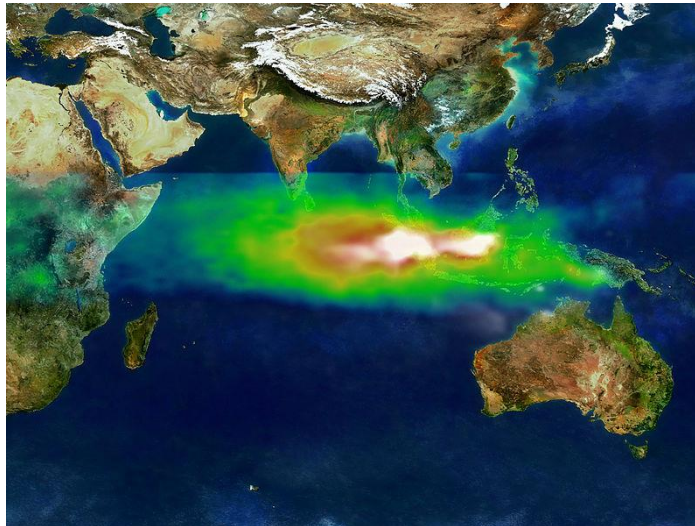


Measurement of Aldehydes such as Formaldehyde in ambient air using the airmoHCHO analyzer

Ozone precursors

- Ozone concentration has multiplied 5 times in the last century in the middle latitudes of the northern hemisphere:
 - From 10 ppb in 1874
 - To approximately 50 ppb today (increase of 1.6% per year)
 - The trend is higher (2.4% a year) over the last decades.¹
- In order to stop this global trend, directives have been written concerning the reduction of ozone precursors emissions (NO_x, VOC like formaldehyde) to define national emission maxima.



¹The International Geosphere-Biosphere Program - World Climate Research Program

²http://visibleearth.nasa.gov/view_rec.php?id=1651

- 100+ different chemicals
- Anthropogenic sources
 - BTEX from road traffic
 - Chlorinated compounds from industries
- Biogenic sources
 - Isoprene and Monoterpenes from trees
 - Natural emissions occur predominantly in the tropics (23° S to 23° N)
- VOCs and PM 2.5 relation
 - 50% of dry mass PM 2.5 are composed by OA: Organic Aerosol
 - 60% SOA Secondary Organic Aerosol from VOCs ^{1,2}



¹ Kanakidou et al. *Atmos. Chem. Phys.*, 5 2005.

² Haddad et al. *Atmos. Chem. Phys. Discuss.*, 2010

- European list 31 VOCs including BTEX and **formaldehyde** (WG13 work on new European list)
 - In Europe, ambient air legislation targets Benzene
 - With annual target value of 5 $\mu\text{g}/\text{m}^3$
- US EPA lists
 - PAMS 56 including BTEX or 58 (including alpha and beta pinenes) – **formaldehyde included**
 - New PAMS 61 including BTEX, 1-3 Butadiene, alpha and beta pinenes – **formaldehyde included**
 - TO14: including BTEX, Cl-VOCs
 - TO15: including BTEX, Cl / Br / O-VOCs

A. Objectives

The main objectives of such measurements are to analyze any trend in ozone precursors, to check the efficiency of emission reduction strategies, to check the consistency of emission inventories and to help attribute emission sources to observe pollution concentrations.

An additional aim is to support the understanding of ozone formation and precursor dispersion processes, as well as the application of photochemical models.

B. Substances

Measurement of ozone precursor substances shall include at least nitrogen oxides (NO and NO₂), and appropriate volatile organic compounds (VOC such as formaldehyde). A list of volatile organic compounds recommended for measurement is given on next slide.

C. Siting

Measurements shall be taken in particular in urban or suburban areas at any monitoring site set up in accordance with the requirements of this Directive and considered appropriate with regard to the monitoring objectives referred to in Section A.

ANNEX X of European directive 2008/50/EC

Ozone precursors

Analyzed by airmoVOC C2 to C6

- C2** Ethane = C2
Ethene / ethylene
- C3** Propane = C3
Propene
isobutane (2-méthyl propane)
- C4** n-butane = C4
Acetylene
trans-2-butène
1-butene
1,3-Butadiene
cis-2-butène
Iso-pentane (2-methyl butane)
- C5** n-pentane =C5
1-pentene
2-methylpentane = I Hexane
- C6** n-hexane =C6
isoprene

Analyzed by airmoVOC C6 to C12

- C6** Benzene
- C7** n-heptane = C7
Toluene
- C8** 2,2,4-trimethylpentane
= Iso Octane
n-octane =C8
Ethylbenzene
m-xylene
p-xylene
o-xylene
- C9** 1,3,5 trimethylbenzene
1,2,4 trimethylbenzene
1,2,3 trimethylbenzene

Analyzed by airmoHCHO

Formaldehyde

Analyzed by ChromaTHC

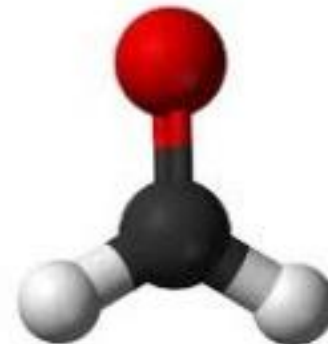
Total non-methane
hydrocarbon



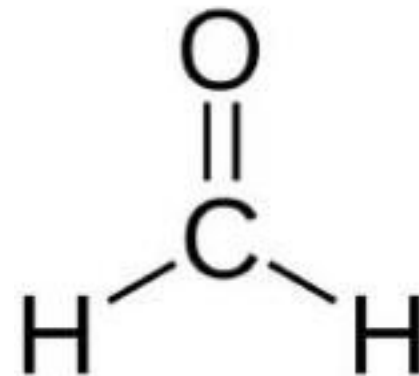
Many other VOCs can be added to this list and monitored with the same system

Why analyze formaldehyde ?

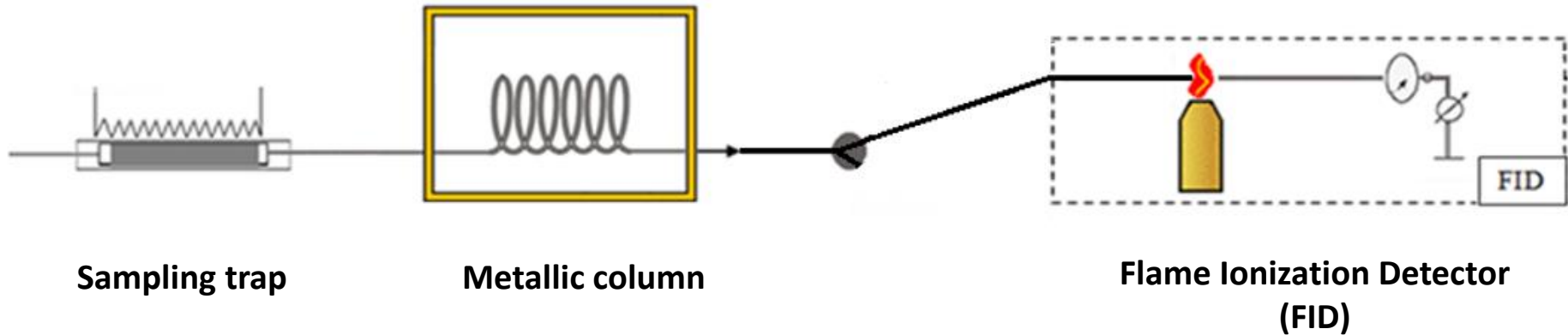
- Formaldehyde is present in :
 - Chemical, pharmaceutical, funeral industries
 - Paper plants
 - Indoor air (paintings, coatings)



- Formaldehyde effects :
 - Irritating, breathing issues (<500 ppb)
 - Carcinogenic (>500 ppb)
 - Risk of death (> 20 ppm)



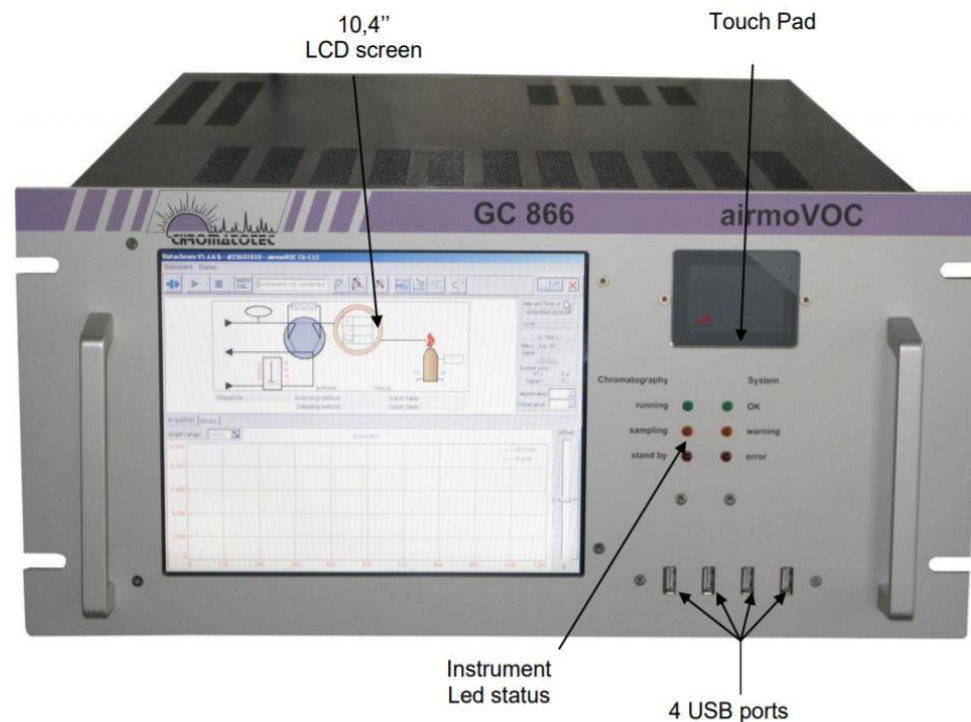
Measurement principle : GC FID



- Separative method
- Identification with retention time
- Linearity for every concentration range

airmoHCHO external overview

- Auto GC-FID
- Embedded computer
- Integrated software
- Air, N₂, H₂ generators can be integrated
- Cabinet version
- Internal calibration with permeation tubes



airmoHCHO internal overview

Pressure regulator for permeation
flow adjustment

Pressure regulator for carrier
gas flow on the column

Permeation oven

Oven with programable
temperature and metallic
column inside

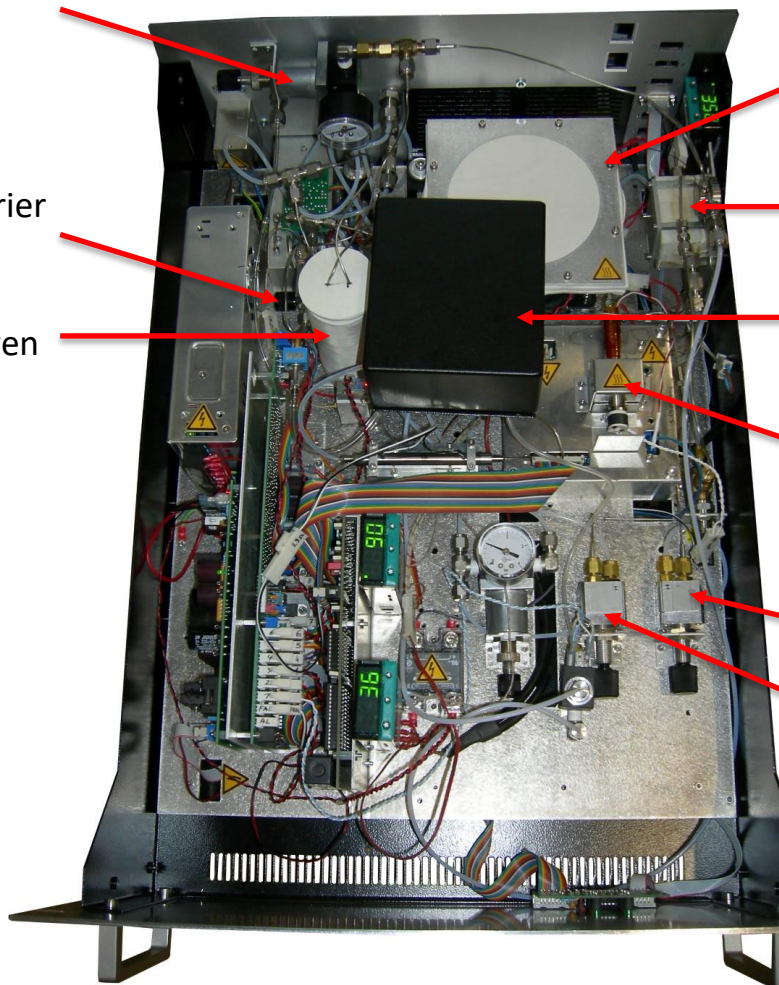
Methanizer

Injection valve 6-ports with
sampling trap and pre-column

FID Detector

H₂ flow regulator for flame

Air flow regulator for flame

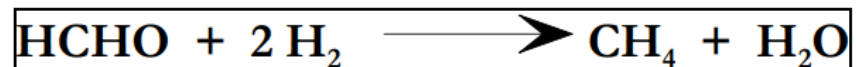


Measurement principle : analysis cycle

- Sampling step :
 - Pre concentrate VOCs in the trap
 - Realized at the end of analysis cycle to reduce cycle time
- Analysis step :
 - Injection of trapped VOCs in the column by thermo desorption
 - Separation in analytical column
 - Methanization of VOCs
 - Detection by FID

- Principle

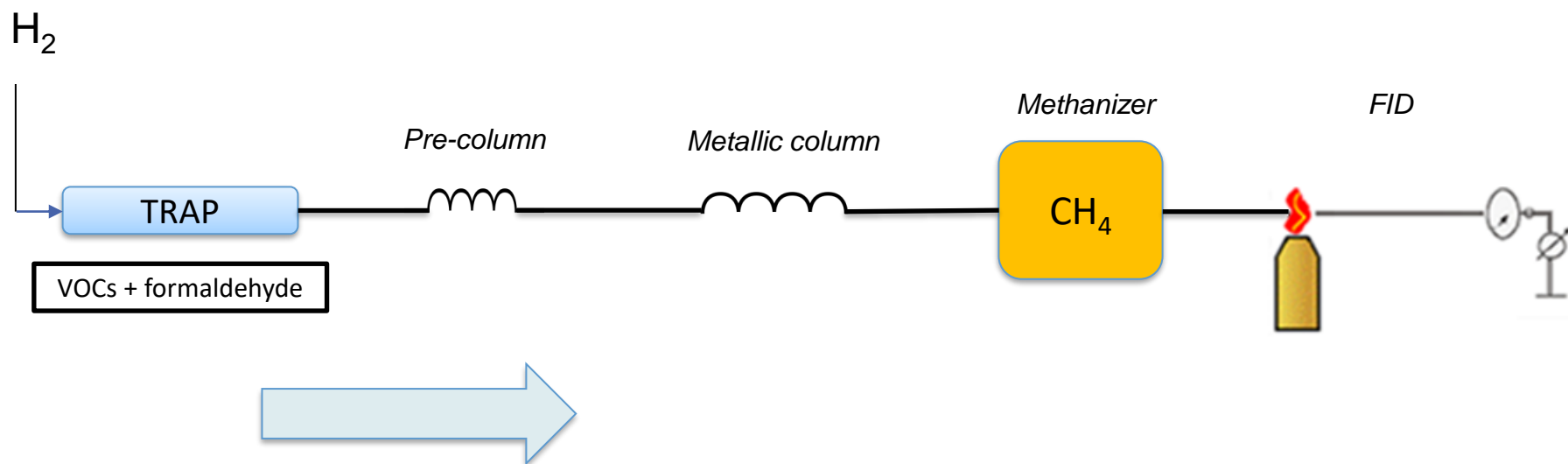
- Transform aldehyde compounds such as formaldehyde to methane
- Using ruthenium to catalyze



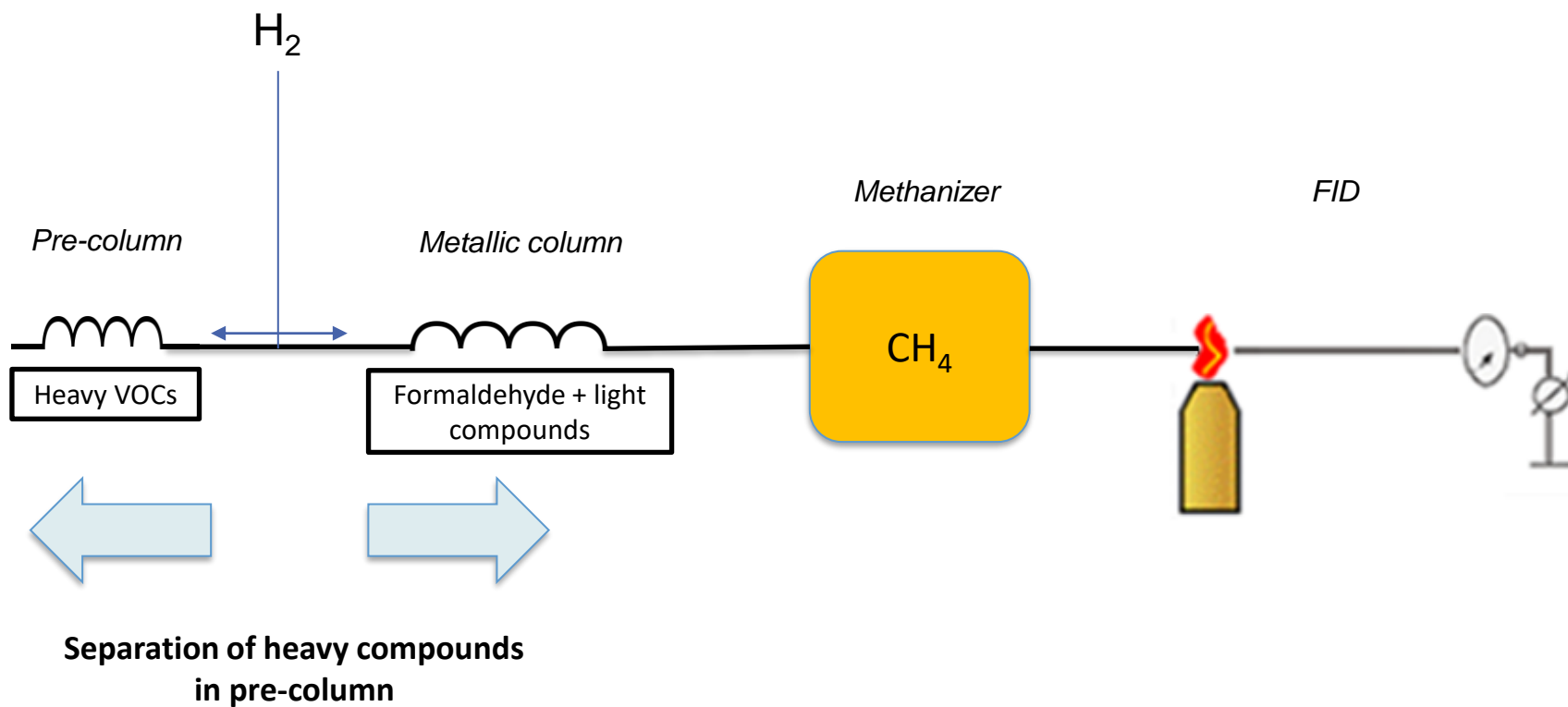
- Advantages

- HCHO has a bad response with FID Detector
- CH₄ is well detected by FID

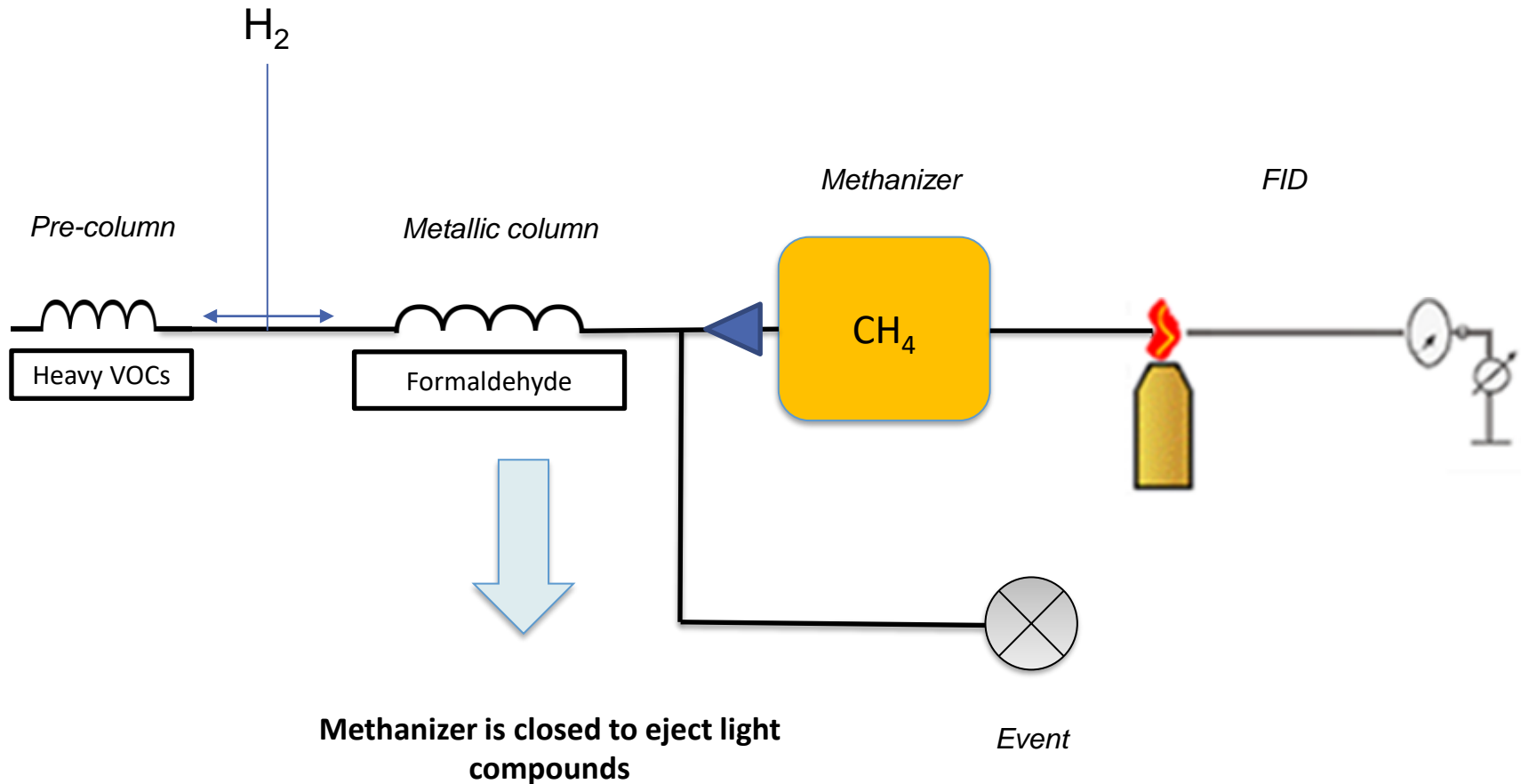
Step 1 : Thermo-desorption



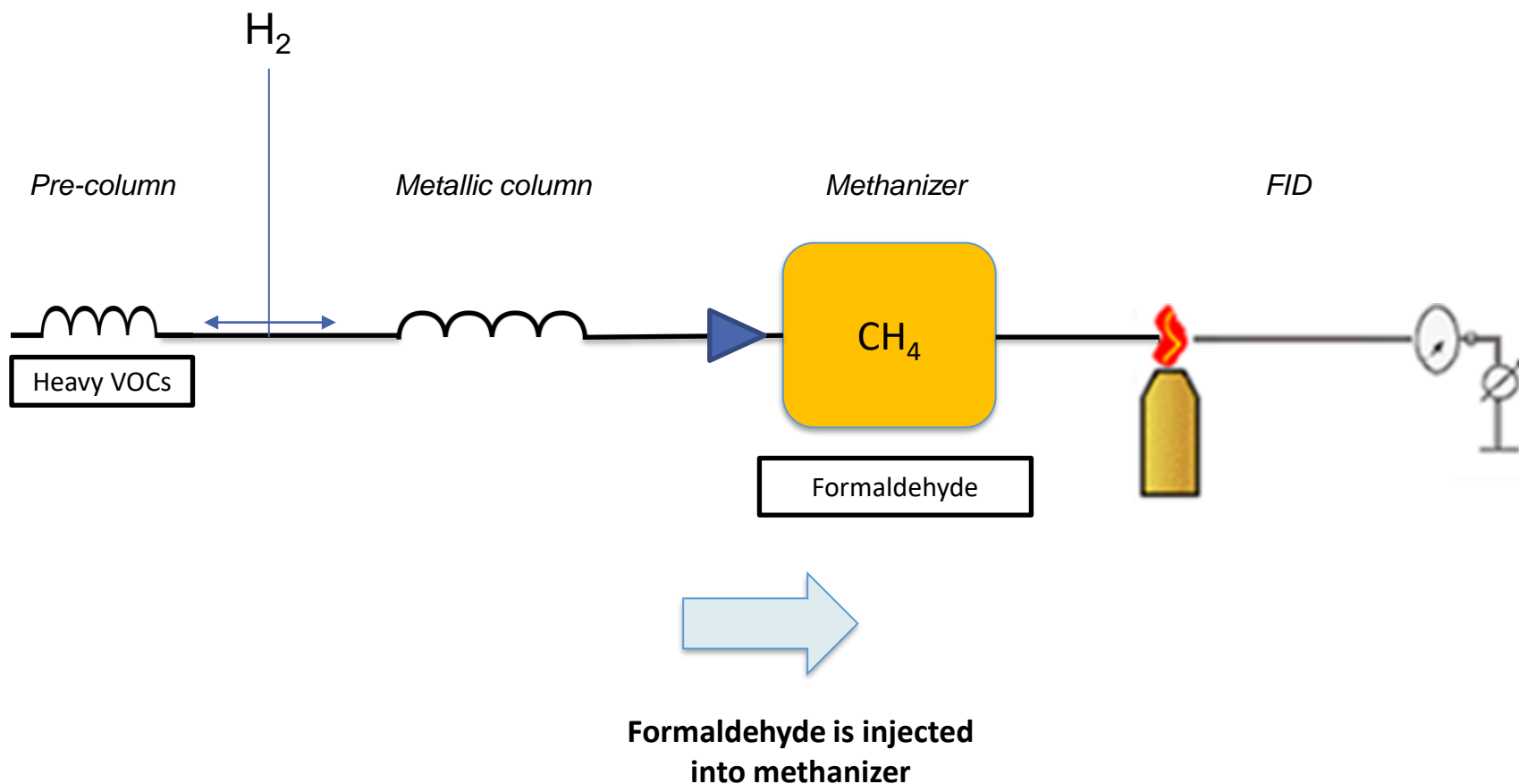
Step 2 : First separation



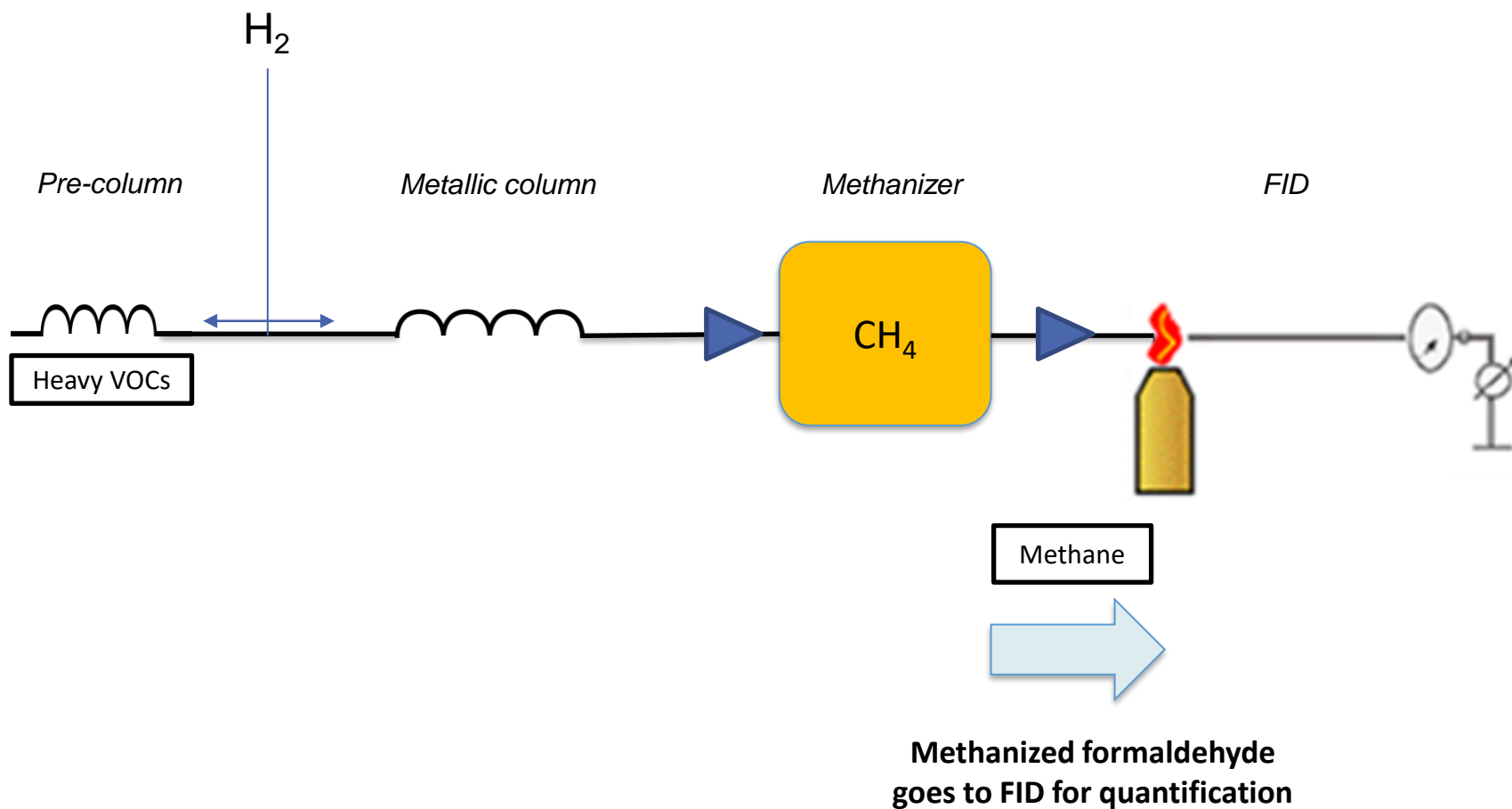
Step 3 : Separation of light compounds



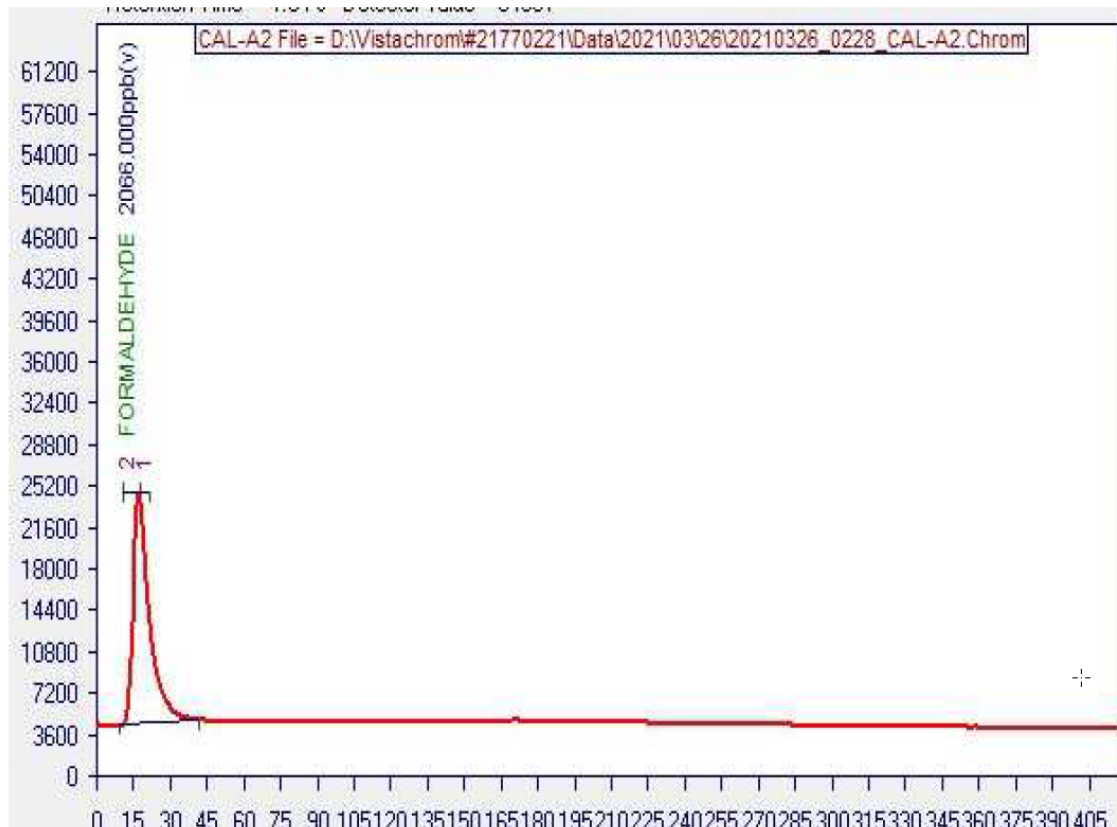
Step 4 : Methanization of formaldehyde



Step 5 : Detection of formaldehyde

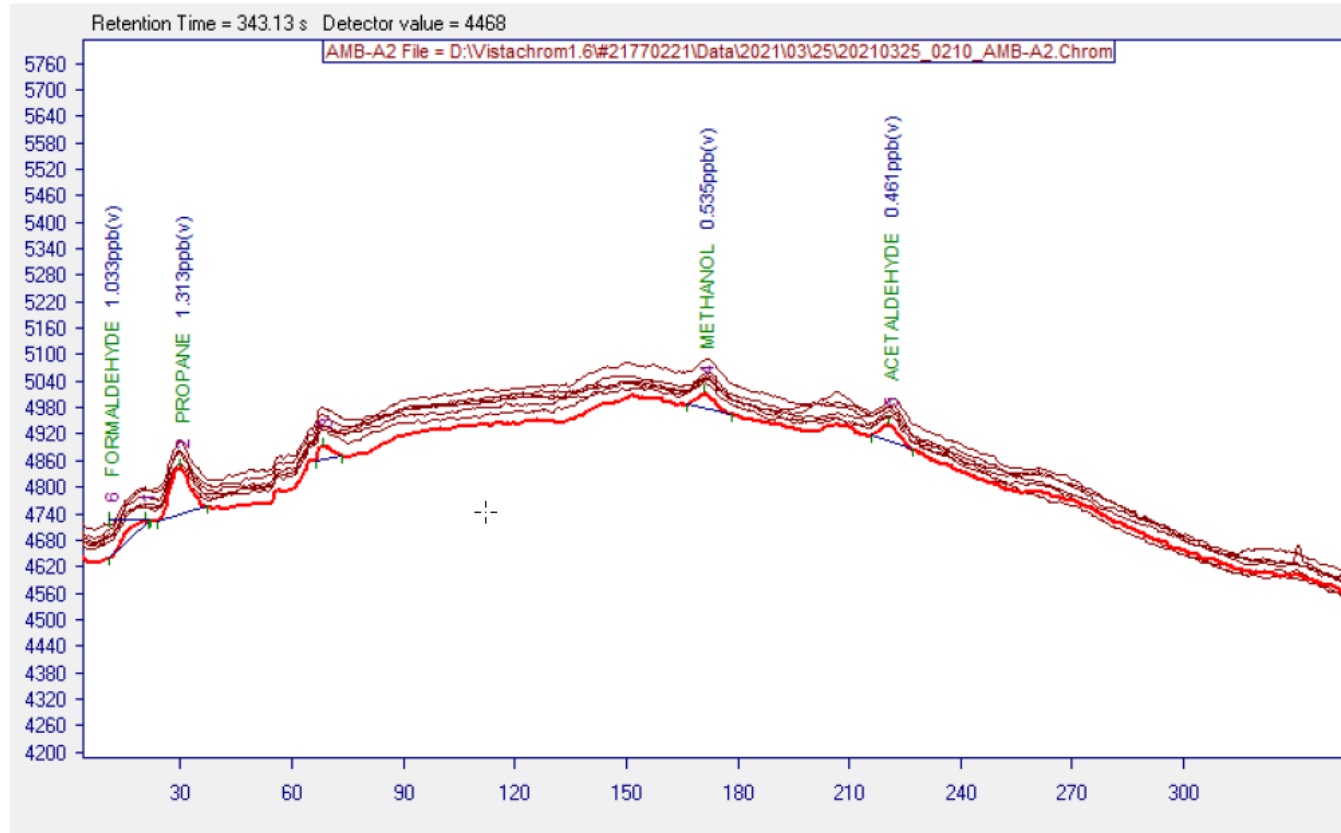


Results for permeation tube analysis



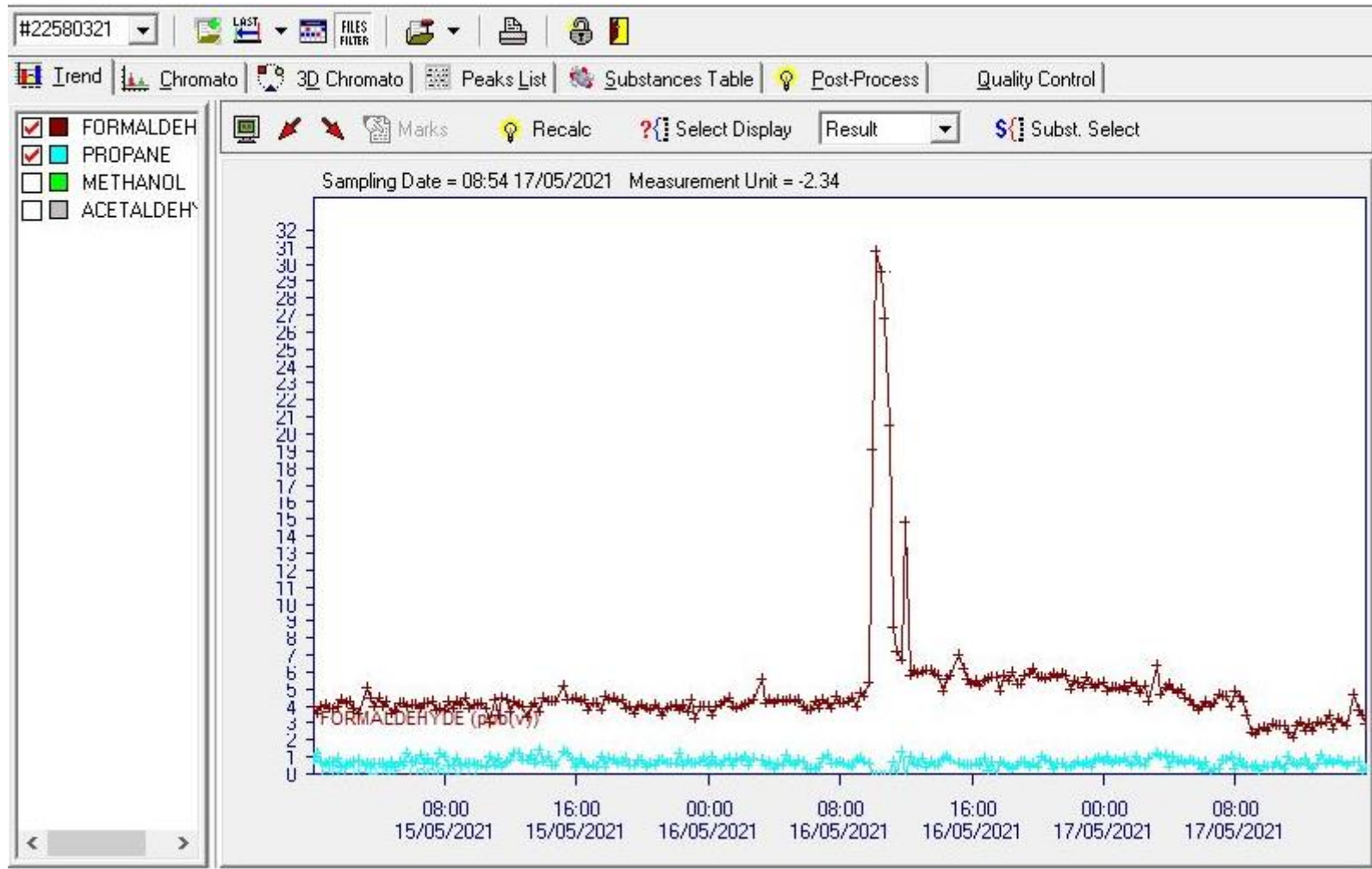
- Configuration permeation tube :
 - [HCHO] = 2023 ppb
 - Gas Temperature : 90° C
 - Gas flow : 111,98 ml/min
 - Sampling time : 300s
 - Acquisition time : 420s
- Results :
 - [HCHO] = 2066 ppb
 - Theoretical deviation : 2%

Ambient air analysis



- Cycle time : 15 min
- Concentration : 1,1 ppb
- Limit of Detection : 0,3 ppb

Ambient air trend



Repeatability

Sampling date	Volume	FORMALDEHYDE in ppb(v)
12/06/2019 18:03	50.76	2968.00
12/06/2019 18:18	50.76	2983.00
22/05/2018 08:33	50.76	3025.00
22/05/2018 14:48	50.76	3040.00
22/05/2018 19:03	50.76	3036.00
23/05/2018 19:18	50.76	3034.00
Average	50.76	3014.33
Standard deviation	0.00	30.85
RSD in %	0.00%	1.02%
Nber of measurements	6	6

Best features airmoHCHO



Online Gas and Liquid Analyzer Experts

- High availability of data with low maintenance in comparison to lab GC
- Flexible: more compounds can be added
- Full remote access capability with total control of the system including: C2C6 autoGC, C6C12 autoGC, airmoCAL MFC, HYDROXYCHROM
- Compact and easy to install in the field
- Customized option like : *automatically switch on a device (i.e., canister) to fill in a canister during pollution event when concentration exceeds limits."*

Advantage of this solution



Online Gas and Liquid Analyzer Experts

- Short cycle time (15 min) compared to ISO 16000-3:2011
- Automatic solution
- No interferences with chromatography
- Visualization of data

Technology comparison

Specification	Reference method DNPH	aerolaser	Laser CRDS	Chromatotec airmoHCHO
Detection principle	Derivatization method with DNPH Spectrometer	Thermal desorption and fluorimetric detection (Hantzsch reaction)		GC with FID and methanizer
LDL	Around 10ppb	Around 0,1ppb		Less than 1 ppb in automatic
Linearity		Linear from 0,1 to 3000ppb with $R^2 > 0,999$		Linear on peak area $R^2 > 0.995$ for each compound at ppb or ppm
Long term stability				RSD on 48 hours $< 2\%$ at 2 ppm for all compounds
Interferences	Other aldehydes	Other aldehydes		Not sensitive to humidity and hydrocarbons.
Compounds measured	Formaldehyde	Formaldehyde		Formaldehyde Methanol Acetaldehyde

Feedback from scientific researchers confirm that other solutions are not able to continuously monitor formaldehyde at low ppb (0-30ppb) range accurately

- Ambient air monitoring in urban and rural areas
- Industrial fence line monitoring
- Transportable version for onsite formaldehyde monitoring
- Chemical, pharmaceutical, funeral industries
- Paper plants
- Indoor air (paintings, coatings) & Clean rooms

- Customers profiles
 - Governmental agencies (EPA, INERIS)
 - Meteorological institutes
 - Universities and Research centers
 - Industrial consortia
 - Petrochemical groups

Example of installation



Emergency mobile van for industrial area with full airmOzone MS

Mobile van:

airmOzone and GCMS design to be installed in fixed or **mobile station**

ReStart in less than 1 hour
No need to tune after transport



Emergency mobile van for waste water treatment plant in Paris with VOCs and sulfurs

Some reference customer

- GIOS Poland (Chief Inspectorate Of Environmental Protection)
 - Ambient air Formaldehyde monitoring in forest area for ultra trace analysis
 - Target is to study the presence and effect of Formaldehyde in ambient air for atmospheric chemistry research

Some reference customer

- ULCO - France
 - “Centre Commun de Mesure” – for industrial site monitoring
 - Customer desired a portable unit to monitor formaldehyde level on industrial sites
 - Easy to set up and start up instrument for campaigns
 - All in one solution for campaigns with analyzer, internal calibration, gas generators, embedded computer



Some reference customer

- Donetsk Region – Ukraine
 - Industrial fence line monitoring for formaldehyde
 - Customer wants to control the emission released in the atmosphere and more especially formaldehyde concentration
 - Level of concentration at ppb-ppm level
 - Online monitoring 24/7
 - Automatic alarms reported by Vistachrom supervisor and through datalogger

airmoHCHO is :

- Very specific to formaldehyde, acetaldehyde and methanol at low ppb level in complex matrices (no interference)
- Automatic quantification limit less than 1ppb
- Automatic data validation at ppb level with internal HCHO permeation tube
- Automatic control of the system with propane standard
- GC instrument which allows quantification and identification of HCHO, acetaldehyde and methanol

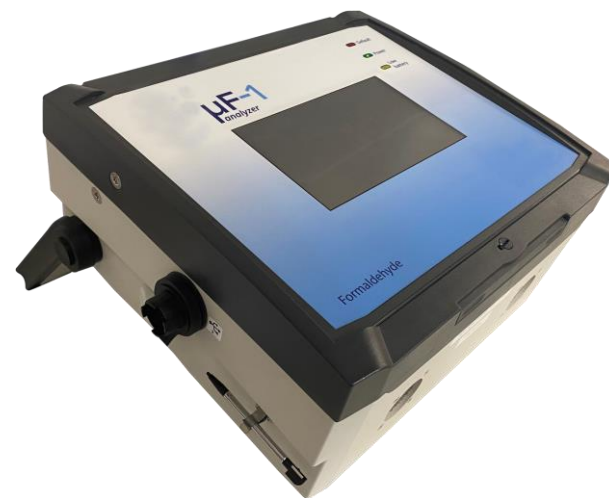
airmoHCHO Keypoints

airmoHCHO is :

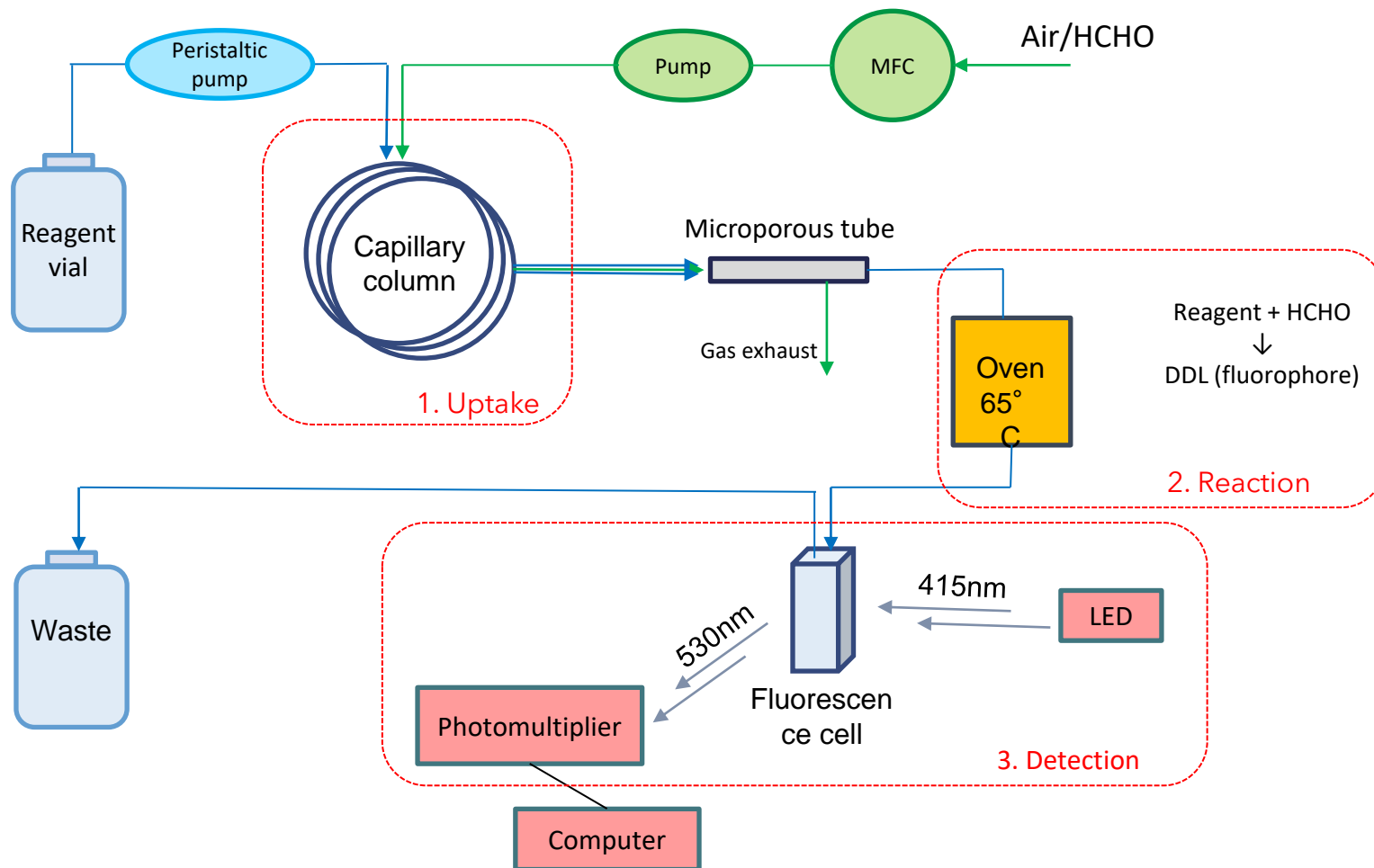
- Designed for process control application
- Continuous online sampling
- Very Low maintenance
- No use of liquid chemical for derivitization
- Fast measurement: Total measurement is 15 minutes - important for identification of punctual events
- Additional system to airmozone and airmozone-MS for full ozone precursors monitoring

New portable micro Formaldehyde analyzer

Dimension	32 cm × 28 cm × 15 cm
Weight	6,5kg
Limit of detection	1 µg/m ³
Linearity range	0 – 400 µg/m ³
Trapping type	Microfluidic annular flow
Derivatization reagent	Fluoral-P (acetylacetone)
Detection type	Fluorescence



Principle Scheme

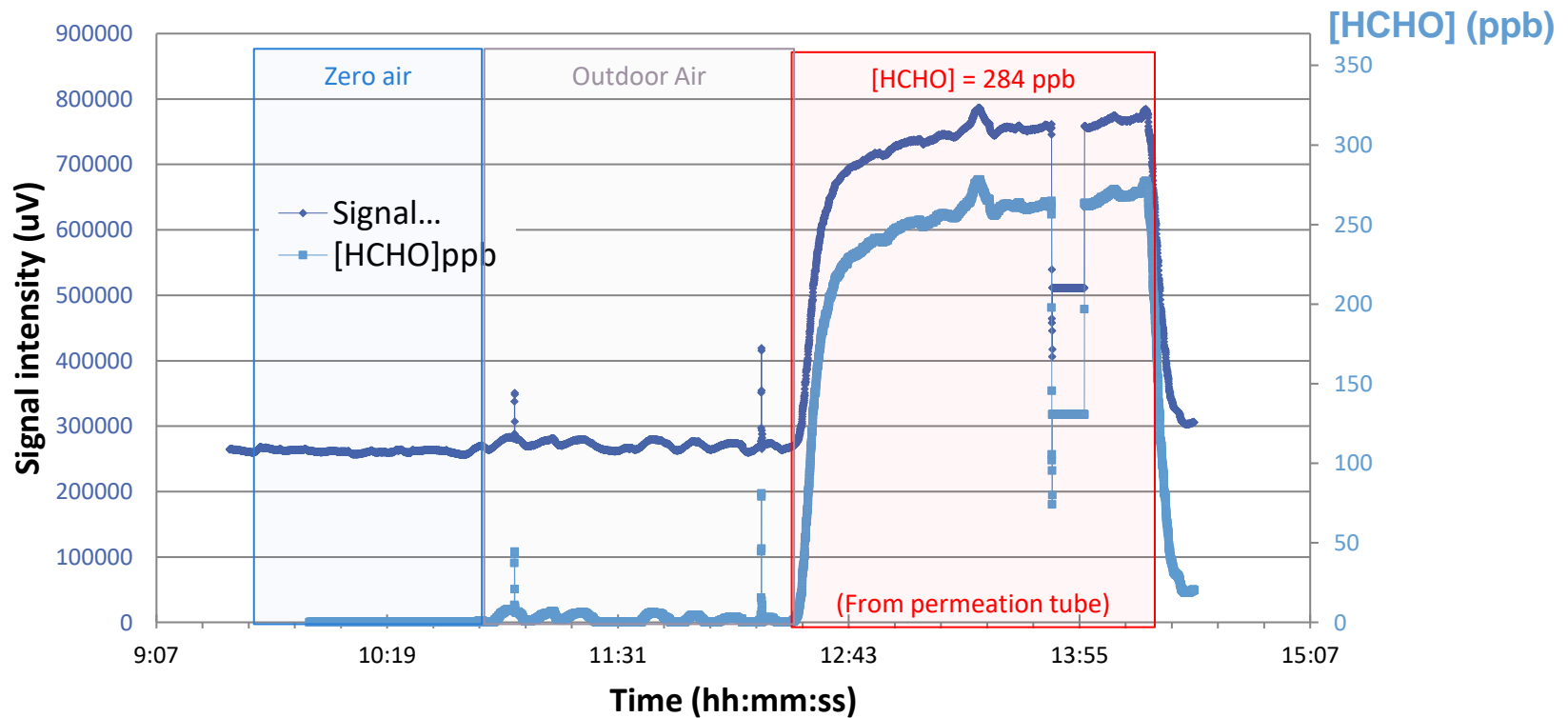


gas
liquid

Principle - Typical curve

- Intensity curve
- Concentration curve ($\mu\text{g}/\text{m}^3$ or ppb)

$\mu\text{F-1}$ sampling tests





**THANK YOU FOR YOUR
ATTENTION!**

Next sales Webinar on portable devices

In September!

Questions ?