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Indoor air quality monitoring with stable carbon isotope ratio of CO_2 in Museum Environments: study for the Leonardo da Vinci's "Last Supper"

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***Abstract* –This work regarded the possible use of stable carbon isotopic ratio of CO_2 to monitor the influence of visitors in the Refectory of Santa Maria delle Grazie (Milan, Italy) which houses one of the most important paintings of Leonardo da Vinci, the *Last Supper*. Indoor air quality is of utmost importance to guarantee the appropriate preservation condition of the painting since the exposure of artwork and materials to gaseous and particulate pollutants emitted from either indoor or outdoor sources contributes to their decay. The results showed a good correlation between the isotopic composition of CO_2 and the tourists inside the museum during the visits and the closure of the museum. The variation of indoor atmospheric $\delta^{13}C$ is related to the presence of visitors in the Refectory and follows their direction from the entrance to the exit. This new methodology can be used as a supplemental and non-invasive tool to help in calibrating microclimatic conditions through the ventilation rate of HVAC and air filtration systems in the museum and to manage the number of visitors per turn.**

Keywords Leonardo's *Last Supper*, indoor carbon dioxide, carbon isotope ratio, active and passive sampling.

I. Introduction

Indoor air pollution is a critical issue in museum environments, where it represents a serious risk for the conservation of the artworks [1-2]. Materials, interacting with the environment, go through chemical and physical modifications with a natural and irreversible process of degradation [3]. Technical standards define acceptable values of environmental conditions for the conservation of artworks, but case-specific investigations are required to identify the potential degradation factors of each artwork and, as a consequence, the appropriate ranges of microclimatic parameters. Threshold concentrations of gaseous molecules and airborne particulate are required to minimize preservation risks [4-8]. To guarantee appropriate conservation of artworks, an appropriate Heat, Ventilation, Air Conditioning, and Cooling system (HVAC) was specifically designed and built for the "Last Supper"; it is coupled with different types of air filters to remove particulate and gaseous pollutants from the air. However, the ventilation rate of systems was fixed while in any museum must be strictly calibrated, according to the number of visitors and the microclimatic conditions using tools in real-time. The guidelines, reported by the ASHRAE Technical Committee regarding the thermodynamic ranges admitted, are based on a precautionary principle instead of scientific criteria.

There is currently no real-time control tool capable of evaluating chemical properties and hygroscopic (deliquescence point) of the aerosol to optimize the functioning of the filtering systems [9].

In the last years, Leonardo da Vinci's *Last Supper* was the most studied painting, particularly related to many difficulties to its restorations. Chemical and physical analysis on environments of the Refectory, where the painting is located, highlighted incompatibilities between restoration and state microclimate conditions. In 1983 the Institute of Conservation and Restoration (ICR) started an important project to improve air quality for the best conservation of the *Last Supper* [10]. The first study of this project highlighted negative effects of the lighting system such as favouring chemical degradation processes, facilitating the deposition of particulate matter, and other pollutants on the surface of the painting [11]. Other effects were associated with SO_2 deposition, produced from the combustion of solid fossil fuels, and considered the most relevant pollutant regarding material deterioration. Thanks to these results, the lighting system was improved and there was a reduction in degradation effects [12, 13].

The identification of the pollution sources and the remediation activities have a significant impact on the organization of museums. This problem highlighted the requirement of appropriate tools to identify pollutants and their sources as well as to verify the performance of the proactive actions [14].

The microclimatic conditions into the Refectory of Santa Maria delle Grazie Church are managed by physically separate the indoor air from the outside through two "filter areas" (area 1 and 2 in Figure 2) at the visitors' entrance and exit doors, and maintaining a slight overpressure to prevent the diffusion of pollutants from the external urban atmosphere. An HVAC system (air exchange rate from the outdoor around 0.67 h^{-1}) with several air filters is installed to remove pollutants in the incoming air [15-17]. Temperature and relative humidity are maintained at constant values of 24–25°C during summer and 20–22 °C in winter, respectively, and RH ~ 50% [18]. Visitors to the museum could be pollutants carriers even in controlled atmosphere conditions, therefore the number of visitors and the length of the visit are kept strictly limited (30 people for 15 min, from 8:00 AM to 5:00 PM for 6 days/week) and their direction is strictly controlled by providing stops in dedicated rooms (area 1 and 2 in the map of Figure 2) to reduce the pollutants they carry.

In a previous paper, it has been reported that diurnal CO_2 levels in the Refectory room frequently reach the threshold concentration of 1000 ppm [18] thus limiting the possibility to increase the number of visitors per turn. Consequently, the museum has several hundred unsatisfied visit requests every year.

In our work, we analysed the effect of visitors on indoor air quality by the measure of CO_2 and its isotopic composition, considering that the breath of visitors could introduce new pollutants into the closed environment, besides fine particles.

Carbon dioxide emitted by humans has a characteristic $\delta^{13}C$ value less than -24.00 ‰. In some scientific works, the isotopic composition of CO_2 was used to assess sources at a local scale to discriminate emissions from vehicles from those generated by the biological activity in urban areas [19 - 24].

Figure 1. The "Last Supper" with visitors.

Generally, isotopic compositions were used to set time constraints on processes and manufacturing of objects and to date human samples (e.g. the ^{14}C technique). Furthermore, the isotopic composition of metals like Sr and Pb isotopes were useful for tracing the origin of a component or a metal [25,26]. In our work, we analysed the possible use of $\delta^{13}C$ values to refer to atmospheric CO_2 as a simple tool for the identification and classification of the source of CO_2 and monitor the influence of tourists on indoor air quality in the Refectory of Santa Maria delle Grazie in Milan, given a possible increase in the number of visitors, thus allowing greater enjoyment of the "Last Supper".

II. MATERIALS AND METHODS

A. Field measurements

The monitoring campaigns were carried out from September - November 2016 and May - July 2017. Carbon dioxide for $\delta^{13}C$ measurements was collected through active and passive sampling techniques. The passive sampler was the commercial RING from Aquaria Srl, where the internal concentric steel cartridge was filled with 500.0 mg of a $CaO/Ca_{12}Al_{14}O_{33}$ 75:25 w/w hydrated sorbent.

The passive samplers were located at about 2.0 m of height in pre-established positions, as depicted in Figure 2, for six days for each measurement, to obtain average concentration values in a week.

The active monitoring was conducted on the same days at the beginning of the monitoring program in September to collect carbon dioxide during the visit of tourists, from 7:00 am to 12:00 am and in the interval between the exit and the entrance of a new group of visitors. Each measurement lasted 15 minutes and several samples were collected to obtain replicate values and confirm the reproducibility of the measurements.

For the active sampling, a tube of ascarite sorbent was used, for the first time, connected to an air pump at a constant flow rate (1L/min) for 15 minutes, on the same side of the painting in front of the visitors, thanks to a small hole from the technical room to the Refectory. The sampling flow rate was checked in continuous by a fluxometer.

B. *Preparation of high reactivity calcium oxide substrate for passive CO_2 capture*

Calcium oxide-based sorbent was prepared as follows: 56.8 g of aluminium nitrate nonahydrate [$Al(NO_3)_3\ 9H_2O$] and 52.4 g of calcium oxide were added into a mixture of distilled water (1.5 L) and 2-propanol (260 mL) so that the weight ratio of calcium oxide to the newly formed mayenite ($Ca_{12}Al_{14}O_{33}$) would become 75:25 w/w. This solution was stirred for 1 h at 75 °C and successively dried at 120 °C for 18 h before being roasted at 500 °C for 3 h in the air. This method produced a fine and porous powder. After calcination, distilled water was added to the mixture and the obtained paste was dried at 120 °C for 2 h and then calcined in air at 800 °C for 1.5 h [19, 20].

All reagents were purchased at reagent grade from SigmaAldrich. Before exposure to CO_2, the sorbent was “activated” by hydrating with water vapor in a closed system for 7 days. Hydration was also necessary to avoid interferences due to variable atmospheric humidity during the exposition.

The crystalline structure of both hydrated and dehydrated sorbents was characterized by XRD analysis.

C. *Preparation of substrate for active CO_2 capture*

Active samplers were prepared using glass tubes with 800 mg Ascarite, 8-20 mesh, as a sorbent for carbon dioxide. All reagents were purchased at reagent grade from SigmaAldrich.

D. *Carbon isotopic ratio analysis*

$\delta^{13}C$ analysis was conducted utilizing a HeliFANplus analyzer equipped with a single beam nondispersive infrared industrial photometer. After the exposure at the sampling locations, the sorbent materials were placed into a glass flask and mixed with 2.5 ml of orthophosphoric acid to develop CO_2 from the carbonates. CO_2 was then gathered into the aluminized breath bags connected with the inlet ports of the NDIR spectrometer for sequential measurements. The NDIR device was connected to a computer, which enables the software-guided measurement and calculation of results. Three samples were analyzed for each determination.

The carbon isotope ratio was expressed in δ‰ relative to V-PDB (Vienna-Pee Dee Belemnite), according to the IUPAC protocol in:

$$\delta^{13}C = [\ (R_{sample} - R_{standard}\ ) \setminus R_{standard}\ ] \times 1000 \quad (1)$$

where R is the ratio between the heavier isotope and the lighter one ($^{13}C/^{12}C$) [27].

III. RESULTS AND DISCUSSION

The influence of visitors in the museum Cenacolo Vinciano was evaluated through stable carbon isotopic composition of carbon dioxide in the atmosphere.

The map of the passive samplers position is reported in Figure 2: arrows suggest the way of visitors (groups of about 30 people) when they entered the museum; circled numbers indicate passive samplers located in different areas (entrance, Refectory with the painting, technical area, bookshop, etc.).

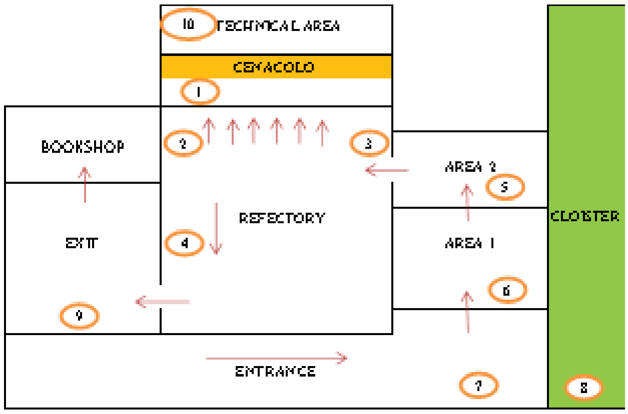

Figure. 2 Map of Museum: the circles represent the position of the passive samplers.

The results of passive sampling are reported in Table 1.

The values of $\delta^{13}C$ (‰) were influenced by the visitors inside the museum and were not very different in the areas analysed: the isotopic average values reflected the average value of human breath which is less than -24‰, as reported in the literature [28]. The $\delta^{13}C$ (‰) values of the technical area (10) resulted higher during the four monitoring campaigns, passing from -21.9 ‰ to -12.0 ‰ because this room is occasionally used by the technical staff to control the diagnostic equipment. This room opens onto the external courtyard of the bookshop and therefore the $\delta^{13}C$ (‰) values found are consistent with that of the external environment.

During the sampling of July, we found different results respect to the previous months, with values generally higher and closer to the external isotopic composition of CO_2. These results could be explained by considering that, to mitigate the elevate summer temperatures, some of the windows on the cloister and the courtyard were opened to the external area and the isotopic values increased, looking alike values of external carbon dioxide.

Table 1. $\delta^{13}C$ (‰) value obtained from passive sampling in different positions.

Passive sampler position	26-30 /09 (2016) $\delta^{13}C$ (‰)	09-14/11 (2016) $\delta^{13}C$ (‰)	23-29/05 (2017) $\delta^{13}C$ (‰)	17-24/07 (2017) $\delta^{13}C$ (‰)
1	-26.2	-29.7	-26.5	-23.3
2	-24.4	-32.1	-27.0	-22.0
3	-27.3	-31.2	-30.6	/
4	-25.1	-31.0	-34.7	-22.2
5	/	-28.3	-33.8	-22.3
6	-22.4	-32.7	-28.8	-17.6
7	-25.5	-37.6	-30.1	-16.1
8	-26.6	-35.6	/	-22.3
9	-25.6	-21.0	/	-19.2
10	-21.9	-20.4	-20.7	-12.0

Interestingly, the results obtained by active sampling confirmed that the carbon isotopic composition of CO_2 collected in the Refectory was strictly related to visitors. The sampling was carried out on September 2016, starting early in the morning, when the museum was still closed and repeatedly during the visit of different groups of visitors, all measurements lasted 15 minutes (the time for each visit). The results are shown in Figure 3.

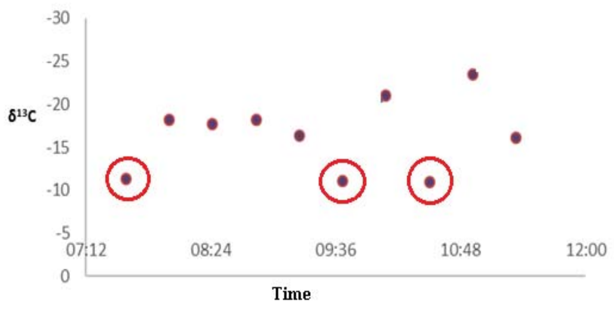

Figure. 3 Stable carbon isotope ratio $\delta^{13}C$ (‰) for active sampling in the Refectory.

Early in the morning, when the museum was closed, the $\delta^{13}C$ value measured was -11.3 ‰. Successively the presence of visitors led the isotopic value to decrease. The points with the red circles correspond to sampling performed before the opening of the museum and in correspondence to the change of the groups of visitors. It can be observed that during the change of groups of visitors, thanks to the HVAC system the air was efficiently exchanged leading to a changing in delta values of CO_2.

Overall, we observed an average of the $\delta^{13}C$ value of this zone, detected by active samplers (-16.4‰), higher than the average value of – 26.4 ‰ detected with the passive samplers positioned in different parts of the Refectory room. This means that close to the painting the ventilation system and the air replacement are very efficient whereas in different positions the CO_2 reflects, on average, the human presence in the room. Active sampling was carried out only in September because the purpose was to detect the change in the carbon isotopic composition of CO_2 at a specific time of day in the presence/absence of visitors. This methodology permits to obtain a single point in time and provide information about contaminant concentration at one point in time, while the passive sampling methodology gives contaminant concentration as an average over the whole deployment period.

CONCLUSIONS

In this work, we looked for CO_2 concentration and isotopic composition that can be linked to the presence of visitors. During the monitoring campaigns, there was clear evidence of the variation of the isotopic composition of CO_2 with the presence of visitors. The value of the isotopic change found with the passive samplers in the Refectory was, on average, determined by the visitors. The most important results were associated with active sampling that showed the variation of $\delta^{13}C$ value in the presence/absence of visitors in the Refectory. Early in the morning $\delta^{13}C$ value was -11.3 ‰, very close to the stable isotope value of carbon dioxide in the urban environments, while during a visit of 30 people the $\delta^{13}C$ decreased to values associated with their presence. This observation indicates that the air exchange system is very effective near the painting. This correlation revealed that $\delta^{13}C$ value could be used as a robust and non-invasive marker for real-time evaluation of the air condition systems in the museums and its monitoring could suggest a strategy for the preventive conservation of artworks and manage the number of visitors per turn. This is also a preliminary study to understand if isotope carbon value could be used to facilitate chemical identification of other pollutants, such as particulate, ammonia, sulfur dioxide, to reduce the damage on fine artworks, architectural and archaeological heritage, suggesting new and correct procedures of preservation such as rationalization of entrances, implementation of air filtration systems and a coherent environmental and architectural conservation approach.

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