Journal of Chromatography A, 1380 (2015) 11–16

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Determination of trichloroanisole and trichlorophenol in wineries' ambient air by passive sampling and thermal desorption–gas chromatography coupled to tandem mass spectrometry

F.J. Camino-Sánchez [a,*], R. Bermúdez-Peinado [b], A. Zafra-Gómez [a], J. Ruíz-García [b], J.L. Vílchez-Quero [a]

[a] Research Group of Analytical Chemistry and Life Sciences, Department of Analytical Chemistry, Campus of Fuentenueva, University of Granada, E-18071 Granada, Spain
[b] DNOTA Medio Ambiente S.L.™, Research Department, E-18220 Granada, Spain

ARTICLE INFO

Article history:
Received 5 November 2014
Received in revised form
19 December 2014
Accepted 22 December 2014
Available online 30 December 2014

Keywords:
Haloanisoles
Halophenols
TD–GC–MS/MS
Winery
Wine taint
Air monitoring

ABSTRACT

The present paper describes the calibration of selected passive samplers used in the quantitation of trichlorophenol and trichloroanisole in wineries' ambient air, by calculating the corresponding sampling rates. The method is based on passive sampling with sorbent tubes and involves thermal desorption–gas chromatography–triple quadrupole mass spectrometry analysis. Three commercially available sorbents were tested using sampling cartridges with a radial design instead of axial ones. The best results were found for Tenax TA™. Sampling rates (*R*-values) for the selected sorbents were determined. Passive sampling was also used for accurately determining the amount of compounds present in the air. Adequate correlation coefficients between the mass of the target analytes and exposure time were obtained. The proposed validated method is a useful tool for the early detection of trichloroanisole and its precursor trichlorophenol in wineries' ambient air while avoiding contamination of wine or winery facilities.

1. Introduction

Chloroanisoles (CAs), particularly 2,4,6-trichloroanisole (TCA), are well-known wine contaminants, responsible for a variety of unpleasant musty aromas and taste. TCA represents a serious economic problem for wineries because wine spoilage can affect a few bottles or even the entire production of wine. TCA has been extensively studied due to the economic impact on the wine market. The sources of contamination are well-known [1] and recent investigations have shown that corks are just one of many possible sources of contamination. These include some kinds of wood preservatives and flame retardants that are used on wineries. In this sense, regular monitoring of these sources is highly recommended [1–3]. TCAs are produced by fungal biodegradation of halophenols (HPs). This degradation is not only caused by the formation of haloanisoles (HAs) from their respective HPs, but also low halogenated HAs can be formed by the removal of chlorine or bromine atoms to produce less chlorinated CAs from tetra- and penta-halophenols [2,4]. Since previous scientific papers have shown these compounds to be responsible for wine taint, 2,4,6-tricholoranisole and 2,4,6-trichlorophenol (TCP), were selected for the present study [3,5,6].

To the best of our knowledge, previous research in this field was limited mainly to the determination of HAs and HPs in wine [7–9], water [4,10] and cork [11,12]. Only one method, previously developed by our research group, has been presented for the detection and quantitation of HAs and HPs in ambient air of wineries on active sampling [13]. In the present work, in order to increase the possibility of monitoring these substances in indoor air, more specifically in wineries' ambient air, the use of passive samplers (PASs) is proposed. PASs have some advantages over active sampling such as the easy handling, cost-effectiveness and no calibrated air pumps are required. PASs are ideal for the calculation of time-weighted average concentrations and no power supply is required, which facilitates simultaneous multiple-point sampling [14–17]. Passive radial samplers were used instead of axial ones allowing for a very large diffusive surface while maintaining the amount of adsorbing material, therefore, improving sensitivity [18,19].

The aim of the present work was to calculate the sampling rates (*R*-values) for TCA and TCP diffused in the indoor air of winery facilities, by measuring their uptake. PASs are calibrated by deriving the

* Corresponding author. Tel.: +34 958 248409; fax: +34 958 243328.
E-mail address: franciscojavier.camino@abbott.com (F.J. Camino-Sánchez).

http://dx.doi.org/10.1016/j.chroma.2014.12.060
0021-9673/

R-value, in $m^3\,h^{-1}$, which is analogous to the equivalent volume of air sampled by the PAS. The efficiency of three commercially available adsorbents was also tested. The mass of the target analytes must be correlated with air concentration and the exposure time. Active sampling was performed simultaneously with the deployment of the PASs in order to determine the concentration of TCA and TCP in the ambient air during experiments. Thermal desorption and subsequent gas chromatography–triple quadrupole mass spectrometry (TD–GC–MS/MS) analysis in Selected Reaction Monitoring (SRM) was used for the analysis of the adsorbed compounds in the tubes and cartridges.

2. Experimental

2.1. Passive sampling theory

The fundamental principle of PAS is that chemicals from ambient air accumulate onto the sampling medium by way of gaseous diffusion. The theoretical principles that explain how chemicals accumulate are well described in the literature [20,21] as well as the calculation procedure of the *R*-values from the uptake measurements [16,22]. The uptake of a gaseous compound from the ambient air to a PAS medium is described as the effective concentration gradient between the air and the sampler. The mass of analyte retained onto the adsorbent (M_{Ad}) is a function of the mass transfer coefficient and the concentration gradient, as defined by the following equation:

$$\frac{dM_{Ad}}{dt} = k_V \cdot A_S \cdot \left(C_{Air} - \frac{C_{Ad}}{K_{Ad}}\right) \quad (1)$$

where A_S is the surface area of the adsorbent (m^2), k_V the mass transfer coefficient ($m\,s^{-1}$), C_{Air} the analyte concentration in the air ($ng\,m^{-3}$), C_{Ad} the analyte's concentration on the adsorbent ($ng\,m^{-3}$), and K_{Ad} the dimensionless adsorbent/air equilibrium partition coefficient. For compounds of high K_{Ad} and low ambient concentration, the mass transfer of the gaseous compound to be determined from ambient air to the sampling medium is controlled by the air mass transfer rate; therefore the mass of analyte adsorbed onto the adsorbent is a linear function of time. Analyte concentration in air can be determined by the following equation:

$$C_{Air} = M_{Ad}(k_V \cdot A_S \cdot t)^{-1} \quad (2)$$

The product of $k_V \times A_S$ is the *R*-value and may be determined experimentally. Sampling rate is expressed as volume per time units, and is equivalent to the air sampling flow rate in conventional active air samplers. k_V is different for each analyte and sorbent material being used, and must be calculated for the different analytes and sorbents. A_S only depends on the geometry of the particular passive sampler, and will be the same for all analytes as long as the same sampling device is used.

2.2. Chemical and reagents

Water (18.2 MΩ cm) was purified using a Milli-Q system from Millipore (Bedford, MA, USA). Pesticide-quality methanol was purchased from Panreac (Barcelona, Spain). Pure standards of 2,4,6-tricholoranisole and 2,4,6-trichlorophenol were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Individual stock standard solutions of each analyte ($400\,mg\,L^{-1}$) were prepared in methanol and stored at −20 °C in the dark. Standard solutions were prepared fresh monthly. Three different adsorbents for passive sampling purchased from Sigma–Aldrich (St. Louis, MO, USA) were evaluated: Radiello cartridge adsorbent filled with Tenax TA™ for sampling phenols, Radiello cartridge adsorbent for sampling anaesthetic gases/vapours with molecular sieve and activated charcoal (30–50 mesh); and Radiello cartridge for sampling BTEX and VOCs with Carbograph 4. Other commercially available materials were ruled out after evaluating their technical specifications. For sampling, passive adsorbent cartridges were placed into Radiello white diffusive holders as recommended by the manufacturer. Glass tubes (Gerstel, Mülheim an der Ruhr, Germany) pre-filled with Tenax GR™ were used for active sampling.

2.3. Instrumentation and software

The gas chromatograph was an Agilent 7890 GC (Agilent Technologies, Palo Alto, CA, USA) equipped with a CIS-4 programmable temperature vapourization (PTV) inlet, a thermal desorption unit (TDU), and a multipurpose (MPS) autosampler to automatically introduce the desorption tubes into the TDU system (Gerstel). The detector was an Agilent 7000B triple quadrupole mass spectrometer equipped with an inert electron-impact ion source. The mass spectrometer operated in SRM mode. Electron impact (EI) ionization at −70 eV was used in both SRM and SIM. Agilent MassHunter B.03.02 was used for control and data analysis. Helium (99.9999% purity) was used as carrier and quench gas (a gas employed in the Agilent 7000 mass spectrometer), and nitrogen (99.999% purity) was used as collision gas; both gases were supplied by PRAXAIR España S.L. (Madrid, Spain). The column was an HP-5MS (5%-phenyl 30 m × 0.25 mm i.d. × 0.25 μm d_f) from Agilent Technologies. A Hewlett Packard 5890-II gas chromatograph (Agilent Technologies) equipped with a split/splitless inlet, a packed inlet and an HP 7673A automatic sampler was also used for the preparation of the calibration tubes. Helium (99.9999% purity) was used as carrier gas. ChemStation version 3.1 software was used for controlling the GC process.

A Zambelli EGO TT pump (Bareggio, Milan, Italy) with a variable intake flow of 5–3000 mL min^{-1} was used for active sampling. A household humidifier was used to diffuse TCA and TCP into the air and to regulate humidity of the ambient air during sampling.

2.4. Analysis of sampling tubes using TD–GC–MS/MS

After passive sampling, adsorbent cartridges were removed from the holder and placed into empty desorption glass tubes. Active sampling tubes fit directly into the desorption unit, therefore no additional manipulation is required after removal from the pump. Desorption tubes, both passive and active, were stored in individual protective vials at −20 °C until analysis. They were then placed in the MPS autosampler, which automatically places them into the thermal desorption unit. Desorption was carried out in solvent vent mode at 300 °C for 8 min. The sample was placed under a 30 mL min^{-1} helium flow and cryo-focused into the CIS-4 inlet cooled with pressurized liquid CO_2 at −20 °C. Finally, the inlet ramped to 300 °C at 12 °C s^{-1} to transfer the analytes into the GC column in splitless mode. The carrier gas was helium in constant flow mode, at 1.2 mL min^{-1}. Initial oven temperature was 70 °C (held for 2 min), the heat was then increased to 150 °C at 25 °C min^{-1}, then to 180 °C at 3 °C min^{-1}, and to a final temperature of 300 °C at 25 °C min^{-1} that was held for 5 min. Total time for the analysis was 25.0 min.

For detection and quantification, the ion intensity of two transitions was monitored for each analyte, the first for quantification and the second for confirmation. The mass spectrometer conditions and the selected transitions are summarized in Table 1. Resolution was adjusted to 1.0 Da for quadrupole 1 and 3. Temperatures of the transfer line, ion source and quadrupole 1 and 2 were 280 °C, 290 °C and 180 °C, respectively. Mass spectrometer autotune was performed on a weekly basis.