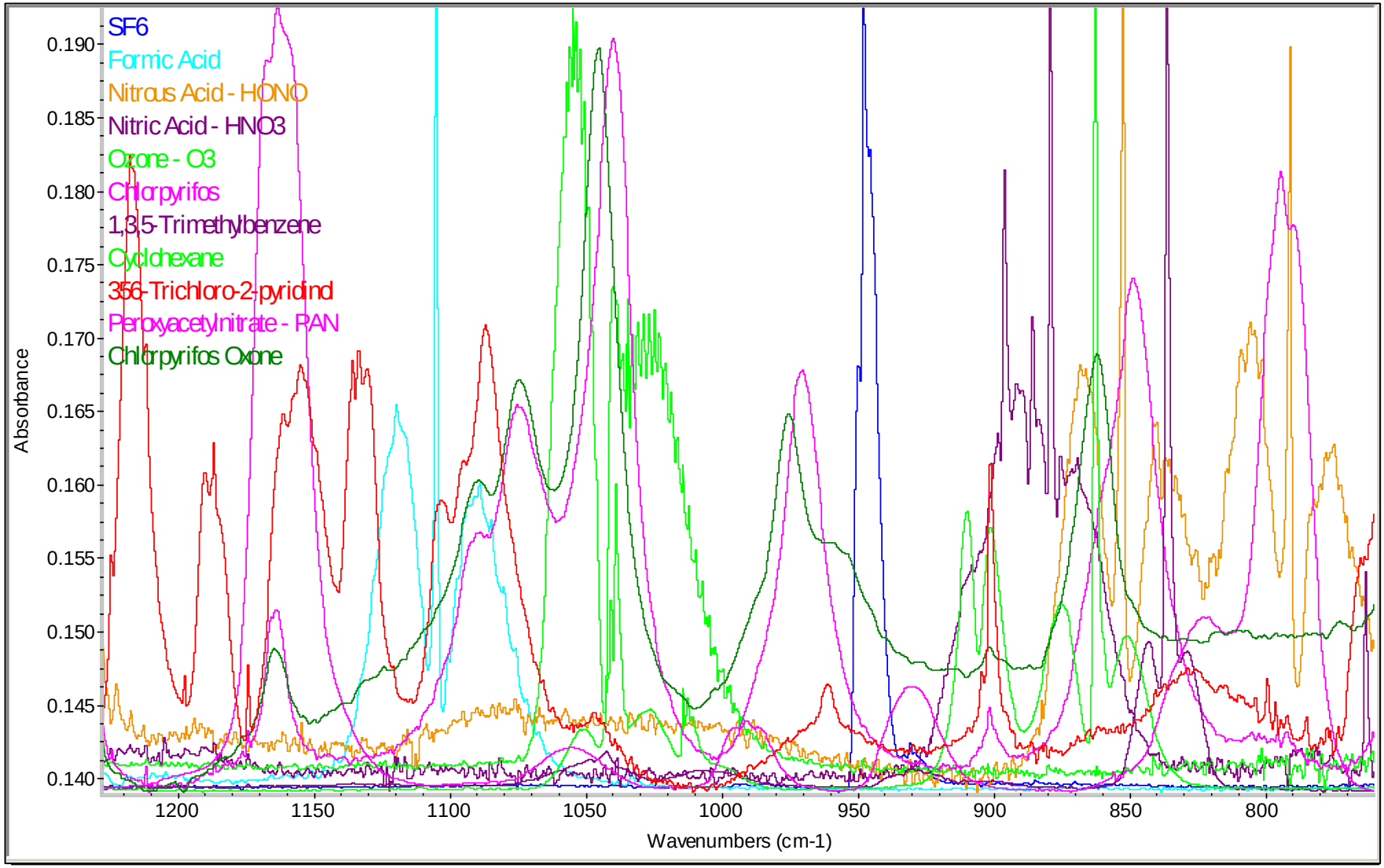
A case study: Chlorpyrifos - Products



A case study: Chlorpyrifos - Products

CEAM
FUNDACIÓN CENTRO DE ESTUDIOS AMBIENTALES DEL MEDITERRÁNEO

Reference spectra of compounds in the mixture

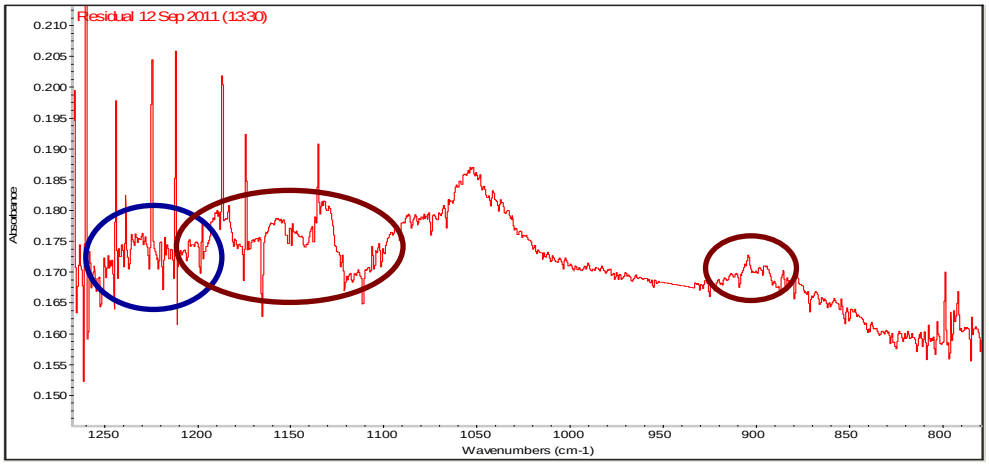


A case study: Chlorpyrifos - Products

COMPOUND	FORMULA	CAS NUMBER	DETECTION LIMIT (ppb)	ACCURACY	ANALYSIS REGION (cm^{-1})
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	2921-88-2	1.7	30.0%	760 - 1225
Chlorpyrifos-oxone	$C_9H_{11}Cl_3NO_4P$	5598-15-2	3.0	30.0%	760 - 1225
1,3,5-Trimethylbenzene	C_9H_{12}	108-67-8	1.3	2.0%	800 - 860
3,5,6-Trichloro-2-pyridinol	$C_5H_2Cl_3NO$	6515-38-4	4.0	30.0%	760 - 1225
O,O-diethylphosphate	$C_4H_{11}O_4P$	598-02-7	2.0	30.0%	760-1225
Chlorhidric acid	HCl	7647-01-0	2.7	30.0%	2700-2900
Cyclohexane	C_6H_{12}	110-82-7	15.3	9.0%	800 - 1100
Cyclohexane	C_6H_{12}	110-82-7	0.7	7.0%	2800 - 2900
Formaldehyde	HCHO	50-00-0	3.0	3.3%	2700 - 2900
Formic acid	HCOOH	64-18-6	0.7	4.5%	1050 - 1150
Glyoxal	$C_2H_2O_2$	107-22-2	2.5	8.0%	2750 - 2900
Chloridric acid	HCl	7647-01-0	2.7	30.0%	2700 - 2900
Nitric acid	HNO_3	7697-37-2	3.4	4.5%	825 - 950
Nitrous acid	HONO	7782-77-6	2.5	7.0%	760 - 900
Methylglyoxal	$C_3H_4O_2$	78-98-8	2.7	15.0%	2750 - 2900
Ozone	O_3	10028-15-6	3.0	10.0%	950 - 1100
Peroxyacetyl Nitrate	$C_2H_3NO_5$	2278-22-0	0.7	3.0%	760 - 1225
Sulfur hexafluoride	SF_6	2551-62-4	0.1	10.0%	920 - 955

A case study: Chlorpyrifos - Products

Residual: Photo-oxidation of CHL

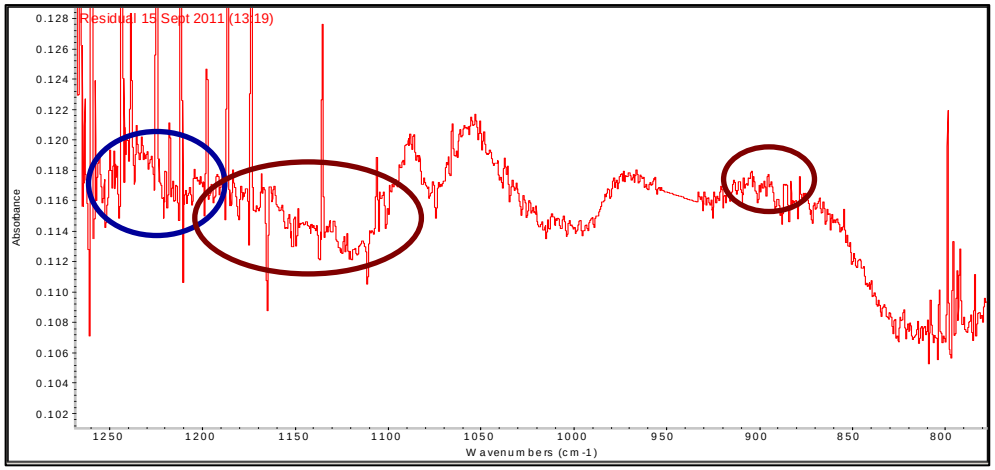


905 cm^{-1}

1120 – 1210 cm^{-1}: $(C_2H_5O)_2P(S)OH$ or desethylchlorpyrifos $(C_5HNCl_3O)(C_2H_5O)P(S)OH$ Compatible with P=S or SO_2 groups

1230 cm^{-1}: (P=O stretch) O,O-diethyl phosphate

Residual: Photo-oxidation of CHLO



Complement Validate mechanisms

Conclusions

DOAS

- Determination of cross section of pesticides

FTIR

- Good time resolution
- Successfully used to study pesticide behavior
- Follow-up of reactives and of products
- Kinetic parameters
  J, photolysis rate constants
  $K(_{OH}, _{O3}, \ldots)$
  Life time
- Confirmation of pathways in reaction mechanisms

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