

RESEARCH ARTICLE

FORMALDEHYDE AND TOTAL ALDEHYDES IN INDOOR AIR OF PUBLIC ENVIRONMENTS BY VOLTAMMETRY

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ABSTRACT

The proposed method involves active sampling, where a sampling pump is used to pull air through a solution and voltammetric analysis of the obtained solutions. No interferences have been observed. In addition, very little sample preparation is required. Analyses were performed in 19 indoor stations and one in outdoor. Measurements were carried out on University environments: Museum of Chemistry, Zoological Museum, libraries, laboratories, corridors, meeting rooms, photocopying room, machine shop and terrace. Formaldehyde concentrations in analyzed samples ranged from 2.6 to 85 $\mu\text{g m}^{-3}$ (median = 32 $\mu\text{g m}^{-3}$), while the sum of others aldehydes ranged from 2 to 25 $\mu\text{g m}^{-3}$ (median = 2.4 $\mu\text{g m}^{-3}$). In the sample Zoological Museum 2, the sum of other aldehydes was very high (400 $\mu\text{g m}^{-3}$). The results demonstrated that artificial ventilation is an efficient system to control indoor air pollution caused by aldehydes emissions.

INTRODUCTION

Studies on indoor air quality are important since people spend more than 80% [1] of their life in confined environments, thus it is necessary to evaluate indoor contaminant concentrations and distributions in order to assess total human exposure to them.

Ozone is a reactive gas and may affect the indoor air quality indirectly through reaction of high molecular volatile organic compounds (VOCs) into formaldehydes, organic acid, ultrafine particles and free radicals [2].

Since in most offices are used printers and photocopiers that emit contaminants (VOCs, ozone, particles, etc.) [2-3] more attention has been paid to them, recently. Aldehydes have several indoor sources, e.g., direct emissions from building materials, wooden artifacts, carpets, stoves and fireplaces, cleaning products, air fresheners various types of clothing and cigarette smoking. Also, formaldehyde is used in the formulation of hair shampoo as antibacterial agent.

Aldehydes are indoor and outdoor chemical pollutants

of particular interest due to their potential impact on health [4-7]. Acute exposure to formaldehyde may cause irritation of the eyes and of respiratory tract, nausea, headache, tiredness and thirst. Chronic exposure has been associated with an increased risk of developing respiratory illnesses [7].

Moreover, considering the deleterious effects of formaldehyde vapours on a wide range of museum objects [8] we carried out analyses in different areas of Library located on Chemistry Departments and in two different museums. This research is also aimed to present to workers the health risks associated with the use aldehydes originating from instrumentation necessary to carry out their work in closed environments.

Our data are discussed and compared with those of previous studies carried out in different countries [8].

To carry out this objective, we developed a reliable, simple, economic and fast method for the determination of formaldehyde and others aldehydes (acetaldehyde, hexanal, etc.) in indoor environments because they cannot be readily measured directly by conventional techniques used in most laboratories [9]. Different methods for the analysis of aldehydes were reported in literature. In particular, a study [9] was conducted to evaluate several techniques for determining formaldehyde in environmental matrices. The first technique is based on the spectroscopic analysis, and the other four used derivatization procedures followed by fluorometric measurements or high-performance liquid chromatography with UV detector. In these cases, formaldehyde was generated by two techniques: in the first, zero air was bubbled through a solution of aqueous formaldehyde to produce gas-phase formaldehyde. Several compounds, as possible interferences, were added to the air mixtures; in the last technique, formaldehyde was generated as a product from controlled irradiations of hydrocarbons and nitrogen oxides in a chamber. The data from each of the techniques were compared against mean values in each sampling period. At a formaldehyde concentration of 10 ppb, each technique showed no evidence for interferences by O₃ (190 ppbv), NO₂ (300 ppbv), SO₂ (20 ppbv) and H₂O₂ (7 ppbv). The agreement for formaldehyde concentrations measured for the photochemical mixtures was similar to that of the mixtures in zero air. In several methods, aldehydes after removal from a cartridge by thermal or solvent desorption or extraction technique are derivatized, and the resulting chromophores are analysed by chromatography and/or spectroscopy. Salthammer [10] found that the acetyl acetone and DNPH methods are equivalent for the analysis of formaldehyde. The DNPH-method yielded slightly lower values, but the deviations were within the analytical error. However, distinctly lower

results were found for pentanal and hexanal with the DNPH-method compared to sampling on Tenax and analysis with thermal desorption GC/MS. Practically, chromatographic methods are slow, laborious and require use of expensive instrumentation. Also, aldehydes are low relative molecular mass compounds that are difficult to determine using GC-MS.

Spectrophotometric methods, involving the pararosaniline-based Schiff reaction, but, unfortunately, colour development is slow and quantification limits are high. Among the spectrometric methods, the reaction with 2,4-pentanedione, since acetaldehyde does not interfere even when present in concentrations 1000 times higher than formaldehyde [11], is the most sensitive and specific methods.

In gas samples aldehydes were analyzed by high performance liquid chromatography as their 2,4-dinitrophenylhydrazine (2,4-DNP) derivatives. Moreover, preparation of 2,4-DNP derivatives requires strong acidic conditions that may cause undesirable reactions, such as decomposition of carbohydrates [12].

Some researchers [13] have developed a portable device to formaldehyde monitoring and carried out indoor air formaldehyde concentration analysis. The absorbance difference of the sensor element was measured in the monitoring device at regular intervals and the result was converted into the formaldehyde concentration. This was possible because they found that the lutidine derivative, that was formed as a yellow product of the reaction between 1-phenyl-1,3-butandione and formaldehyde, was stable in porous glass for at least six months. Under several indoor conditions, the detection limit of the device is 5 µg m⁻³h⁻¹.

Several sensing devices are available for continuous formaldehyde monitoring including a luminescence-based gas sensor, a silicon-based gas sensors, a nickel oxide film sensor, quartz crystal microbalance-based sensors and Cd-In oxides sensor [12]. However, their sensitivity is inadequate to evaluate formaldehyde concentrations in indoor environments.

In a recent unpublished study, we measured the concentrations of formaldehyde in several rooms for surgeries and laboratories of chemical-clinical analysis. We used a portable multiple gas detector (Brüel and Kjær type-1302) whose operation is based on the photo-acoustic measurement of the absorption of infrared radiation. The concentrations of formaldehyde, in the investigated stations, where the chemical product was used, were very high (80-120 µg m⁻³ in a case and 146-516 µg m⁻³ in others) while, in the neighboring environments (corridors, offices, etc.) analita concentrations were in the same order of magnitude compared to those of the present paper. The negative aspect about the use of the mentioned

portable instrumentation depend on periodic calibration that can be performed only by provider.

The method developed in this paper to measuring aldehydes involves active sampling, where a sampling pump is used to pull air through a solution of ammonium citrate. For the determination of aldehydes in the obtained solutions, analyses were carried out by voltammetry.

Voltammetric methods are used for single and simultaneous analysis of several compounds. The history, theoretical background and applications of voltammetry are well known [14]. Many applications of voltammetry technique for the determination of interesting compounds in environmental and toxicological fields in several matrices are reported [15,16], but to the best of our knowledge, there are no reports on the application of the electrochemical method for the determination of traces of aldehydes in environmental matrices.

In this study, we used the differential pulsed voltammetry (DPV) to measure the concentrations of formaldehyde and total aldehydes. Unlike conventional stripping approaches (anodic and cathodic stripping voltammetry), which based on an electrolytic nature of preconcentration step, DPV approach in contrast is based on the differential measure of the faradic current after the application of a potential pulse at the working electrode, with great sensitivity and resolution. Consequently, the voltammetric technique can be successfully applied for analyzing compounds in environmental matrices either with moderate sample preparation.

MATERIALS AND METHODS

Sampling

A total of twenty samples were collected: 19 indoor stations and one in outdoor (terrace) (Figure 1) in Palermo (Italy) that is a densely populated town-city (about 850,000 inhabitants) with a heavy load of vehicular traffic and major craft and industrial activities are located within the urban area. It is characterized by conspicuous air pollution [17].

The first measurements were focused on different places of University: museum, libraries (n°4), laboratories (n°3), corridors (n°2), meeting rooms (n°2), photocopying room, machine shop and terrace (outdoor). The second series of indoor measurements were conducted in different areas and times in the Zoological Museum (n°4).

The measurements of aldehydes concentrations were conducted from June 2011 to March 2012. All the measurements were triplicate in the same location on the same day.

The Chemistry Museum is housed in a new building (constructed after 1990) while those of the Zoological Museum is in an ancient structure. Both museums

have wood tables and shelves and are furnished with antique wood furniture. Chemistry museum has no windows that can be opened and is equipped with a forced ventilation system while Zoological Museum has a natural ventilation system. Inside both museums smoking is strictly forbidden. The Chemistry Museum is usually open only for short periods of time, while Zoological Museum is usually open for visitors, schools, researchers and internal students for longer periods of time. Additional measurements were performed in a photocopy centre equipped with an efficient circulation and purification system and air conditioning.

Aldehydes were collected using a sampler (Explorer mod. ZB1, Zambelli, Italy) with a pump drawing air through a glass fiber filter (47 mm in diameter) to stop particulate, two traps containing ammonium citrate $0.1 \text{ mol L}^{-1} \text{ M}$ to collect aldehydes from the air.

The sampling solutions were weighed before and after the sampling. Preliminary tests have shown that, during the sampling period, the pH (6.5) of the absorbent solutions does not undergo appreciable variations. Flow rates of 1 L min^{-1} were monitored at the start and end of each sampling period. During the sampling period (3-4 hours), the volume of sampled air was recorded. Approximately a volume of 200 L of air was drawn through the sampling apparatus. Increased periods of sampling can be performed when longer-term averages are needed.

The sampling period is particularly appropriate to museum and libraries studies where an instantaneous measurement might not reflect the mean pollutant concentrations surrounding workers and objects held in closed spaces for a long time.

Reagents

All chemicals used were of analytical reagent grade and were used without further purification. Formaldehyde stock solution 37% for analysis was purchased from Aldrich, Milano. All solutions were prepared in Milli Q water.

Formaldehyde and acetaldehyde stock solutions of $1 \text{ g}\cdot\text{L}^{-1}$ were prepared by diluting the appropriate amount of compounds in Milli Q water in a volumetric flask. The formaldehyde stock solution was titrated as reported in Manual of Analytical Methods (NIOSH, 1994) [19] and stored in the dark and under refrigeration in order to minimize decomposition. Standard solutions at lower concentrations were prepared daily by diluting the stock solution with water. Hydrazine sulfate solutions (1%) were prepared daily from analytical grade reagents (Carlo Erba, Milano, Italy).

Analytical method

Aldehydes can be determined by voltammetry in either basic or acid solution. The derivatives of carbonyl compounds are more easily determined

than the free carbonyl compounds themselves, with which complicating side reactions such as hydration, acetal formation, or enolization tend to lower the concentration of the free carbonyl group. In this paper, the solutions obtained by the sampling (in the presence of 0.1 M ammonium citrate, as supporting electrolyte (pH 6.5) and 1% hydrazine sulphate) allowed to stand for at least 5 min before the voltammetric analysis is run. By reacting with hydrazine under acidic conditions, aldehydes can be quantitatively converted into a hydrazone:

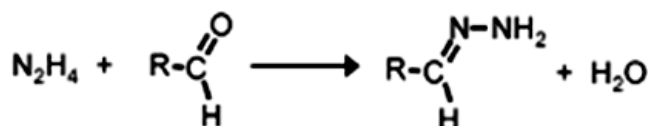


Fig. 1a Reaction between hydrazine and aldehydes into hydrazone

Once formed, hydrazone adduct is stable. No variation of the voltammetric signal was observed after 60 minutes of standing. The reaction of hydrazine with the other aldehydes (acetaldehyde, hexanal, etc.) is not immediate, and a reaction time of 5 min was observed to be adequate. The reduction of the hydrazone at the electrode is a two-electron process, and the signal (current) is proportional to aldehyde concentration.

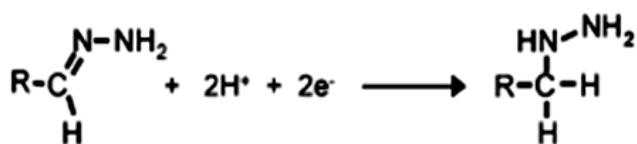


Fig. 1b Reduction of the hydrazone at the electrode during voltammetric measures

The sample solutions were analyzed by differential pulse voltammetry (DPV) using a Polarograph Amel Model 433-A. The operating conditions are reported in Table 1.

The solutions were deaerated with analytical grade nitrogen (99.998%) at the start of each experiment for 300 s and a flow of gas was maintained over the solution during the measure to prevent oxygen interference.

Subsequently, a potential changing from -950 to -1350 mV in the differential pulse mode was applied to the working electrode and current, due to the hydrazones reduction, was measured at -970 mV (versus Ag/AgCl) for formaldehyde and at -1150 mV for all aldehydes expressed as acetaldehyde; their intensities (areas or heights of voltammetric peaks) being proportional to concentration of aldehydes.

Quantitative measurements were performed using the standard addition procedure. Calibration graphs were built using data from measurements and evaluated by the least squares linear regression method.

Once the most ideal and suitable chemical conditions

and instrumental parameters for the voltammetric determination were established, calibration plots for the analyzed compounds were recorded to estimate the analytical characteristics of the developed method.

Quality control and assurance

All the vessels and flasks were cleaned before use by rinsing three times with hot HNO₃ (1%) and three times with water purified by Milli Q System. The linearity of the method was evaluated as follows:

Under the optimum conditions, very good linear correlations were obtained between the monitored voltammetric peaks and the concentrations in the range 0.25-25 µg L⁻¹. Least-square treatment of the calibration graphs (Figures 2,3) yielded the following regression equations:

$$i \text{ (nA)} = 1.108 + 7.63 C \text{ (}\mu\text{g}\cdot\text{m}^{-3}\text{)} \text{ (for formaldehyde),}$$

$$R^2 = 0.999 \text{ } n = 9$$

$$i \text{ (nA)} = 0.31 + 5.46 C \text{ (}\mu\text{g}\cdot\text{m}^{-3}\text{)} \text{ (for acetaldehyde),}$$

$$R^2 = 0.999 \text{ } n = 9$$

where *i* is the peak current, *C* the analysed compounds concentrations and *r* the correlation coefficient (*r* is a measure of the strength of the straight-line or linear relationship between the variables. The correlation coefficient can vary between +1 and -1. Coefficient of determination is symbolized by R² because it is square of the coefficient of correlation).

Samples were analyzed by standard addition method whereby the standard solution was added directly to an aliquots of solutions obtained by bubbling air into the solution of ammonium citrate. This method was used because sample matrix and possible interferences could also contribute to the analytical signal, a situation known as the matrix effect, thus making it impossible to compare the analytical signal (in our case current) between sample and standard using the traditional calibration curve approach.

The method of standard addition is a type of quantitative analysis approach often used in analytical chemistry whereby. This method is used in situations where sample matrix also contributes to the analytical signal, a situation known as the matrix effect, thus making it impossible to compare the analytical signal between sample and standard using the traditional calibration curve approach.

Using the intercept (negative) on the calibration curve, the employed volumes of solutions and the air volume sampled, we calculate the concentration of aldehydes in the different stations.

Detection and quantification limits

The detection and quantification limits were established. The detection limit (LOD), estimated on the basis of seven determinations of the blanks (*b*), as *b*+3*s* (three times the background noise (IUPAC criterion), was 0.4 µg m⁻³ for formaldehyde and 0.2 µg m⁻³ for all others compounds. Quantification

limits (LOQ) for analyte [19], calculated on the basis of seven determinations of the blanks as ten times the standard deviation of the blanks for formaldehyde and acetaldehyde are respectively 1.1 and 0.8 $\mu\text{g m}^{-3}$. Considering the analyzed solutions obtained from sampling, the LODs values for formaldehyde and other aldehydes correspond to about 0.8 and 0.4 $\mu\text{g L}^{-1}$ respectively.

As field blanks we used solutions of ammonium citrate 0.1 mol L^{-1} . The blank values of analytical procedure analyzed concomitantly with the samples remained always below the quantification limits (LOD).

Reproducibility

The reproducibility of the sampling was preliminarily checked by analyzing for the aldehydes three different samples of air collected at different points of the same environment the same morning. The standard deviation on sampling (about 10%) with respect to that of the whole analytical process was negligible.

The high sensitivity of voltammetry is accompanied by very good reproducibility. To evaluate the precision of the analysis, three replicates of the same sample were analyzed. The relative standard deviations of the replicates on the concentrations of formaldehyde and others aldehydes are respectively 3% to 5% and are satisfactory for determinations at the $\mu\text{g m}^{-3}$ level.

Accuracy

Because a reference certified standard of environmental matrices (air) containing the analytes taken into account in this work was not commercially available, the accuracy of the method was checked by determining the recovery of a known amount of formaldehyde and acetaldehyde added, before the sampling, to a portion of the ammonium citrate solution previously analyzed. The values of the recovery obtained by the standard addition method were 98% for formaldehyde and 95% for the other aldehydes.

RESULTS AND DISCUSSION

Table 2 summarizes the concentrations of aldehydes measured in the 20 environments using the voltammetric method by us optimized. The most important advantage of this method is its selectivity for the considered compounds. No interferences from bisulphites and other compounds have been observed. In addition, very little sample preparation is required.

All reported data were blank corrected. All the formaldehyde concentrations were above the detection limit of method, evaluated 1.1 $\mu\text{g m}^{-3}$. In some cases, sum of other aldehydes were similar to quantification limit (0.8 $\mu\text{g m}^{-3}$).

Formaldehyde concentrations ranged from 2.6 to 85 $\mu\text{g m}^{-3}$ (median = 32 $\mu\text{g m}^{-3}$), while the sum of others

aldehydes ranged from 2 to 25 $\mu\text{g m}^{-3}$ (median = 2.4 $\mu\text{g m}^{-3}$). Only in a case (station n° 17, Zoological Museum 2), the sum of other aldehydes was very high (400 $\mu\text{g m}^{-3}$) (Figure 4).

Formaldehyde and other aldehydes were measured in the air outside the buildings only in one case (n° 14, terrace), however, the presence of volatile compounds in outdoor air is known to have little influence on indoor concentrations because the outdoor concentrations of aldehydes are much lower than indoor. In a study [20] the mean outdoor concentration was found to be 18 $\mu\text{g}\cdot\text{m}^{-3}$ that it is equal to ours.

Our mean formaldehyde indoor concentration of 32 $\mu\text{g m}^{-3}$ is in good agreement with measured in several homes in the Strasbourg French city (33 $\mu\text{g m}^{-3}$) [21]; and with those (30 $\mu\text{g m}^{-3}$) measured by Nicolas in Canada [22]; but is higher than that of 20 $\mu\text{g m}^{-3}$ reported by Lui [23] in a study performed in homes in United States.

In good agreement with several researchers, it has been shown that indoor concentrations of our compounds are generally much higher than outdoors [24,25] also indoor and outdoor concentrations are not correlated [26].

The observed elevated concentrations of formaldehyde in Zoological Museum (mean value = 54 $\mu\text{g}\cdot\text{m}^{-3}$) could depend on the presence in the environments of numerous specimens preserved in jars containing formalin solution, of several old stuffed animal and from absence of artificial ventilation. Also, Zoological Museum is located in a historical foundation with the fabric and fittings completed in 1894. The shelving, along walls on two levels, is made of wood, which, as the lignocellulosic material, probably contributes to the observed high concentration of formaldehyde concentration. Very high total aldehydes concentration have been measured in Zoological Museum (400 $\mu\text{g m}^{-3}$) where a numerous groups of visitors were presents during the sampling.

Levels of formaldehyde in indoor air samples collected in the Museum of Chemistry, Laboratory A1 and corridor of Organic Department appeared high (50 $\mu\text{g m}^{-3}$) compared with the values (median = 18 $\mu\text{g m}^{-3}$) found in the other indoor areas of the same building. In contrast with Zoological Museum, Chemistry Museum is located in a recent building and is equipped with wood shelving along walls. Lab tables, display cases and cabinets are made of wood recently restored. The used products (paints, resin, dyes, etc), probably, contributes to the observed concentration of formaldehyde.

Measurements were also carried out in the corridor, which is a large open space adjacent to the museum, and the formaldehyde concentrations slightly decreased (27 $\mu\text{g m}^{-3}$).

In this study, the indoor air of a room containing a photocopier (n°8) was monitored. The results

confirmed similar values concentration of aldehydes than those measured in the corridors and open spaces. Formaldehyde was detected in all of the 4 libraries and the concentrations were very similar ($18 \mu\text{g}\cdot\text{m}^{-3}$) while the sum of the others aldehydes were, except in one case (sample n°4), similar than the quantification limit. Concentrations of formaldehyde in the indoor air samples collected in the University libraries, located in the inner Chemical Departments, were generally lower than those collected in other Department's spaces.

Formaldehyde concentrations in libraries are lower than those reported by Fantuzzi [26] for 16 libraries of the University of Modena, those ranged from 1.7 to $67.8 \mu\text{g m}^{-3}$ with an average value of $33 \mu\text{g m}^{-3}$. Similarly to formaldehyde level, the sum of others aldehydes concentration was lower in library of Palermo University (from 2 to $6 \mu\text{g m}^{-3}$) than that in library of Modena, where hexanal concentration of $8.6 \mu\text{g}\cdot\text{m}^{-3}$ has been also detected.

In laboratories, where four triplicate air samples were collected, the formaldehyde mean concentrations ranged between 18 and $50 \mu\text{g m}^{-3}$, while those of acetaldehyde from 2.0 to $25 \mu\text{g}\cdot\text{m}^{-3}$. Aldehydes mean concentrations in the laboratory A1 were higher than those observed in the other. This evidence can be explain by considering that, in these environments, solutions were prepared daily for analysis of aldehydes, while voltammetric measurements were carried out in a different lab (n°9).

Many studies measuring formaldehyde concentrations in indoor air suggest that the concentrations are often higher than those outside. In most cases, especially in the environment equipped with air recirculation system, our results do not agree with this finding, as indoor and outdoor levels were very similar, perhaps due to the air recycling caused by ventilation system. Results demonstrated that artificial ventilation as in the case of laboratory photocopies (n°15), is an efficient system to control indoor air pollution caused by aldehydes emissions.

Not taking into account the concentration measured in the station where once was obtained a value much greater than the mean, the high indoor/outdoor ratios of formaldehyde and acetaldehyde (about 12 and 3 , respectively) confirm the existence of indoor aldehydes sources (stored materials, activities, etc.). Therefore, the indoor exposure represents the maximal fraction of the daily human exposure.

In the mechanical and electronic workshop (n°13), in which it is performed maintenance of equipment of the department, the concentrations of formaldehyde ($32 \mu\text{g m}^{-3}$) was relatively higher than those measured in others areas of departments. In this environment, paints, lubricants and solvents are commonly used that could be the source of the pollutants considered in this work.

International regulations and guidelines concerning

to emissions of and exposures to formaldehyde have been set in several countries and range from 60 to $500 \mu\text{g m}^{-3}$ with a tendency for $120 \mu\text{g m}^{-3}$. Data from our research show values below this limit. According to the World Health Organization [28], the lowest formaldehyde concentration that has been related with nose and throat irritation after short-term exposure is $100 \mu\text{g}\cdot\text{m}^{-3}$ (WHO, 2000) [29], therefore this recommended maximal value is for a 30-min average exposition to formaldehyde. In this study, no places show formaldehyde values exceeding this concentration. Other recommended values were established, for example, Health and Welfare Canada's exposure guideline for formaldehyde in residential air is $120 \mu\text{g m}^{-3}$ as a 5-min average and a target concentration of $60 \mu\text{g}/\text{m}^3$ is recommended (Health and Welfare Canada, 1987) [30]. Furthermore, the recommended levels are valid for short-term exposures (5–30 min).

The mean concentration of formaldehyde ($32 \mu\text{g m}^{-3}$) found in the 19 indoor environments were higher than the indoor air quality guideline value for a long-term exposure to, fixed to $10 \mu\text{g m}^{-3}$ in France. If this last value is taken as a reference, all places investigated in this study, excluding the site where the air was purified (station n° 15), show concentrations below this value. Considering that a worker (researchers, teachers, secretaries, etc.) or a student spends about 70–80% of its time in indoor environment, estimation of the health effects under these conditions, lower concentrations but longer exposure time, merit more attention.

Students attending the courses of sciences generally handle solvents during laboratory work or presenting natural science museum may be exposed to little higher or similar aldehydes levels compared to students attending the colleges of social and/or humanistic sciences, whose typical academic activities are associated with paper, printer, photocopier or computer work. However, exposure data that confirm this hypothesis have not been widely reported in the literature.

CONCLUSIONS

The results of this study show that concentrations of total aldehydes in laboratory, libraries and museum environments, excluding a case, are in the range between 4.6 and $75 \mu\text{g m}^{-3}$. The elevated concentrations of formaldehyde in Zoological Museum could depend on the presence in the environments of numerous specimens preserved in jars containing formalin solution, of several old stuffed animals and from absence of artificial ventilation. Only in a case, at Zoological Museum, where several visitors were present during the sampling, the sum of other aldehydes was very high.

The lowest concentrations of aldehydes were recorded

in the laboratory of photocopies because artificial ventilation results an efficient system to control indoor air pollution.

In general, artificial ventilation could be provided to limit the exposition to such and similar pollutants in indoor air of public environments. The lack of knowledge concerning the consequence of volatile aldehydes and other organic volatiles compound, on library and museum remains a cause for concern. Additional studies needs to be carried out to increase the knowledge on the damage caused by aldehydes on heritage materials inside libraries, museum and archives.

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REFERENCES

1. Benner A, Gordon, GE Wise SA.. Mobile sources of atmospheric polycyclic aromatic hydrocarbons: a roadway tunnel study. *Environmental Science and Technology*, 1989, 23: 1269-77.
2. Kagi Naoki, Fujii Shuji, HoribaYouhei, Namiki Norikazu, OhtaniYoshio, Emi Hitoshi, Tamura Hajime & KimYong Shik, Indoor air quality for chemical and ultrafine particle contaminants from printers, *Building and Environment*, 2007, 42: 1949–1954.
3. Marchand C, Bulliot B, Le Calve S, Mirabel Ph. Aldehyde measurements in indoor environments in Strasbourg (France). *Atmospheric Environment*, 2006, 40: 1336–45.
4. IARC (1995). International Agency for Research on Cancer. (IARC) Monographs on the evaluation of carcinogenic risks to human. Wood Dust and Formaldehyde, 62. IARC. Lyone.
5. IARC (2004). Overall Evaluation of Carcinogenicity to Humans. Formaldehyde, Monographs Series, vol. 88. International Agency for Research on Cancer, Lyon, France.
6. IARC (2006). Monographs on the Evaluation of Carcinogenic Risks to Humans, Formaldehyde, 2-Butoxyethanol and 1-tert-Butoxypropan-2-ol, vol. 88, WHO, Geneva.
7. WHO (2001) Formaldehyde, Air Quality Guidelines, 2nd ed., WHO Regional Office for Europe, Copenhagen, Denmark. p. 1 (Chapter 5.8).
8. Gibson LT, Kerr WJ, Nordon A, Reglinski J, Robertson C, Turnbulla L, Watt CM, Cheung A, Johnstone W. On-site determination of formaldehyde: A low cost measurement device for museum environments, *Analitica Chimica Acta*, 2008, 623: 109–116.
9. Kleindienst TE, Shepson, PB, Nero CM, Arnts RR, Tejada SB, Mackay GI, Mayne, Schiff LK, Lind HI, Kok JA, Lazrus GL, Dasgupta PK, Dong S. An Incomparision of formaldehyde measurement techniques at ambient concentration, *Atmospheric Environment*, 1967, 22 (9) 1931-39.
10. Salthammer T, Mentese S. Comparison of analytical techniques for the determination of aldehydes in test chambers, *Chemosphere*, 2008, 73: 1351–1356.
11. Pinheiro H LC, de Andrade V. M, de Paula Pereira P A, de Andrade Jailson B. Spectrofluorimetric determination of formaldehyde in air after collection onto silica cartridges coated with Fluoral P, *Microchemical Journal*, 2004, 78: 15– 20.
12. Kataoka H, Kondo T, Sumida A. Gas chromatographic determination of aldehydes in combustion smoke samples, *Analytica Chimica Acta*, 1998, 358: 269-75.
13. MaruoYY, Nakamura J. Portable formaldehyde monitoring device using porous glass sensor and its applications in indoor air quality studies, *Analytica Chimica Acta*, 2011, 702: 247– 253.
14. Skoog DA, Leary J. *Chimica Analitica Strumentale*, Edises, Napoli, 2000.
15. Orecchio S, Amorello D , Carollo C. Voltammetric determination of platinum in perfusate and blood: Preliminary data on pharmacokinetic study of arterial infusion with oxaliplatin. *Microchemical Journal*, 2012, 100: 72–76.
16. Amorello D, Orecchio S. Micro determination of dithiocarbamates in pesticide formulations using voltammetry, *Microchemical Journal*, 2013, 110: 334–339.
17. Orecchio S, Amorello D. Platinum levels in urban soils from Palermo (Italy); analytical method using voltammetry. *Microchemical Journal*, 2011, 99: 283–288.
18. Orecchio S, Amorello D. Platinum and rhodium associated with the leaves of Nerium oleander L.; analytical method using voltammetry; assessment of air quality in the Palermo (Italy) area, *Journal of Hazardous Materials*. 2010, 174: 720–27.
19. NIOSH. Manual of Analytical Methods (NMAM), Fourth Edition, Peter M.L. Editor, Cincinnati, Ohio 1994.
20. Baez A, Padilla H, Garcia R, Torres MC, Rosas I, Belmont R. Carbonyl levels in indoor and outdoor air in Mexico City and Xalapa, Mexico. *The Science of the Total Environment*. 2003, 302: 211–26.
21. C. Marchand, B. Bulliot, S. Le Calve, Ph. Mirabel, Aldehyde measurements in indoor environments in Strasbourg (France). *Atmospheric Environment* 40 2006, 1336–45.
22. Gilbert N, Guay M, Miller JD, Judek S, Chan C, Dales RE. Levels and determinants of formaldehyde, acetaldehyde, and acrolein in residential indoor air in Prince Edward Island, Canada. *Environmental Research*, 2005, 99: 11–17.

23. Liu W, Zhang J, Zhang L, Turpin BJ, Weisel CP, Morandi MT, Stock H, Colome S, Korn LR. Estimating contributions of indoor and outdoor sources to indoor carbonyl concentrations in three urban areas of the United States. *Atmospheric Environment*, 2006, 40: 2202-14.
24. Bell RW, Chapman RE, Kruschel BD, Spencer MJ. Windsor Air Quality Study: Personal Exposure Survey Results. Toronto, Queen's Publisher for Ontario 1994.
25. Kinney PL, Chillrud SN, Ramstrom S, Ross J, Spengler JD. Exposures to multiple air toxics in New York City. *Environmental Health Perspectives*, 2002, 110 (Suppl. 4): 539-46.
26. Jurvelin J, Vartiainen M, Jantunen M., Pasanen P. (). Personal exposure levels and microenvironmental concentrations of formaldehyde and acetaldehyde in the Helsinki metropolitan area, Finland. *Journal American Air Waste Manage Associate*. 2001, 51: 17-24.
27. Fantuzzi G., Aggazzotti G., Righi E., Cavazzuti L., Predieri G., Franceschelli A, Indoor air quality in the university libraries of Modena (Italy). *Science of the Total Environment*, 193 1996, 49-56.
28. Health and Welfare Canada 1987. Exposure Guidelines for Residential Indoor Air Quality. Department of National Health and Welfare, Ottawa, Ontario www.hc-sc.gc.ca/hecs-sesc/air_quality/.
29. WHO 2000. Air quality guideline for Europe, WHO Regional Publications, European series no. 91, eprise/main/WHO/InformationSources/Publications/Catalogue/20010910-6.
30. Afsset. Valeurs guides de qualité d'air intérieur, Le formaldehyde, Rapport du groupe de travail janvier, 2007 78.