TRAINING SESSIONS

18th October 2021

Innovative packaging solutions for storage and conservation of 20th century cultural heritage of artefacts based on cellulose derivative

HIGH O_2 BARRIER AND ACTIVE PACKAGING

ACTIVE ACID ADSORBERS

MULTI-SCALE MODELLING

GAS DETECTION SENSORS

PACKAGING WITH MODULAR DESIGN

CURATIVE PACKAGES

NEMOSINE has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760801.

Nanostructured materials and innovative transduction systems: detection of harmful contaminants in cultural heritage protection

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Biosensor srl

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Biosensor srl work field

- Biosensor srl is a SME born in 2003
- Biosensor Srl is based in Via di Olmetti 44, Formello Industrial Zone (RM), which operates in the production and marketing of sensors and biosensors. The Biosensor has two secondary offices in Campania and Friuli.
- Multitask-research company with interests in nanotechnology and biotechnology for environmental, agri-food and biomedical applications
- Wide experience in coordination of bio/sensors based on EU projects

European

Euro Trans Bio

sharing cost, risk and skills of innovation

Space

esa

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Ministero dello Sviluppo Economico

Filas

Finanziaria laziale di sviluppo

Ministero delle Attività Produttive

Ministero dell'Ambiente e della Tutela del Territorio e del Mare

provinciattiva spa

INVITALIA

Biosensor work in NEMOSINE project

- Development of sensors suitable to monitor gases involved in film deterioration
- Optimize the sensitivity and specificity of the sensors using different materials and array configurations
- Generate algorithms/software to process the signal from the sensor(s)

Summary

- Cultural heritage artifact: what is monitored and why
- Current degradation monitoring techniques
- New monitoring solutions developed: working principles and results
- Best sensing solution: software developed and validation on real samples
- Conclusion and future perspectives

Cellulose-based cultural heritage artifacts

- Cellulose and cellulose derived polymers had large use between end XIX and first half XX century
- Used to produce numerous kinds of artifacts from decoration to technical
- Interest in production of cinematographic and photographic films:
  - Cellulose Nitrate (1898 – 1951)
  - Cellulose Acetate (1934 – 1980s)

Monitoring of cultural heritage artifacts: why?

- Cellulose nitrate and cellulose acetate undergo spontaneous degradation over time
- If left unchecked ends in total degradation (destruction) of film/photo support
- Different degradation pathways depending on material
  - Cellulose acetate
    - First water-dependent slow step
    - Fast autocatalytic step after certain acetic acid concentrations reached
  - Cellulose nitrate
    - Complex degradation process involving both nitric oxides and nitric acid

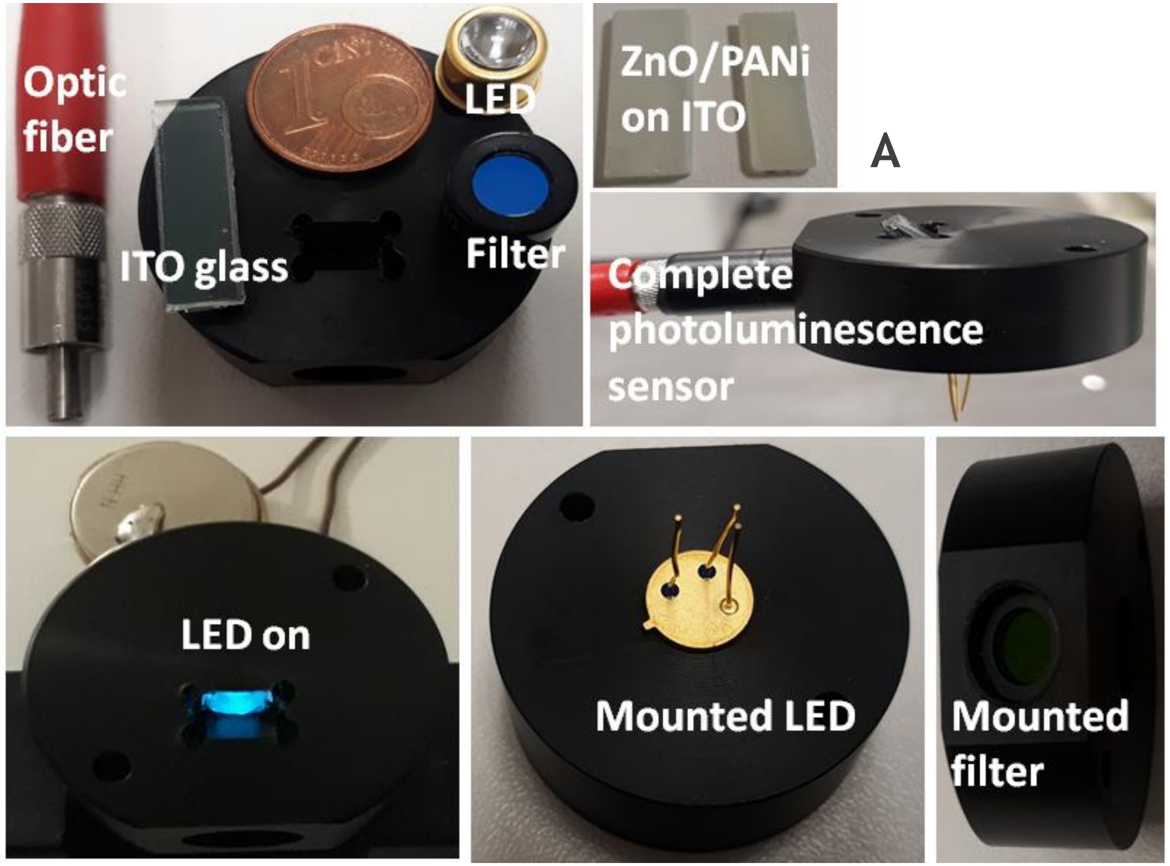
Monitoring of cultural heritage artifacts: how?

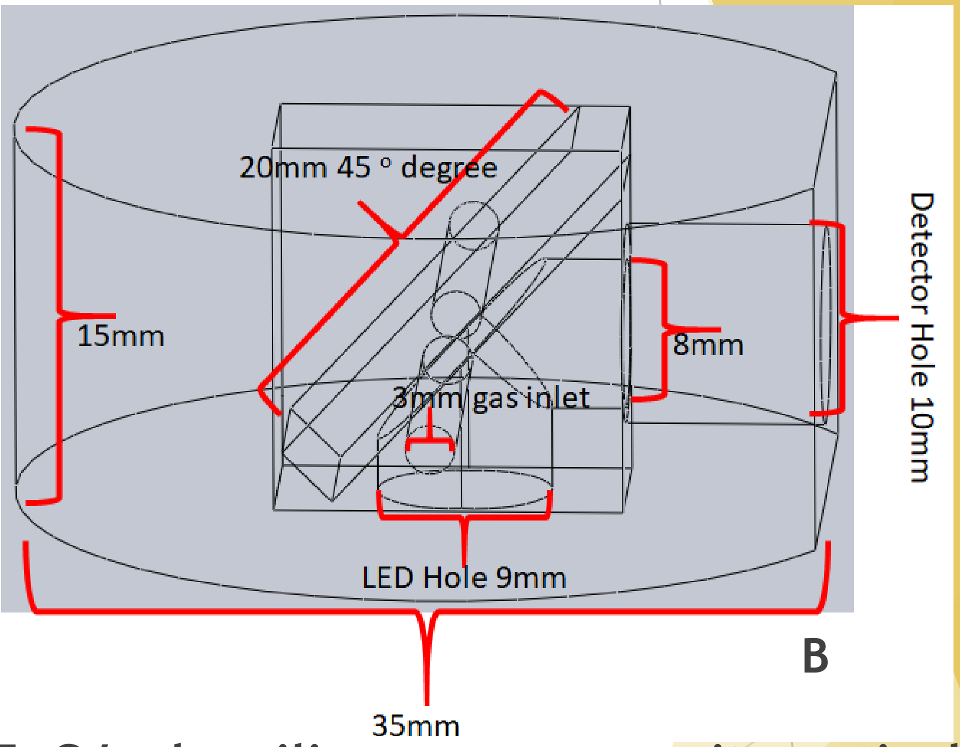
Current monitoring solution to track cellulose support degradation:

- Cellulose acetate → Visual examination of film status
  → Degradation evaluation via A-D strips
- Cellulose nitrate → Visual examination of film status

Conservation institutes request: system for real-time monitoring of volatiles involved in degradation process of cellulose derivative-based films

First developed solution: fluorescence-based instrument based on nanostructured ZnO-Polyaniline

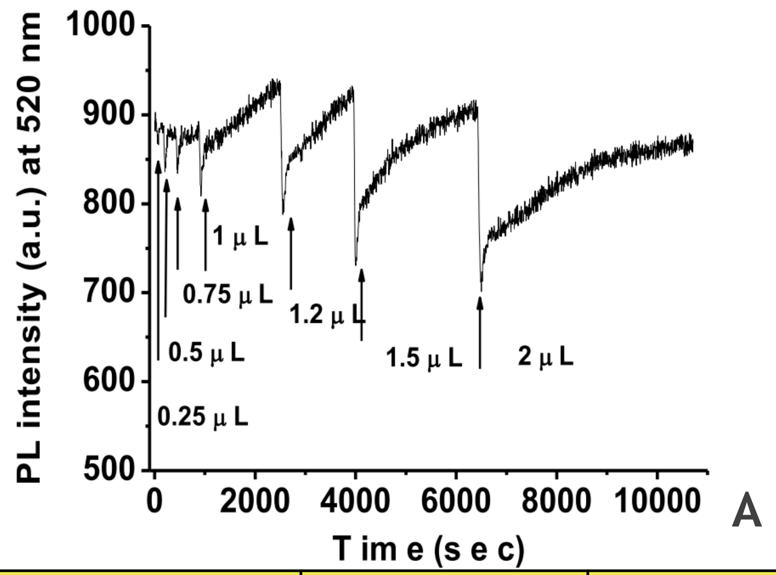


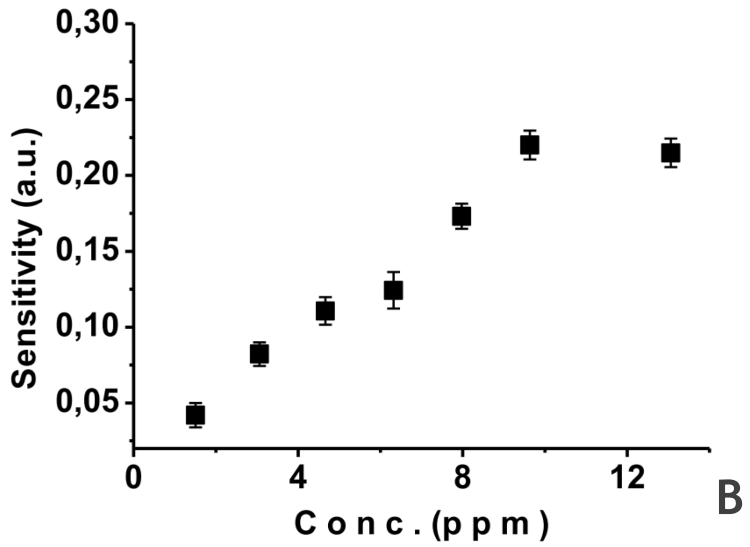


M. Turemis, D. Zappi, M.T. Giardi, G. Basile, A. Ramanaviciene, A. Kapralovs, A. Ramanavicius, R. Viter, ZnO/polyaniline composite based photoluminescence sensor for the determination of acetic acid vapor, Talanta. 211 (2020) 120658. https://doi.org/10.1016/j.talanta.2019.120658.

ZnO/polyaniline nanocomposite optical gas sensor for the determination of acetic acid at room temperatures. (A) Components and assembly of the sensor; (B) Internal structure of the sensing element

First proposed solution: analytical parameters





LOD	Linearity range	Response time	Recovery time	Stability	Selectivity	Resistance against continual exposure to analyte
1,2 ppm	3,6 - 10 ppm	30 s	max 40 minutes	Up to 30 days	No signal when exposed to common interferents	resistive against concentrations of acetic acid in linearity range (1-13 ppm)

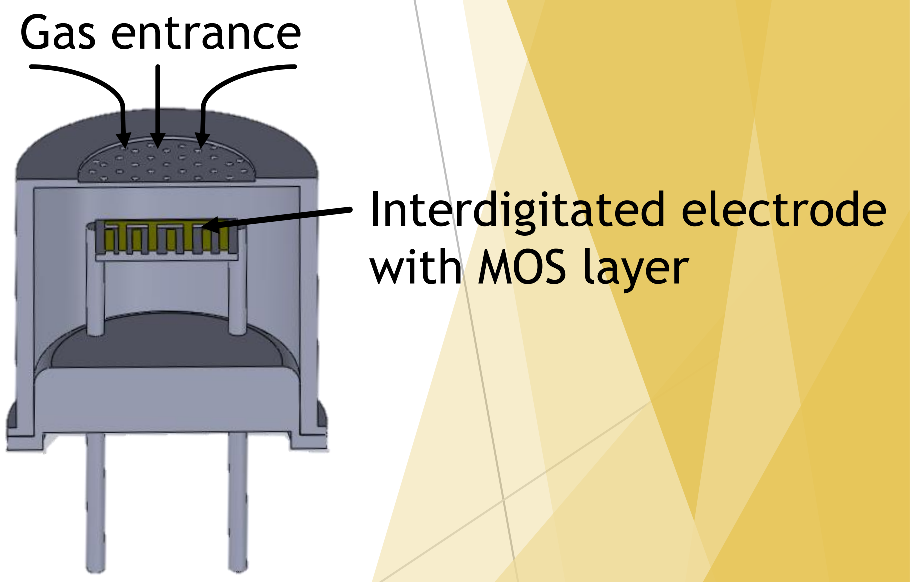
Response curves (A), calibration curve (B) and analytical parameters (table) of developed photoluminescence sensor

- Developed instrument can detect acetic acid vapor at low concentrations
- Small to no interference from other volatiles commonly released by films (i.e., short-chain alcohols, camphor, methylene chloride, butanol, cyclohexane)

- Cons: instrument is too big and power-consuming to be efficiently integrated in film boxes
- Next steps focused on development of low-power, miniaturized solutions, easy to integrate in existing film boxes / new film boxes of same overall size and shape

Second developed solution: Metal Oxide semiconductor (MOS), operating principles

- MOS sensors consist of sensing material layer deposited on top of interdigitated electrode pattern with integrated heating system
- Interaction between target gas and sensing layer causes variation of measured system
- Measured resistance variations correlate with concentration of target gas

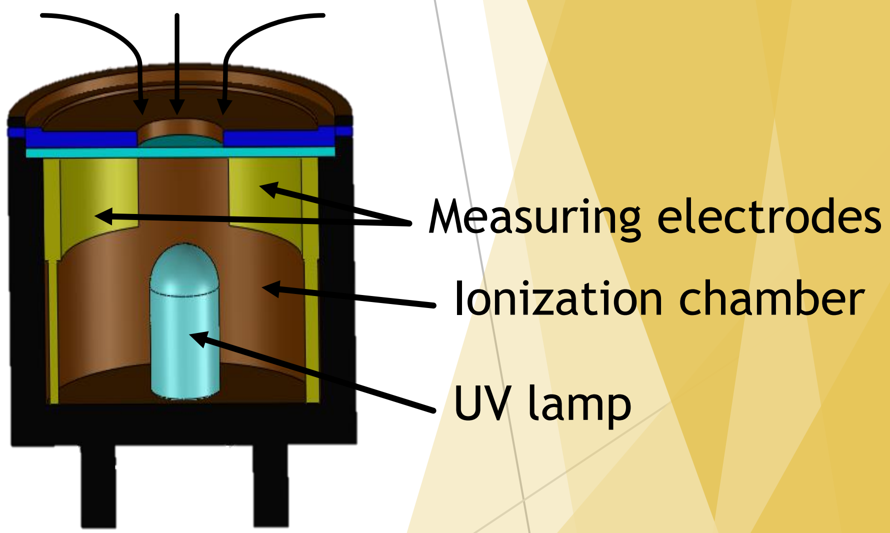


Metal Oxide semiconductor (MOS) for “air quality” evaluation

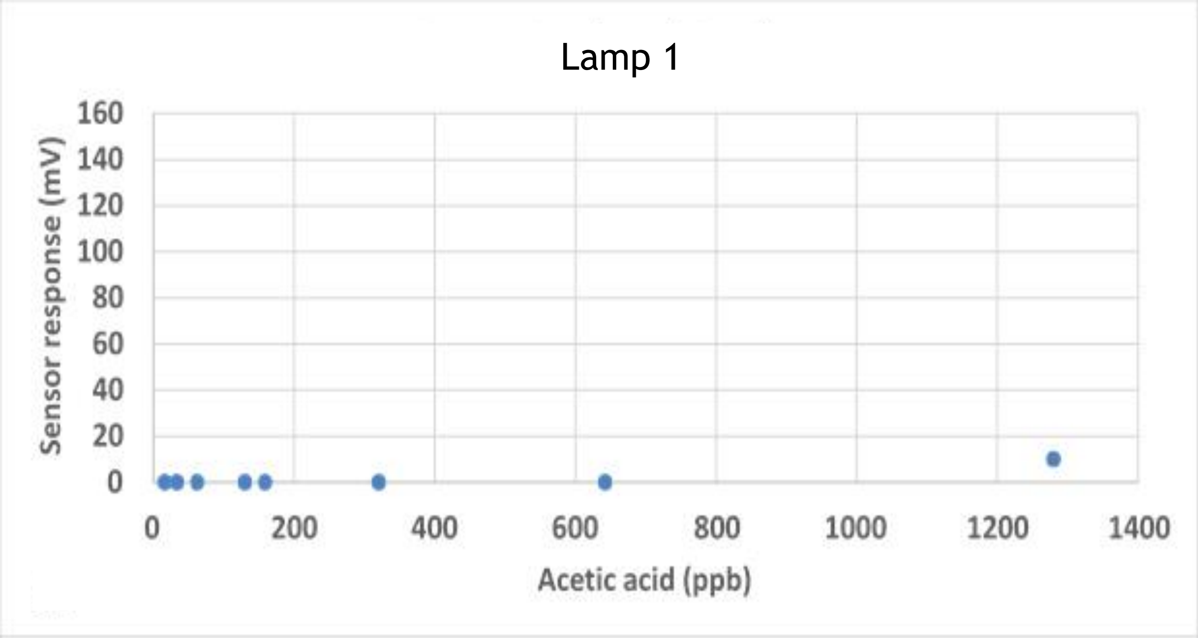
- Sensor showed good responsivity to acetic acid (LOD = 300 ppb)
- Sensor suffered interference from other volatiles released by films
- Alternative sensing solutions researched to minimize interferent volatiles effects

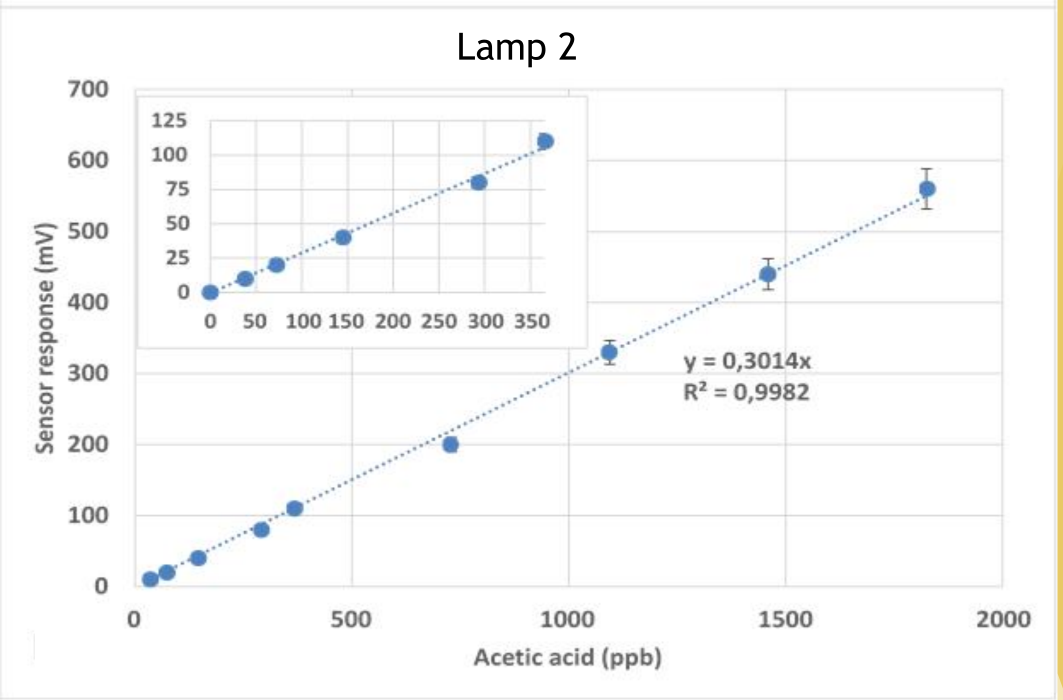
Third developed solution: parallel Photo-Ionization detectors (PIDs)

- PIDs measure volatile organic compounds in air by photo ionization
- VOCs are ionized if light photon of energy greater than the ionization potential interacts with a molecule of the gas sample
- Ionizing photons produced by integrated UV lamp
- Two maximize system selectivity, array assembled with two parallel PIDs employing UV lamps with different photon excitation energy



PIDs array results





- Array responded selectively to acetic acid
- Accurate response down to 50 ppb
- Negligible response from interferents

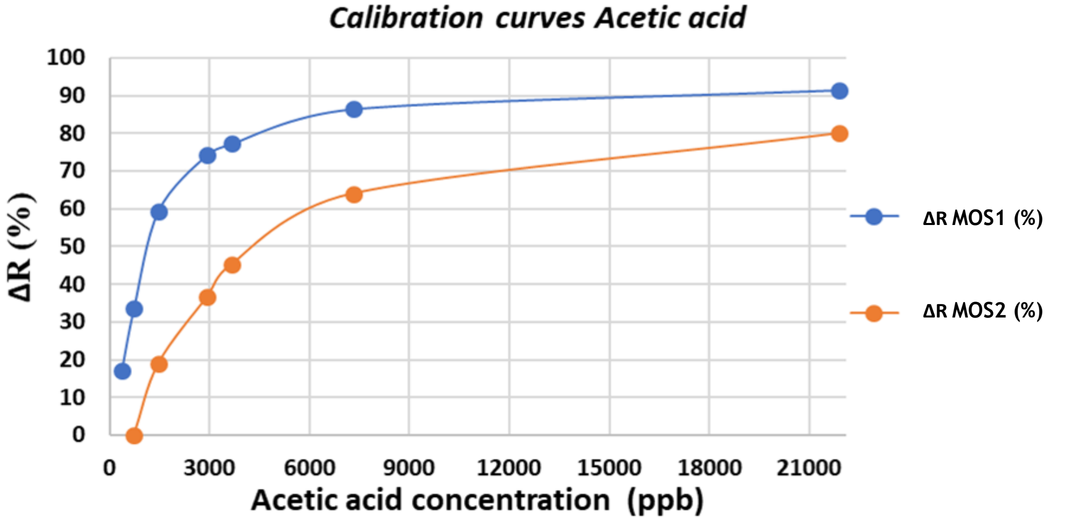
PID array: integration problems

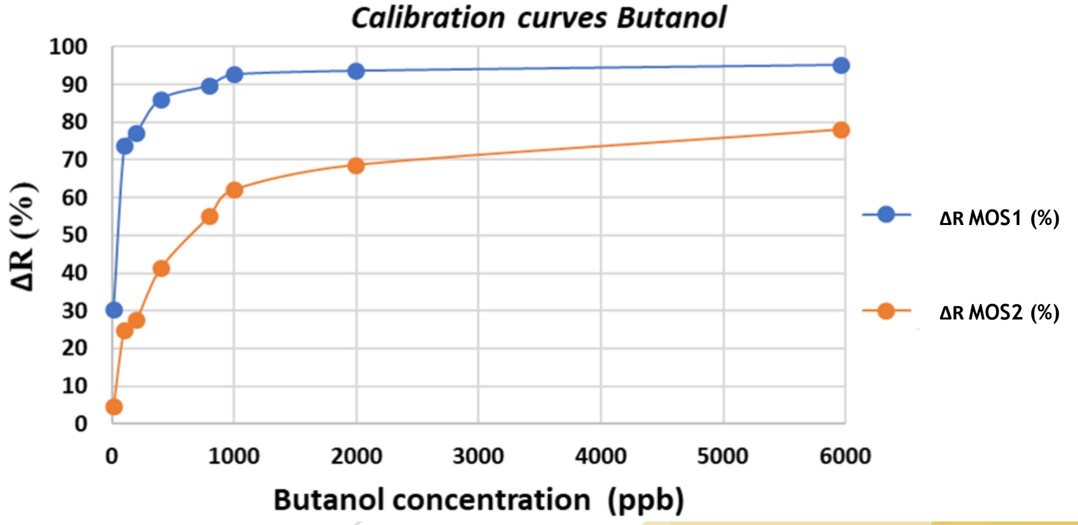
- PIDs array proved useful for detection of acetic acid vapor at lab level

- Not suitable for detection in film boxes due to:
  - High energy consumption
  - Short lifetime of UV lamp (± 6 months)
  - High cost of PIDs

Fourth developed solution: Array of MOS sensors using different sensing layers

- Array assembled using two MOS with different sensing layers
- Materials of layer chosen for different response toward target volatiles and interferents
- Responses obtained show different response of array when exposed to different volatiles





Fourth developed solution: data processing

- Biosensor developed software to process data from multiarray
- Software uses mathematical solving system to calculate concentration of acetic acid vapor, regardless of interferents
- System applied to film samples provided by partners (Fratelli Alinari, DFF, OEAW, INSTITUT VALENCIÀ DE CULTURA (Filmoteca Valenciana)), using as reference classical validation system (A-D strips)

Fourth developed system: validation

Code	Film Name	Owner	Result with AD strips (ppm)	Result with BIOS1+BIOS2 sensors (ppm)
Alinari sample 0	3 photos: Construction site	ALINARI	18.0 - 20.0	17.03
Alinari sample 1	Photo of office	ALINARI	≤ 0.5	0.455
Alinari sample 2	Photo of industrial machinery shop	ALINARI	≤ 0.5	0.362
Alinari sample 3	Photo of electrical equipment	ALINARI	≤ 0.5	0.493
Alinari sample 4	Technical specification for equipment	ALINARI	0.5-1.0	0.884
Alinari sample 5	Various symbols on pentagram	ALINARI	0.5-1.0	0.94
Alinari sample 6	Photo of office reception	ALINARI	0.5-1.0	0.92
Alinari sample 7	Photo of art piece	ALINARI	0.5-1.0	1.00
Alinari sample 8	3 photos: 1 people dining, 2 and 3 press conference	ALINARI	≤ 0.5	0.383
Alinari sample 9	Photo of building	ALINARI	1.0 - 2.0	1.86
Alinari sample 10	Photo of Italian street	ALINARI	1.0 - 2.0	1.91
Alinari sample 11	2 photo reels: column and archeological pieces	ALINARI	≤ 0.5	0.477
Alinari sample 12	3 photos: TV show	ALINARI	≤ 0.5	0.475
Alinari - B/W photo films	5 photos: 1 inside of office, 2 outside of historical building, 3 inside of restaurant, 4 man admiring paintings, 5 people discussing	ALINARI	0.5-1.0	0.815
Alinari - B/W photo reel	3 photos: official meeting	ALINARI	1.0 - 2.0	1.32
Alinari - red hue photo films	3 photos: 1 airplane storage, 2 and 3 photos inside homes at Christmas	ALINARI	0.5-1.0	0.813
Alinari - color photo film	Photo of Pantheon - Rome	ALINARI	0.5-1.0	0.969
00010820	Publicidad Rico Famosa	INSTITUT VALENCIÀ DE CULTURA (Filmoteca Valenciana)	>20	>20
00011242	Febus Comic 4 Publicidad	INSTITUT VALENCIÀ DE CULTURA (Filmoteca Valenciana	0.5-1.0	1.034
00015797 CulturArts 5	"Easy street" (Charlot en la calle de la tranquilidad)	INSTITUT VALENCIÀ DE CULTURA (Filmoteca Valenciana)	8-18	11.981
00015798 CulturArts 7	Canario Roj	INSTITUT VALENCIÀ DE CULTURA (Filmoteca Valenciana)	3-5	2.560
00015799 CulturArts 6	Maigret en el caso de la condesa	INSTITUT VALENCIÀ DE CULTURA (Filmoteca Valenciana)	0.5-1.0	0.597
006113	Las Truchas	INSTITUT VALENCIÀ DE CULTURA (Filmoteca Valenciana)	0.5-1.0	1.078
DFF_12_21	Das Wachsfigurenkabinett	DFF	≤ 0.5	0.679
DFF_12_556	Nosferatu	DFF	≤ 0.5	0.660
DFF_12_584	Das lied der Nachtigall	DFF	≤ 0.5	0.255
DFF_3.01.35.01	Fire	DFF	≤ 0.5	< 0.030
DFF_3.01.35.03	Herbstgeschichte	DFF	≤ 0.5	< 0.030
DFF_3.01.35.04	La parola Amore esiste	DFF	≤ 0.5	< 0.030
DFF_3.01.35.16	Leolo	DFF	≤ 0.5	< 0.030
DFF_50_500A	Bergbauern (Kurzfilm)	DFF	≤ 0.5	0.365
88		OEAW	1-2	1.099
90		OEAW	>20	37.540
94 gr Rolle		OEAW	≤ 0.5	0.417
96		OEAW	≤ 0.5	0.290
Carsta 62		OEAW	≤ 0.5	0.722
Carsta 63		OEAW	1-2	1.614
Carsta 64		OEAW	≤ 0.5	0.382
Carsta 65		OEAW	0.5-1	0.864
Film 99	Memento	OEAW	>20	>20
SCS 00060-1	FBI sucht Lemmy Caution	OEAW	1-2	1.687
SCS 00060-4	FBI sucht Lemmy Caution	OEAW	>20	>20
SCS 00060-5	D FBI sucht Lemmy Caution Pos. Kopie Nr. 12	OEAW	3-5	5.215
SCS 00061-3	Lemmy Caution schlägt zu	OEAW	>20	>20
SCS_00057A	Der 20. Juli 1944	OEAW	>20	>20
SCS_00058A	Nordlicht	OEAW	6-8	6.277
SCS_00059	Deutsche Wochenschau	OEAW	>20	>20
SCS_00060-3	FBI sucht Lemmy Caution	OEAW	10-15	13.085

Conclusions

- Developed MOS sensor array proved capable of detecting acetic acid at very low concentrations (30 ppb)
- Quantification not influenced by presence of other volatiles
- Measurements on real samples in agreement with official acetic acid quantification method (A-D strips) but much faster (≈15 minutes MOS array vs ≥1 day with A-D strips)

Future perspectives

Working to create solutions

- Compact
- Low energy consumption
- Easy to integrate with current reel storing systems
- Capable of simultaneously monitor condition of multiple films in archive

Global gas sensor market size valued at $823.1 million in 2019, projected to reach $1,336.2 million by 2027

Possible to foresee application of developed solution in other fields, leveraging the specific sensing properties of different nanomaterials (alone or in sensor arrays)

Source: Gas Sensor Market :Global Opportunity Analysis and Industry Forecast, 2020-2027, Allied Market Research

Acknowledgments

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  - IRIS and ULISBOA for technical and theoretical support
  - OEAW, DFF, INSTITUT VALENCIÀ DE CULTURA (Filmoteca Valenciana) and Fratelli Alinari for providing the film samples used for the array validation

Thanks for your attention

COMPANY WEBPAGE

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