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Julien Kammer, Francois Truong, Christophe Boissard, Anne-Laure Soulié, Anne-Laurence Dupont, et al.. Quantitative and qualitative assessment of VOCs emitted from cellulose acetate movie films by PTR-ToF-MS. Journal of Cultural Heritage, 2021, 47, pp.50-58. 10.1016/j.culher.2020.09.004 . hal-03047421

HAL Id: hal-03047421
https://hal.science/hal-03047421

Submitted on 13 Feb 2023

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Version of Record: https://www.sciencedirect.com/science/article/pii/S129620742030443X
Manuscript_a35a06bfb7a94020c987bd518682bd4e

Quantitative and Qualitative Assessment of VOCs emitted from Cellulose Acetate Movie Films by PTR-ToF-MS

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Abstract
Cellulose acetate (CA) has been widely used since the second half of the 20th century as a transparent support for photographs and movie films in order to replace the flammable cellulose nitrate. Over time, hydrolysis occurs and the deacetylation of the CA produces acetic acid (AA), a well-known phenomenon in film archives, the so-called "vinegar syndrome". However, beside AA, other off-gassing compounds may be present, and very few studies have been devoted to their quantitative and qualitative assessment. Proton Transfer Reaction "Time-of-Flight" Mass Spectrometer (PTR-ToF-MS) combines high sensitivity with high mass resolution for real-time detection of multiple Volatile Organic Compounds (VOCs). This technique was used to evaluate the air composition from 41 films dated from the second half of the 20th century, which showed different degradation levels (ranked using A-D strips®: level 0 to 1.5). More than 100 VOCs were detected, and their distribution was different from one film to another. AA was the most abundant VOC in 27 film cans. In others, it was either N,N dimethylformamide (DMF), butanol, acetaldehyde acetone or formic acid. This study shows that PTR-MS is a powerful tool to monitor in real-time, and non-invasively, objects degradation in a museum environment via the quantitative and qualitative analysis of their VOCs emissions, and that this can be used for hierarchical cluster analysis classification.

Keywords: cellulose acetate, VOCs, PTR-ToF-MS, movie film, vinegar syndrome

Highlights
- PTR-ToF-MS was used for the first time for real-time full qualitative and quantitative detection of VOCs released by 41 historical movie films on a cellulose acetate base
- Around 100 different organic ions were attributed to VOCs emitted from films
- Acetic acid, acetaldehyde, acetone, butanol, DMF, formic acid, methanol, propanoic acid dominated the VOC mixture composition
- Over 41 films, acetic acid was the most abundant VOC for 27 films reels, butanol for 6, DMF for 3 formic acid for 2, acetaldehyde for 2, acetone for 1.

1. Introduction, context of the study

• Vinegar syndrome mitigation

Cellulose acetate (CA) has been widely used since the second half of the 20th century as a transparent base for photographs and movie films in order to replace the flammable cellulose nitrate. First considered as having a good lifetime expectancy, it was realized in the 1980's that its shelf-life was much shorter and that, depending on the climatic environment, tangible degradation could happen in less than 30 years (1). Hydrolysis occurs and the deacetylation of the CA generates acetic acid (AA), a well-known phenomenon in film archives, so-called "vinegar syndrome". The process is autocatalytic as the acetic acid produced speeds up further degradation. Embrittlement and film distortion can also occur due to the loss of plasticizers. The CA base shrinkage may reach 0.7% in ten years and up to 10% in extreme cases (2). AA concentration builds up in the film reel and increases the film degradation level, the latter being usually

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assessed using A-D strips® (3). These calibrated pH indicators (Table 1) allow ranking the film condition from 0 (good condition) to 3 (critical condition) based on a color change from blue, to green and yellow (4). Films in critical condition (A-D strips® 2 to 3) need to be kept in cold storage. For films in good condition or in an early stage of degradation, the use of sorbents might be a suitable and sustainable option to trap the AA and to curb the degradation process. For this purpose, zeolites have been introduced (5) as acid scavengers by Kodak and Fuji companies (under the name KeepWell®) for preserving movie films in the 1990's (6). However, the impact of zeolites is mainly due to the air moisture adsorption that slows down the hydrolysis of CA, rather than to AA adsorption. Those products were discontinued. Recent developments in chemistry brought to light a new family of compounds, Metal Organic Frameworks (MOFs) that appear as a promising alternative (7). MOFs are hybrid ordered porous solids and are built up from metal subunits connected to each other through multitopic organic complexing linkers. The very large number of combinations of linkers and metal nodes leads to a wide range of structures with tunable pore sizes/shapes and polarity, suitable for the selective adsorption of VOCs. MOFs can be designed to trap AA off-gassing from films bases, this is the objective of a EU funded project so called "NEMOSINE" (https://nemosineproject.eu/). However, to better adjust the MOF to the needs, it is necessary to first identify which VOCs are produced by movie films in storage and at which rate. This study aimed at assessing qualitatively and quantitatively the VOCs emitted by 41 movie films on CA base produced after the 1950's, in black and white or color, and from different brands. Films that are in the first stages of degradation (A-D strips® from 0 to 1.5) were the focus of this study.

- **VOCs emitting from CA and their identification**

In the literature, when considering the degradation of CA, acetic acid is most often cited (8). In fact, the presence of AA is easily identified by its smell, and it is also the most relevant indicator of CA-based film decay. However, the CA film base is a synthetic polymer with a wide range of formulations, including different types of additives such as triphenylphosphate (flame retardant), phthalates (plasticizers), manufacturing residual solvents, and other by-products that may be released over time (9). A study of the indoor air quality in movie films storage in USA indicated the presence of acetone, butanol, cyclohexane, trichloroethane, methylene chloride, 1,2-dichloropropane (10). However, to our knowledge, no research has been devoted to the complete quantitative and qualitative characterization of VOCs emitted from film reels, nor to their emission rates. A common method for VOCs sampling consists on trapping by physisorption on a solid substrate such as active charcoal, silica gel, molecular sieves, porous polymers, etc. The selectivity of the adsorbent may require to combine different types of adsorbents. In the field of cultural heritage, polymeric fibers (Solid Phase Micro Extraction, SPME) or sampling tubes (TENAX, Carbosieve, etc.) have been used (11, 12, 13). The adsorbent is left in contact with the surrounding air (passive sampling) or a certain volume of air (14) is flushed over the sample (active sampling). After the sampling, the chemical compounds are thermally desorbed (from 80 to 300°C) for analysis using gas chromatography coupled with mass spectrometry. Thermodesorption methods are straightforward and they allow the identification, and often the quantitation, of VOCs. However, they also have some drawbacks. They may not allow the measurement of emission rates and the risk of chemical reactions occurring on the sorbent (15, 16, 17) or during the thermal desorption, if the species are not stable at high temperature (18), cannot be excluded. Adsorbed acids may react and decompose, and carbonyl compounds can interact with water, ozone or NOx (19). The exposure time, the location of the SPME fiber with respect to the emissive material, and the temperature, all have an impact of the fiber performance (20). Other analytical approaches such as EGA-GC–MS (21), based on a thermodesorption phase have identical shortcomings and they require a sample that is not always possible with heritage objects..The adsorbent must have a breakthrough volume adjusted to the VOCs concentration (22, 23). Ultimately, the VOCs speciation and concentration might not reflect the real ambient air composition. Direct analysis of VOCs in real time allows avoiding these intermediary uncontrolled steps of sample preparation. For example, DART- MS (direct analysis in real time-time of Flight mass spectroscopy) has been applied to the qualitative and quantitative analysis of pollutants in environmental contaminants (24). Select ion flow tube mass spectrometry (SIFT-MS) (25) has been applied to obtain quantitative real time VOCs release from comics books (26).

- **PTR-MS for VOCs quantification**

Proton transfer mass spectrometry (PTR-MS) is another promising technique that has been initially developed for monitoring atmospheric VOCs by Werner Lindinger (27). The principle of the PTR-ToF-MS has already been extensively described elsewhere (28, 30, 31). It allows in-situ and on-line monitoring of pollutants and VOCs at high sensitivity – up to pptv levels (parts per trillion in volume)-, short integration time and has been widely

used for environmental research, biological research, food science, etc. The principle is based on the ionization of VOCs by proton transfer. The primary ions (mainly H_3O^+) are produced in the ion source by a hollow cathode discharge applied on high purity water vapour flow. The proton transfer reaction between the formed H_3O^+ and neutral analyte molecules (M) occurs in the drift tube ($M + H_3O^+ \rightarrow MH^+ + H_2O$). The reaction only occurs if the analyte has a higher proton affinity than water. As a consequence, this technique is not adapted to n-alkanes because they have a lower proton affinity than water. However, those are not the most abundant volatile organic compounds expected during CA degradation. Proton transfer may occur on every collision without high excess of energy. Such a soft chemical ionization, unlike electron impact ionization, does not induce sever fragmentation of the VOCs molecules. As a result, a cleaner mass spectra is produced (compared to electron impact), allowing to identify VOCs at their corresponding mass+1 (1 for the transferred proton). Recently, the association with time of flight detectors (PTR-ToF-MS) greatly improved the ability of PTR-MS to analyze VOCs. The improved mass resolution of PTR-ToF-MS (up to 8000) allows to separate isobaric compounds (28). However, because of the principle of mass spectrometry, some uncertainties could remain in determining the actual compound in case of a few isomers corresponding to the same exact molecular weight. PTR-ToF-MS was applied for the first time to a batch of historical movie films. The aim of this study was to characterize VOCs emitted by a series of film reels, to verify whether AA was the most abundant VOC. The speciation of VOCs and the magnitude of their emissions was compared, and films have been clustered based on their emissions.

2. Materials and methods

- **Films Samples**

41 movie films on Ca base (Table 2) were selected from the collection of the French film archive among about one million film reels. They are stored in a vault which is maintained at 16°C, 45% RH. The film reels are housed in polypropylene vented by tiny holes on the side of the cans (produced by Orcaplast company). The selected samples are 35 mm CA films, housed in 28 cm diameter containers, from different manufacturers, color and black-and-white, produced during the second half of the 20th century. They presented various acidity levels (A-D strips® ranking from 0 to 1.5), the latter were assessed after the PTR-MS analysis.

- **Methods for PTR-MS film analysis**

A PTFE (polytetrafluoroethylene) dynamic chamber adapted from the Genard-Zielinski et al. (29) device was used (Fig. 1). It consisted in a 40 cm diameter and 30 cm height cylinder enclosed by a 50 µm thick PTFE film. The film cans were brought to the laboratory for the VOCs analysis. Just before use, the film container was opened and the lower part of the container with the film reel was placed in the analysis chamber (Fig. 2). The chamber was continuously flushed with ambient air using and external PTFE pump. The flow inside the chamber was set to 13 L min^{-1}, and was controlled using a mass flow controller (Bronkhorst), providing a residence time above 3 min. The air was uniformly distributed in the chamber thanks to a PTFE ring tubing with small holes every centimetre. The film reels were introduced in the chamber from the top. The experiments were carried out in 3 main steps:

- Measuring the air at the chamber inlet during 5 minutes
- Measuring the air in the empty chamber during 5 minutes
- Measuring the VOC concentration of the film reel during at least 5 minutes, until the equilibrium inside the chamber was reached.

An example of a typical experiment following the 3 steps described above is presented on figure 3.

VOCs emitted by film reels were investigated online using a Proton Transfer Reaction – Time of Flight – Mass Spectrometry (PTR-ToF-MS 1000 Ultra, Ionicon). The air was sampled at 0.4 L min^{-1} through a 1-meter long Teflon tubing with 1/8 inches then 1/16 inches diameter. The tubing was heated at 75 °C to avoid any loss of semi-volatiles or sticky compounds. During the experiments, the PTR-ToF-MS operated in standard conditions. The pressure in the drift tube was set at 2.8 mbar at 80 °C, and a drift voltage at 500 V. These conditions provide an E/N ratio about 117 Td (where E is the electric field strength and N the gas number density, 1 Td = 10^{-17} V cm^{-2}). Such an E/N was reported to be a good compromise to limit the fragmentation and the influence of ambient relative humidity (32, 33). Instrument background signal was estimated using a catalyser that convert VOCs to CO_2 using a molybdenum hoven heated at 300°C.

VOC mixing ratios (MR_{VOC}, in pbb) were estimated as following: $MR_{VOC} = 1.657e^{-11} \frac{U_{drift} \cdot T_{drift}^2}{k_{VOC} \cdot p_{drift}^2} \frac{VOC^+}{H_3O^+} \frac{Tr_{H_3O^+}}{Tr_{VOC^+}}$

Where U_{drift} is the drift tube voltage (V), T_{drift} is the drift tube temperature (K), k_{VOC} is the VOC protonation rate constant (in cm^3 s^{-1}), p_{drift} is the drift tube pressure (bar), VOC^+ and H_3O^+ are the protonated VOC and

primary ions signal (cps, counts per seconds), $Tr_{H_3O^+}$ and Tr_{VOC^+} are transmission values (unitless) of the primary ions and the considered VOC, respectively. In this study, we used m/z 21.022 corresponding to H_3O^+ isotope ($H_3{}^{18}O^+$, 487.56 isotope multiplier factor) and m/z 39.033 corresponding to the first water cluster H2O.H3O+ isotope ($H_2{}^{18}O$.$H_3{}^{18}O^+$, 244.43 isotope multiplier factor) as primary ion signals. Calibration was performed by adjusting the transmission curve using a gas standard containing 15 VOCs around 1 ppmv mixing ratio, diluted using the air flow from the catalyser. During the experiment, the mass spectra from m/z 14 to m/z 500 were recorded every second with a TOF scan of 25 kHz.

The VOC content is either provided in ppbv in the emission chamber or in emission rate of VOC (E) in nanogramme per kilogramme of film and per second (ng kg^{-1} s^{-1}). This emission rate was calculated using the following calculation

$$Emr = (Q (C_{movie} – C_{blank}))/ m_{movie}$$

Emr is the film emission rate of a VOC in ng kg^{-1} s^{-1}
Q is the air flow inside the chamber
C_{movie} and C_{blank} are the concentration of VOC during the emission phase and in the blank (respectively)
m_{movie} is the mass of the analyzed movie film

For a VOC, the uncertainty associated to the PTR-TOF-MS can be defined as 3 times the standard deviation of the signal measured for a gas standard and/or during background/blank measurements. During our experiments, the uncertainty was typically below a ppb. Thus, it remains far below the concentrations measured in the experiment that could reach values higher than 1 ppm in the emission chamber. The mass resolution of the instrument was > 2000 at m/z 79 (corresponding to benzene in the gas standard). A mass calibration has been performed for each experiment (1 experiment corresponding to one movie), based on the signal of H3O+ and H2O.H3O+ isotopes (at m/z 21.022 and m/z 39.033), acetone which is naturally abundant in the air (at m/z 59.0497) and two ions corresponding to an internal calibrant that diffused in the drift tube (di-iodobenzene at m/z 330.8375 and m/z 203.9431). Using these ions for the mass calibration, the mass accuracy was typically a few ppm over the full range of m/z.

Some VOCs can be identified directly from their molecular weight. However, the molecular weight may correspond to several isomers that undergo proton addition and are indistinguishable to the PTR-ToF-MS. In that case, the molecular formula is given. Some compounds may be fragmented. For instance, butanol undergoes hydrolysis (loss of a water molecule) and it is known (34) that iso-butanol and tert-butanol are fully fragmented in $C4H9^+$ while n-butanol produces 95% of $C4H9^+$ and 5% of $C4H11O^+$ (25). In this study C4H8 will be assigned to butanol.

3. Results and discussion

- **VOCs emission**

121 different VOCs were identified during the 41 movie films reel analysis still encased in the lower part of their plastic container. VOC emissions from a plastic container were also measured and very few VOCs were observed with negligible emissions, which were mostly attributed to the movie film that was previously inside (such as AA for example). Around 50 VOCS were in the range from m/z 33 to m/z 223. Some film reels had a low VOCs emission, the total volatile organic compounds (TVOC) being just a few ng kg^{-1} s^{-1}, while others emitted over 1000 ng kg^{-1} s^{-1} (Table 3). Those emission rates were stable over more than 10 minutes. In this batch, the film reels that produced the highest rate of VOCs emitted either mostly AA or N,N dimethylformamide (DMF)! AA was the most abundant emitted VOC for 27 films out of 41, then it was butanol (6 films), DMF (3 films), acetaldehyde (2 films), formic acid (2 films), acetone (1 film). These VOCs other than AA arise from residues or/and additives used during the CA film manufacturing, as well as from degradation products. However, further understanding of the VOCs provenance has not been attempted in this study. When the TVOC from a film reel increased, the number of individual VOCs that contributed to 99% of the TVOC in ppbv rapidly dropped to only 8 to 10 VOCs (Fig. 4). Adding all the VOCs emitted by the 41 films, the VOC mixture that dominated in abundance (over 200 ppbv per VOC) and occurrence was composed of acetic acid, acetaldehyde, acetone, butanol, DMF, formic acid, methanol, and propanoic acid. This VOCs mixture was emitted by more than 50% of the film reels (Fig. 5). The emission profile varied from one film to another (Table4). This may reflect characteristics which are either linked to the film constituents or their breakdown. So far, previous VOCs studies of CA did not evidence emissions with such a specific low molecular weight oxygenated compounds profile. A few reasons can explain this. First, those analyses were performed on 3D

objects in display cases which have a higher ventilation rate than a movie film reel in a container. Additionally, a movie film is a CA support coated with a gelatin layer containing silver or dyes and residual processing chemicals. The latter may add a few more VOCs to the ones emitted by CA. But, chiefly, these earlier studies were based on SPME-GC-MS, which seems more efficient for sampling and analysing acetic acid and heavier compounds such as 2-ethyl-1-hexanol, phenol, tetrachloroethylene diethyl phthalate and dimethyl phthalate than the lighter VOCs that were detected by PTR-ToF-MS (20, 35, 36).

- **A-D strips evaluation and AA content**

After the PTR-ToF-MS analysis, the acidity level in the films containers was assessed using A-D strips® and compared to the concentration of AA (Fig.6). Most of the film reels which had over 1 ppmv of AA matched an A-D strip® level of 1 to 1.5. However, some discrepancies were noticed for films with a low concentration of AA - between 10 and 140 ppbv - that had an A-D strip® level of 1.0. Yet, we do not have a clear understanding of those differences. They could be due to the fact that A-D strips® ranking is a subjective and discontinuous classification, whereas PTR-ToF-Ms is an objective and continuous measurement. The A-D strips® assess the AA accumulated in a closed container during 24 hours at room temperature. This is a static process that allows the slow diffusion of AA from the core to the surface of the reel where the A-D strip® is exposed. PTR-ToF-MS is a dynamic process that measures the concentration of AA constantly emitted in a flow of fresh air, which may shift the equilibrium in the VOCs composition, and especially AA concentration. Those specificities may contribute to the differences observed.

- **Films Agglomerative Hierarchical Clustering**

The PTR-ToF-MS analysis reveals different VOCs distribution from one film to another; differences in the range of relative concentration of VOCs but also differences in the chemical composition (Table 4). When comparing emission profiles, clear similarities and differences that should allow to use the emission profile for fingerprinting were noticed. We applied the XLSTAT version 2020.1 software for hierarchical cluster analysis (HCA) in order to explore similarities and hidden patterns VOCs emissions in the matrix (41 films x 121 VOCs) and to attempt clustering the films based on their emission characteristics. The clusters we obtained corresponded to the predominant VOC in 90% of the cases. We can distinguish 5 classes (Fig.7, Tab.4) corresponding to films most abundant VOCs emission: C1 for acetic acid, C2 for butanol, C3 for DMF, C4 for formic acid. C5 represents only one film (F13) with a very low emission level that is probably not significant. Class C1, gathers two distinct sub-classes with different profile emissions, however, without information on the film (brand, batch emulsion number, chemical composition, etc.), it is not possible to draw further conclusions and link a type/brand of film characteristic to a specific profile. This clustering method was well suited to the data set and the objectives of the study. We have tried other approaches such as k-means, especially to confirm the most significant number of clusters. The results were similar, no finer and more logical sorting could be obtained. Bayesian statistic would suit best if we have more information about all the movie films and a larger dataset, further option would be to do a chemometric approach by implementing an ATR-FTIR analysis of the CTA film support in the data set.

Conclusion

This first attempt of using PTR-Tof-MS on a batch of cellulose acetate movie films to assess the VOCs gives new insights on VOCs distribution in a film reel and allows comparing with other film reels. More than 100 different VOCs emitted by the 41 movie films with an A-D strip® level from 0 to 1.5 were harvested. Occasional discrepancies between the A-D strips® level and the acetic acid concentration were noticed. The TVOCs concentration values spanned from a few ppbv to almost 4.7 ppmv for one of the film reels. The number of significant VOCs dropped to about 10 when the concentration of TVOC was above 0.5 ppmv. Besides AA

(27/41), the other most frequent VOCs were either butanol (6/41), acetaldehyde (2/41), DMF (3/41), formic acid (2/41) or acetone (1/41). This might reflect different films origin, manufacturing treatment or degradation levels. Film clustering by hierarchical cluster analysis resulted in 5 classes corresponding to films that emitted mostly acetic acid, DMF, butanol, formic acid and acetaldehyde. However, with no further information on the chemical composition of the films or the film batch manufacturing number, it was not possible to link the defined classes to a particular film characteristic. This study provided in depth knowledge about the nature of the VOCs and the differences from one film reel to another, it will help for introducing appropriate MOF adsorbents for improving long-term preservation. VOCs assessment using PTR-MS is a powerful and promising tool for cultural heritage as it provides numerous and interesting chemical information, non-invasively, in real-time and in ambient air. It is a fast and sensitive technique, with short integration time that can allow the classification of cultural heritage objects based on their emissions and /or degradation level.

Acknowledgments:

The authors would like to thank Pr. Nathalie Steunou from Versailles Saint-Quentin University. Work was done as part of the NEMOSINE project (https://nemosineproject.eu/, accessed in April 2020). This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement Nº 760801.

Declarations of interest: none

Data and materials availability

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Research aim

Cellulose acetate (CA) materials are at risk in heritage collections because tangible degradation can occur in less than 30 years. Thus, the deacetylation of CA generates acetic acid (AA), a phenomenon well known in film archives as the "vinegar syndrome". The process is autocatalytic, as the acetic acid produced accelerates further degradation. Studies are underway to introduce Metal Organic Frameworks (MOFs) to trap AA releases, however, to better adjust the MOF to the needs, it is necessary to identify which VOCs are produced by motion picture films and at what rate. This study aims to qualitatively and quantitatively assesses the VOCs emitted from a selection of 41 motion picture films using Proton Transfer Mass Spectrometry (PTR-MS).

Caption for figures

Table 1: A-D strips® levels and color changes related to amount of acetic acid in the air in parts per million

Table 2: List of films provided by the French Film Archives (CNC)

Table 3: VOCs Emission rate (Emr) and most abundant VOCs for the 41 film reels

Table 4: Emission rate (10^{-3}ppbv/kg.s) of the 8 most significant VOCs (in gray, most abundant VOC) for the 41 film reels analysed.

Fig.1: Set-up for analyzing the VOC emission from a movie film. After measuring the VOCs concentration in the air and in the empty chamber for measuring a blank, the film is placed in the 37,6 L Teflon chamber for around 3 minutes with a 13 L min^{-1} air flow. (MFC: Mass Flow Controller).

Fig.2: Photo of the analytical set-up, on the left on the table the Teflon analytical chamber containing a film and on the right the PTR-ToF-MS.

Fig. 3: Measurement of the AA concentration of a film reel versus time in seconds. From 0 to 300 seconds measurement of the air, from 300 to 600 seconds measurement of the empty test chamber, at 600 seconds, the film is placed in the test chamber.

Fig. 4: Number of VOCs (contributing to 99% of the TVOC) in a film reel as a function of the concentration of TVOCs in the film container (each dot corresponding to a film reel).

Fig. 5: Number of film reels emitting a VOC as a function of this VOC concentration cumulated for the 41 film containers (each dot corresponding to a VOC).

Fig. 6: Correlation of the AD-strip level with the acetic acid concentration for the 41 film reels (each dot represents the measurement in a film container).

Fig.7: Dendogram and classes, average linkage clustering using correlation based on film emissions (software XLSTAT Version 2020.1).

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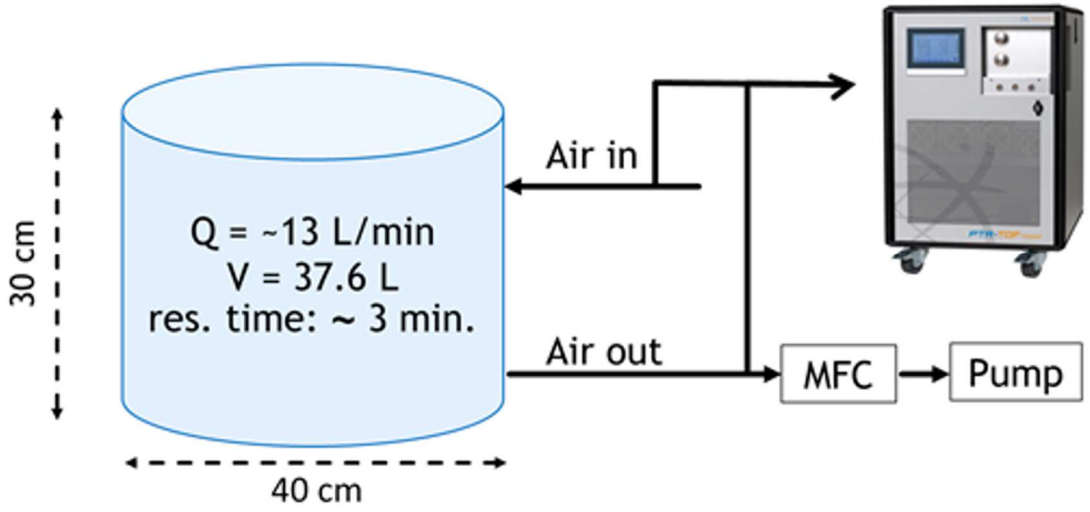

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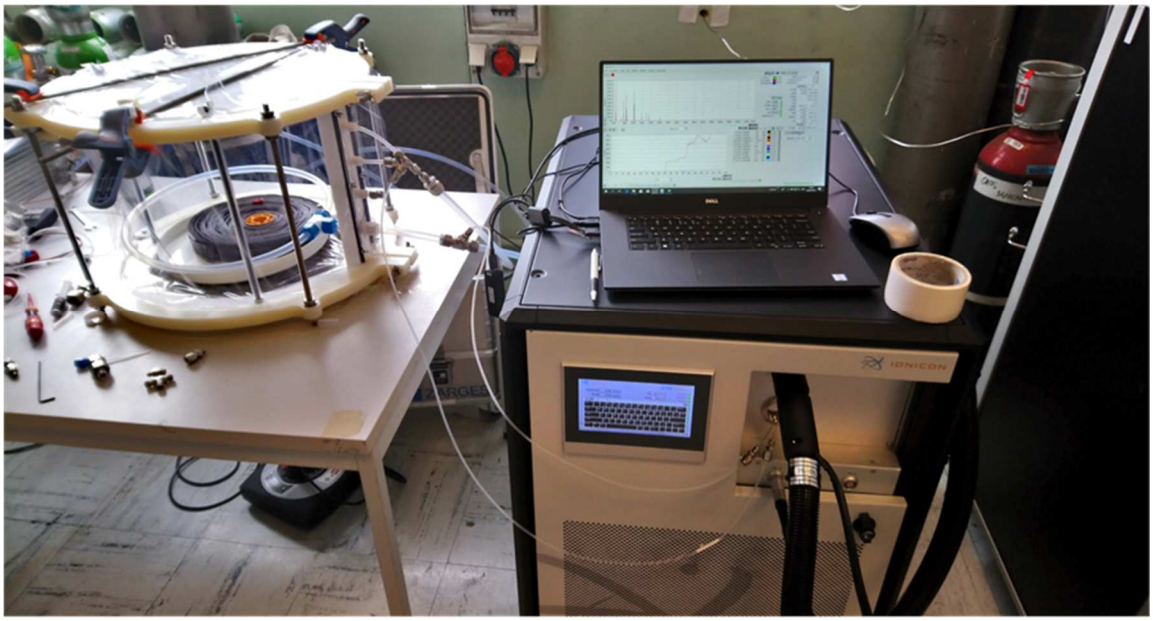

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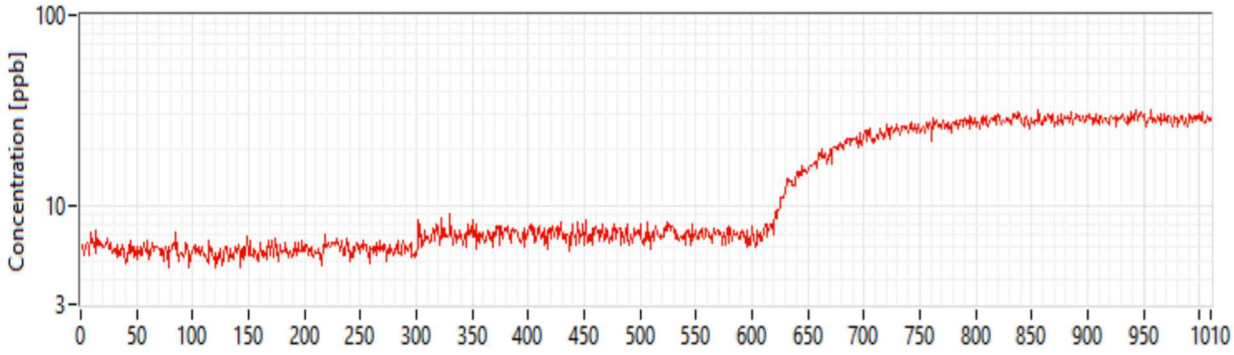

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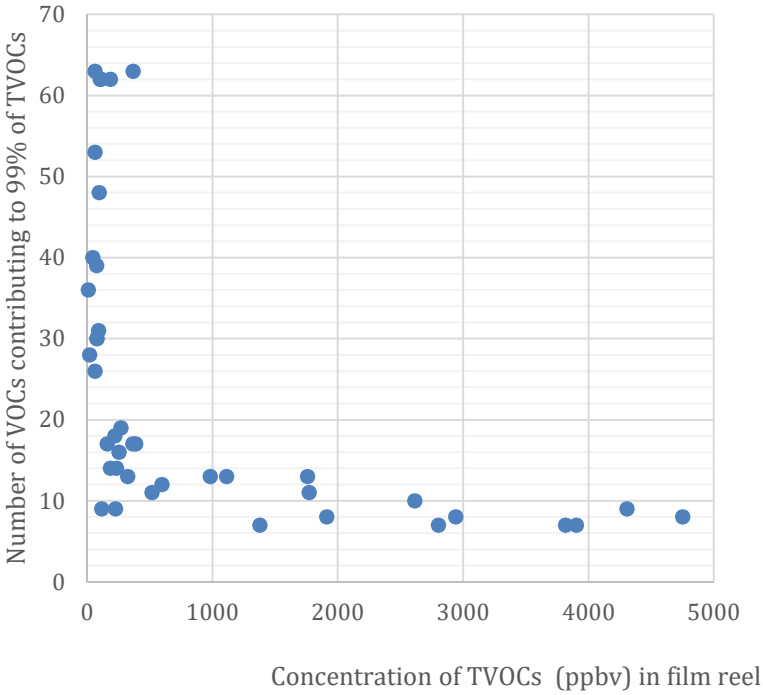

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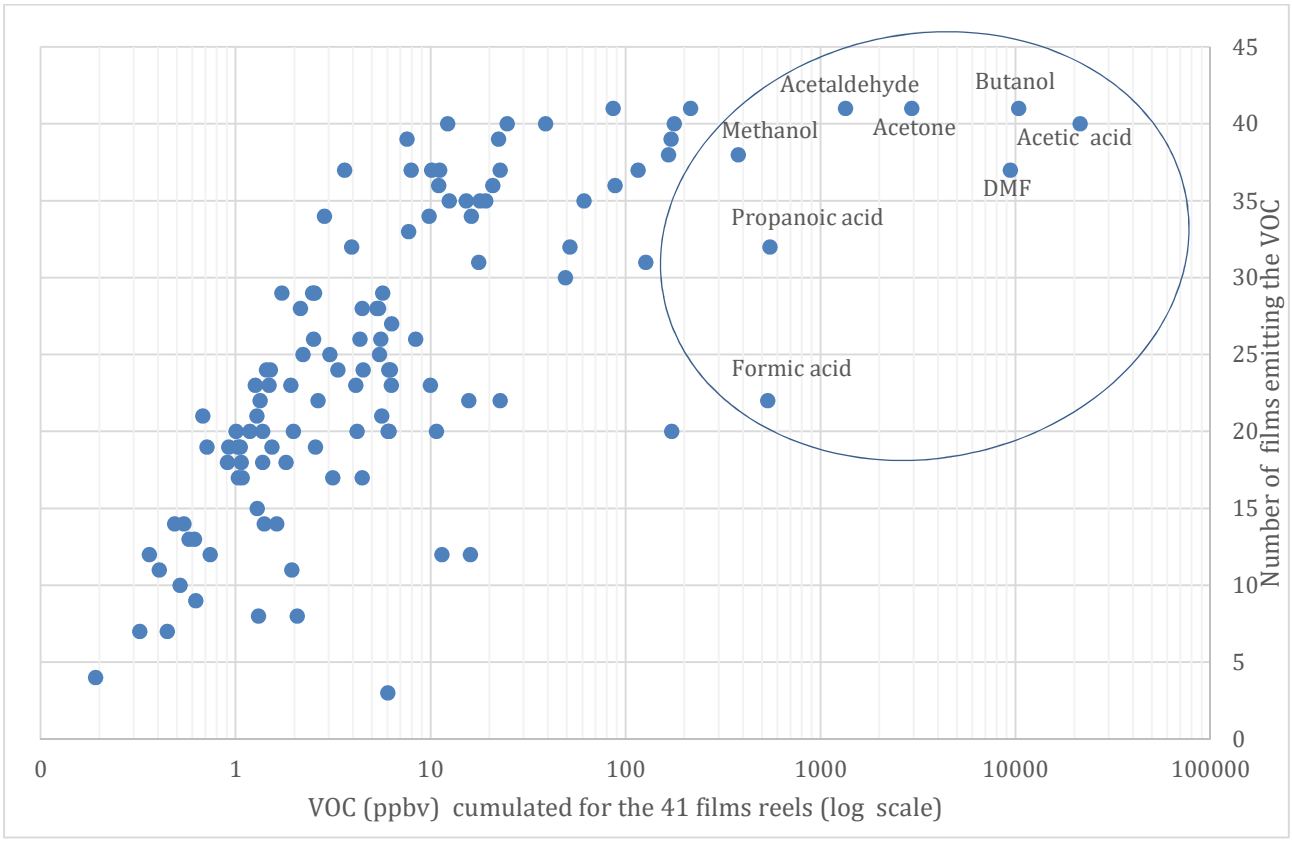


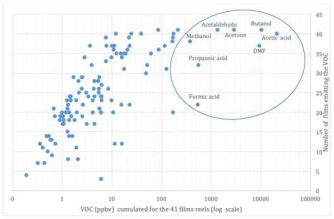
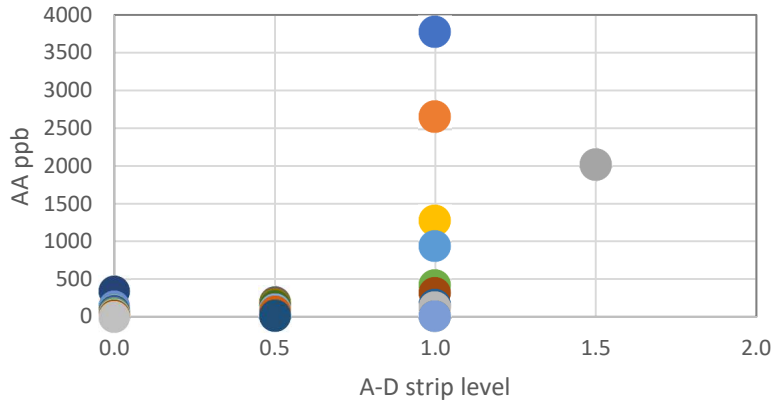


Fig. 6: Correlation of the AD-strip level with the acetic acid concentration for the 41 film reels (each dot represents the measurement in a film container)



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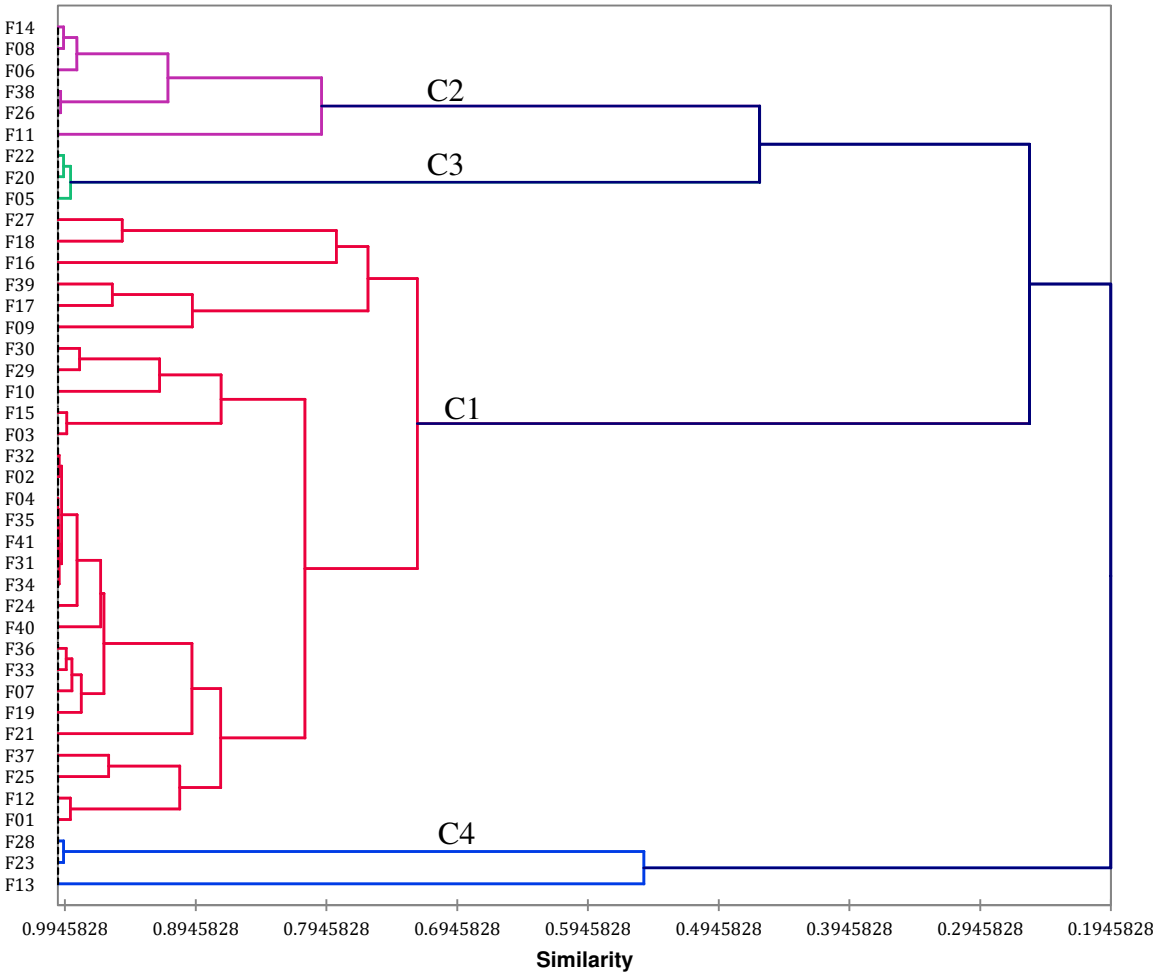

Table 1: A-D strips® levels and color changes related to amount of acetic acid in the air in parts per million

A-D strips® level	Acetic acid (ppmv)	Color	Color sample
0	-	Blue	
0.5	-		
1	1-2	Blue-green	
1.5	3-5		
2	6-8	Yellow-green	
2.5	-		
3	18-20	Yellow	

Table 2: List of films provided by the French Film Archives (CNC)

Movie title	Ref	Type	Sound	A-D strips ®level	Film brand
Absence	F01	B&W	optical	0.0	Kodak (1972)
By the Sea	F02	B&W	optical	1.0	Agfa Gevaert
Céline et Julie vont en bateau...	F03	-	magnetic	0.0	Unknown
In the park 1/2	F04	B&W	optical	1.0	Kodak
Conflit	F05	B&W	silent	0.0	Eastman (1990)
Coup double	F06	color	optical	1.0	Kodak
El Gran calavera	F07	B&W	optical	1.0	Agfa
Espoir	F08	B&W	optical	0.0	Unknown
Fin de série	F09	color	optical	0.5	Eastman (1989)
Fitzcarraldo	F10	-	magnetic	0.0	Unknown
Harpya	F11	color	optical	1..0	Eastman Color (1979)
In the park 2/2	F12	B&W	optical	1.0	Kodak (1961)
La Jeune fille d'en face	F13	B&W	silent	0.0	Agfa Gevaert
Le Fakir du grand hôtel	F14	B&W	silent	0.0	Eastman (1990)
Le Genou de Claire	F15	-	magnetic	0.0	Unknown
Le Monde à l'heure de la France	F16	color	optical	0.0	Eastman Color (1975)
Le Pays beau	F17	color	optical	0.5	Fujicolor
L'Industrie de l'ardoise dans les Alpes	F18	color	silent	0.0	Eastman
Love Happy	F19	B&W	optical	0.0	Agfa Gevaert
Many a Slip	F20	B&W	silent	0.0	Eastman (1980)
Masquerage	F21	B&W	optical	0.0	Gevaert Belgium
Mephisto 41	F22	B&W	silent	0.0	Eastman
Nuits sans sommeil	F23	-	magnetic	1.0	Unknown
Partout, l'électricité	F24	color	optical	1.5	Kodak (1969)
Patatomanie	F25	color	magnetic	0.5	Eastman Color (1971)
Pauvre Pierrot	F26	color	silent	0.0	Eastman (1989)
Pierre de Ronsard, vendômois	F27	color	optical	0.5	Eastman Color (1970)
Quai Bourbon	F28	-	magnetic	1.0	Unknown
Se permute 2/10	F29	-	magnetic	0.5	Unknown
Se permute 9/10	F30	-	magnetic	0.5	Unknown
Smultronstället	F31	B&W	optical	0.5	Orwo
Tanna	F32	color	optical	1.0	Unknown
The Circus	F33	B&W	optical	0.0	Agfa Gevaert
The Count 1/2	F34	-	magnetic	1.0	Unknown
The Count 2/2	F35	-	magnetic	1.0	Unknown
The Great Dictator	F36	B&W	optical	0.5	Agfa Gevaert
The Hick Chick	F37	color	optical	0.5	Unknown
The Victim	F38	color	silent	0.0	Eastman

Un axe impérial : "La Route Napoléon"	F39	color	optical	1.0	Eastman (1991)
White Zombie	F40	B&W	optical	0.0	Agfa Gevaert
Without reservations	F41	-	magnetic	1.0	Unknown

Table 3: VOCs Emission rate (Emr) and most abundant VOCs for the 41 film reels

Ref	TVOC Emr ng/kg.s	TVOC Emr ppbv/kg.s	TVOC Concentration ppbv	Top emitted VOC	% of the top emitted VOC	% of AA
F01	39	0.43	159	AA	54%	
F02	105	1.13	384	AA	84%	
F03	22	0.22	110	AA	27%	
F04	802	8.79	3815	AA	97%	
F05	1012	10.17	4304	DMF	52%	3%
F06	503	5.84	1909	Butanol	68%	9%
F07	49	0.54	183	AA	74%	
F08	42	0.49	224	Butanol	78%	6%
F09	115	1.32	594	Acetone	41%	32%
F10	16	0.16	73	AA	42%	
F11	443	5.29	1756	Butanol	32%	25%
F12	59	0.67	231	AA	55%	
F13	3	0.04	16	Acetaldehyde	44%	0%
F14	204	2.34	981	Butanol	87%	5%
F15	19	0.19	102	AA	29%	
F16	27	0.33	94	AA	19%	
F17	69	0.77	322	AA	43%	
F18	2	0.03	7	AA	36%	
F19	20	0.21	76	AA	51%	
F20	1263	12.55	4749	DMF	55%	7%
F21	23	0.24	88	AA	52%	
F22	772	7.59	2938	DMF	61%	2%
F23	74	0.75	365	Formic acid	34%	3%
F24	712	7.77	2612	AA	77%	
F25	79	0.91	253	AA	38%	
F26	231	2.69	515	Butanol	50%	7%
F27	44	0.54	221	Acetaldehyde	37%	31%
F28	46	0.48	183	Formic acid	31%	6%
F29	21	0.19	62	AA	23%	
F30	20	0.19	62	AA	28%	
F31	28	0.31	113	AA	90%	
F32	265	2.83	1111	AA	85%	
F33	21	0.23	77	AA	63%	
F34	298	3.30	1375	AA	92%	
F35	819	8.99	3901	AA	97%	
F36	33	0.36	43	AA	58%	
F37	115	1.34	362	AA	45%	

F38	381	4.45	1770	Butanol	55%	5%
F39	112	1.25	269	AA	48%	
F40	22	0.17	61	AA	55%	
F41	588	6.46	2802	AA	95%	

Table 4: Emission rate (10^{-3}ppbv/kg.s) of the 8 most significant VOCs (in gray, most abundant VOC) for the 41 film reels analysed

Ref	Emr Methanol	Emr Acetaldehyde	Emr Formic acid	Emr Butanol	Emr Acetone	Emr Acetic acid	Emr DMF	Emr Propanoic acid	Class
F01	21.2	9.6	-	114.6	8.8	232.8	1.4	-	C1
F02	14.2	35.7	1.0	26.9	9.6	943.5	0.7	0.9	C1
F03	4.7	23.0	15.2	12.0	4.2	57.8	1.2	2.4	C1
F04	41.0	31.7	41.9	29.0	11.8	8495.6	1.2	3.2	C1
F07	4.5	5.0	-	91.0	4.3	400.2	4.1	0.9	C1
F10	0.1	14.3	27.9	9.5	1.7	68.8	0.9	0.3	C1
F12	8.1	9.2	-	221.8	9.8	365.1	1.2	0.9	C1
F15	2.4	23.3	10.2	10.0	3.7	54.7	0.8	1.5	C1
F16	19.3	51.0	-	37.6	45.9	63.9	1.0	0.5	C1
F17	10.3	38.1	1.5	60.6	225.9	332.7	56.1	7.8	C1
F18	1.6	7.2	-	0.9	4.1	11.1	-	-	C1
F19	5.8	6.1	-	32.2	4.0	106.3	2.3	0.4	C1
F21	-	1.8	-	9.1	5.1	123.9	0.5	-	C1
F24	58.8	194.4	13.2	83.7	1030.3	6000.3	1.6	4.5	C1
F25	12.1	179.8	-	144.2	123.6	346.2	3.9	1.7	C1
F27	7.6	200.2	-	25.7	94.4	166.5	2.3	-	C1
F29	-	22.1	37.3	15.9	1.4	43.6	0.6	0.5	C1
F30	-	17.8	39.4	13.0	2.0	53.3	0.6	-	C1
F31	7.7	-	-	5.1	4.8	280.2	0.3	-	C1
F32	10.6	48.1	10.8	143.3	14.7	2397.2	0.5	1.8	C1
F33	3.8	6.5	-	33.0	4.8	146.5	0.4	0.3	C1
F34	12.0	21.9	147.0	17.0	9.7	3036.9	1.3	-	C1
F35	47.1	47.8	29.4	26.0	14.5	8694.7	1.3	4.0	C1
F36	15.2	5.3	-	33.2	5.3	211.2	1.3	2.0	C1
F37	21.1	120.6	12.6	239.8	195.4	603.0	13.2	20.5	C1
F39	5.7	52.7	3.6	52.1	257.8	600.0	79.0	6.0	C1
F40	0.5	2.7	-	7.0	1.8	93.3	0.3	0.0	C1
F41	29.9	22.4	128.9	22.3	13.2	6121.1	2.2	0.0	C1
F09	15.1	86.5	3.7	134.7	547.4	428.9	19.4	14.3	C1
F11	157.2	822.2	26.8	1673.1	1028.6	1271.5	46.7	27.7	C2
F06	31.6	168.5	2.6	3964.6	898.0	498.2	1.1	6.5	C2
F08	9.7	1.6	-	383.8	45.0	32.1	1.3	1.0	C2
F14	25.8	6.3	-	2031.0	68.0	110.7	-	12.0	C2
F26	52.8	131.5	-	1348.6	822.8	177.7	-	30.9	C2
F38	78.7	197.9	-	2437.2	1314.9	206.3	-	50.4	C2
F05	79.0	5.2	5.0	3831.4	126.3	324.9	5297.5	257.0	C3
F20	48.9	12.3	4.8	3965.4	87.0	885.8	6916.5	377.0	C3
F22	30.6	9.8	-	2386.4	30.4	148.8	4628.8	207.1	C3
F23	0.1	212.8	256.5	13.8	6.0	24.9	1.5	5.1	C4
F28	5.5	130.1	149.5	13.7	5.1	28.1	1.2	4.3	C4
F13	0.9	17.9	-	4.9	1.6	-	2.1	-	C5