Microchemical Journal 114 (2014) 187–191

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Determination of selected phthalates by gas chromatography–mass spectrometry in mural paintings from Palermo (Italy)

Santino Orecchio *, Roberta Indelicato, Salvatore Barreca

Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche, Università di Palermo, Viale delle Scienze, I-90128 Palermo, Italy

ARTICLE INFO

Article history:
Received 22 November 2013
Received in revised form 26 November 2013
Accepted 26 November 2013
Available online 4 December 2013

Keywords:
Mural paintings
Phthalates
GC-MS
Restore
Construction

ABSTRACT

Phthalate esters for decades, and probably even now, were used as softeners in water-based paintings. In general, these compounds are dangerous owing to their carcinogenicity and reproductive effects. Phthalates are not chemically but only physically bound to the matrices, hence, they may be leached into the environment and are ubiquitously found in environmental matrices. Considering that, construction is one of most important fields in Europe, and probably worldwide, with respect to its economic, technological and environmental impact.

In the present work the phthalate esters content of several mural paintings was evaluated by gas chromatography–mass spectrometry (GC-MS). Because, this issue is especially important to ensure proper security measurements during processes that could involve particulate inhalation, the total concentrations of 15 compounds in the analyzed mural paintings, ranged from 0.8 to 236 mg/Kg d.w. with an average of 39.4 mg/Kg d.w. The highest concentration was found in a mural painting sampled in an apartment built about 50 years ago, though, building age was not significantly correlated with the levels of total and single PAEs. Among the monitored phthalates, only four (bis(2-ethylhexyl) phthalate, diisobutyl phthalate, Di-n-butyl phthalate and diethyl phthalate) were detected in appreciable quantities. Benzyl butyl phthalate was relevant only for one sample and, at trace levels, only for two samples. In all tested mural paintings, except two samples, predominates the bis(2-ethylhexyl) phthalate (DEHP) (from 30 to 100% of total). In general, occasionally, dinonyl phthalate (DNP) was used as an alternative to DEHP, however, in our case, its occurrence was not found. Diisobutyl phthalate (DiBP) was detected in seven samples and ranged from 0.17 to 13.2 mg/Kg d.w.

1. Introduction

Indoor environments can be a sources and/or a repository of many kinds of pollutants [1,2] and it is necessary to evaluate their indoor sources, concentrations and distributions in order to assess human exposure to them, especially for children, elderly and sick people, because of their behavioral factors and longer indoor residence time [3].

The hazardous air pollutants are defined by the United State Environmental Protection Agency (EPA), among which there are polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), heavy metals (lead, chrome compounds etc.) usually deposited on surfaces of buildings located in anthropized areas [4]. Also, if a renovation or restore effort is planned for a property, construction workers and building occupants may need to be protected from hazardous substances. Most studies have focused on heavy metals, volatile organic compounds (VOCs), pesticides and less attention has been paid to potential health risks of exposure to persistent and semi-volatile endocrine-disrupting chemicals (EDCs) such as phthalic acid esters, generally called phthalates (PAEs) in the indoor environment [5]. Numerous household products, building materials and pest control activities are known as major sources of endocrine disruptor chemicals (EDCs). Traditionally, food consumption has been considered a primary route of exposure to contaminants like those measured in the present study. However, it is becoming clear that exposure through ingestion and/or inhalation of indoor dust may be comparable to corresponding food consumption especially for younger children [6]. It has been suggested that indoor dust is highly contaminated by phthalates and many other hazardous chemicals and thus indoor residential exposure may be a greater contributor to overall exposure than diet [7].

Phthalate esters for decades, and probably even now, were used as softeners in water-based synthetic paintings. Dinbutylphthalate (DBP) and Bis(2-ethylhexyl) phthalate (DEHP) are the most employed. Softeners are released from the painted surface for a long time after it has been applied [8]. Surfaces and structures, such as house walls painted with phthalates based paintings, can be a concern to construction workers engaged in demolition, restore and paint removal activities if they are not protected from hazardous dust inhalation.

Phthalates with higher molecular weights, such as bis(2-ethylhexyl) phthalate, are largely used as additives softeners and plasticizers, while those with lower molecular weights (diethyl, di-n-butyl and dimethyl phthalate) are components of industrial solvents, adhesive, wax, ink, pharmaceutical products, insecticide materials, and cosmetic [9]. DEHP was found in medical disposals devices and in a number of medicine

* Corresponding author. Tel.: +39 091 23897968.
E-mail address: santino.orecchio@unipa.it (S. Orecchio).

0026-265X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.microc.2013.11.015

coatings. Some compounds are contained in cleaning solutions for contact lenses [10] and in food packaging films [11].

Phthalates are not chemically but only physically bound to the matrices, hence, they may be leached into the environment and are ubiquitously found in dust, air, water, soils, and sediments [2,12–15].

Unfortunately, the phthalate concentrations that can be mobilized from surfaces are not usually determined. This issue is especially important to ensure proper security measurements during processes that could involve particulate inhalation. Construction is one of most important fields in Europe, and probably worldwide, with respect to its economic, technological, and environmental impact. In this context, important issues arise: construction, restore and demolition hazardous materials, in particular dusts that can be inhaled. Construction, renovation and repair dusts are generated in these processes, and during transporting, storing and handling construction materials. This may also be verified when certain construction processes are undertaken. Some works regarding other pollutants in construction materials are concentrated on PCBs in joint sealing materials and how this class of chemicals have spread into the environment and surrounding materials [16]. In the last years, Unites States Environmental Protection Agency (EPA) [17] sponsored a program aimed at reducing lead-based paint emissions in the environment from use, demolition and renovation of buildings but no actions has been taken about other dangerous substances such as phthalate esters. Protracted residence times and work on building matrices containing dangerous substances in the indoor environment increase possibility of exposure to contaminants by 1000-fold compared to outdoor exposures [18]. Levels of phthalates in indoor air and dust are often higher than outdoor levels [19,20].

Among the hazardous pollutants [20], phthalate esters are dangerous owing to their carcinogenicity and reproductive effects [21]. Phthalates, generally, are colorless and odourless liquids having high boiling points (228–380 °C), low volatility, insolubility in water and predominantly fat solubility. Excluding the dimethyl phthalate (DMP), which belong to the group of VOCs, PAEs are classified as semi-volatile organic compounds. There are no naturally occurring PAEs, therefore all phthalates found in environmental matrices can be accredited only to man-made materials. PAEs are emitted into the atmosphere as particulates and gasses [22]. Weschler [22] argues that, the less volatile PAEs are more likely to be deposited on the indoor surfaces bound to particles in wet and dry deposition. In particular, for compounds of intermediate vapor pressure, a temperature-dependent gas/particle portioning of PAEs will occur, and thus, they are subject to both wet and dry deposition in gaseous and particle-bound form. The transport, residence time, fate, and reactions of PAEs in atmosphere are widely controlled by their gas-particle partitioning [23]. About indoor pollution, indoor environments increase the lifetime of substances adsorbed to the dust by minimizing or eliminating the natural decomposition processes catalyzed by natural light and rain [24].

Moreover, numerous household products, building materials, and pest control activities are known as major sources of endocrine-disrupting chemicals. Evidence for the adverse effects of this class of substances on human health is mounting [5,7,19,22,21,25–27]. Thus, there is the need to acquire more information about the occurrence of EDCs in indoor matrices and the associated potential risk.

Workers manufacturing materials containing phthalates are greatly exposed and have shown to have urinary metabolite concentrations that often exceed those at the 95th percentile of the common population [28]. Such as reported PAEs are not very volatile, but they readily form aerosols that may be inhaled in particular during work with high temperature processes [29]. In addition, dermal exposures could potentially play a role in low temperature operations; on the other hand, due to their chemical characteristics (lipophilicity), dermal phthalate absorption is assumed to below or negligible. Several authors [29–31] claim that this theory might be not true because among phthalates exposed workers performing low temperature processes was found the presence of urinary PAEs metabolites. Gaudin [30] founds elevated urinary 5cx-MEPP metabolite concentrations (median 107.5 g/L) among workers preparing a DEHP-containing material at room temperature. In a study [31], workers refinishing phthalate-containing sealants at room temperatures had 20 times higher metabolite concentrations than the control group.

The principal aim of this study was to determine the concentrations and distribution of 15 PAEs presents in the surface layer of walls (mural paintings) of some buildings. In order, to get a better insight in environmental levels and distribution of these compounds, reliable analytical methods are required capable of measuring a large range of PAEs at low concentrations. There are some studies on the concentrations of PAEs in different matrices [2,7,10] but information about the occurrence and distribution of PAEs in mural paintings materials are absent.

One of the analytical difficulties that may occur with building materials is the complexity of matrices and differences in their compositions. Therefore, it is need check the validity of the analytical method using the material to be analyzed. In this paper we report an analytical method for 15 PAEs which adopts and improves previous knowledge and affords better results on the concentration levels and the distribution of phthalates in wall paintings.

GC/MS was used to quantify PAEs in samples taken from wall surface of eight building located in Palermo, in an attempt to demonstrate the presence and the hazards of substances, often not even known to the specific operators and managers.

2. Experimental

2.1. Study area

The buildings taken in consideration in this study are located in Palermo area (Italy). Palermo is a densely populated city (about 850,000 inhabitants). It is characterized by conspicuous air pollution [1,32–37]. The town is situated on the north-western coast of the island along the wide bay Piana di Palermo and is overlooked by Mt. Pellegrino (600 m above sea level). Palermo is a typically European town in building style and is generally built in stone (tuff), clay bricks and concrete.

In order to determine a possible pattern in usage of PAEs in the Palermo area, sampling was conducted in different parts of the town, in different types of buildings of different ages (Table 1). The samples were taken, during 2012 from the surface of the walls from eight buildings and were collected by scraping off the layers or removing fragments; care was taken to ensure that the samples were representative of the single room. From each surface, a total of 5 samples were collected. About 25 g of the material were placed in glass containers. The samples were refrigerated (4 °C), avoiding the exposure to light, and taken to the laboratory where they were frozen (−20 °C) until the analysis was performed. About 2 g of homogenized samples of mural painting were dried at 105 °C for overnight. The water content was determined by weight loss and was utilized to correlate all the results with dry weight. Before each analysis the samples were finely pulverized in a mortar.

Table 1
Descriptive profile of sampling station.

n°	Characteristic of station	Age of building
Mur 1	Stair of a building build around 1990.	23
Mur 2	Bedroom of an apartment on the first floor	25
Mur 3	Stair of the previous station	25
Mur 4	Living room of house dating from 1950 to 1 floor renovated 13 years ago.	63
Mur 5	Kitchen of an apartment on the top floor.	15
Mur 6	Garage	43
Mur 7	Kitchen	30
Mur 8	Kitchen	5