



ELSEVIER

Contents lists available at ScienceDirect

Talanta

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

Atmospheric pressure solid analysis probe coupled to quadrupole-time of flight mass spectrometry as a tool for screening and semi-quantitative approach of polycyclic aromatic hydrocarbons, nitro-polycyclic aromatic hydrocarbons and oxo-polycyclic aromatic hydrocarbons in complex matrices

Daniel Carrizo^a, Celia Domeño^a, Isabel Nerín^b, Pilar Alfaro^a, Cristina Nerín^{a,*}

^a Aragon Institute of Engineering Research (I3A), EINA, Department of Analytical Chemistry, University of Zaragoza, María de Luna 3, 50018 Zaragoza, Spain
^b Smoking Cessation Unit, Department of Medicine, Psychiatry and Dermatology, Faculty of Medicine, University of Zaragoza, Domingo Miral s/n, 50009 Zaragoza, Spain

ARTICLE INFO

Article history:

Received 25 April 2014

Received in revised form

9 July 2014

Accepted 11 July 2014

Available online 22 July 2014

Keywords:

Direct analysis

Polycyclic aromatic hydrocarbons

Screening

Organic pollutants

Ambient ionization mass spectrometry

Tobacco

Cancer

ABSTRACT

A new screening and semi-quantitative approach has been developed for direct analysis of polycyclic aromatic hydrocarbons (PAHs) and their nitro and oxo derivatives in environmental and biological matrices using atmospheric pressure solid analysis probe (ASAP) quadrupole-time of flight mass spectrometry (Q-TOF-MS). The instrumental parameters were optimized for the analysis of all these compounds, without previous sample treatment, in soil, motor oil, atmospheric particles (ashes) and biological samples such as urine and saliva of smokers and non-smokers. Ion source parameters in the MS were found to be the key parameters, with little variation within PAHs families. The optimized corona current was 4 μ A, sample cone voltage 80 V for PAHs, nitro-PAHs and oxo-PAHs, while the desolvation temperatures varied from 300 °C to 500 °C. The analytical method performance was checked using a certified reference material. Two deuterated compounds were used as internal standards for semi-quantitative purposes together with the pure individual standard for each compound and the corresponding calibration plot. The compounds nitro PAH 9-nitroanthracene and oxo-PAH 1,4-naphthalenedione, were found in saliva and urine in a range below 1 μ g/g while the range of PAHs in these samples was below 2 μ g/g. Environmental samples provided higher concentration of all pollutants than urine and saliva.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The quality control requirements are more and more demanding, especially in areas of food and health, where consumers have a high concern about the likely contamination or affection to their health. The number of samples requiring analysis has increased dramatically in the last years as well as the required sensitivity of the current analytical procedures [1]. These characteristics imply a high cost of the analysis. For this reason, fast screening procedures are gaining importance, as they permit the evaluation of the presence or absence of specific compounds in the samples that may require a further analysis in depth. These screening methods, most of them based on mass spectrometry (MS), are now promoted in a wide variety of areas.

Ambient mass spectrometry (Ambient MS) analysis has experienced a very rapid development during the last 7 years. This technique is defined as mass spectrometric analysis with minimal or no sample preparation using direct sampling and ionization at ambient conditions [2] and it represents the ideal tool for screening analysis. With the introduction of direct analysis in real time (DART) [3] and desorption electrospray ionization (DESI) [4], the analysis of samples without any prior treatment became possible for the first time [2]. In the DART technique, the sample is placed in a stream of helium that contains ionized atmospheric gases (such as water vapor and oxygen), and the analytes in the sample are ionized in open air in the laboratory environment. Desorption electrospray ionization (DESI) is carried out by directing charged droplets produced from a pneumatically-assisted electrospray onto a surface to be analyzed at atmospheric conditions. Ions of chemical species present on the surface, usually a paper impregnated in the sample, are produced through the interaction of charged droplets and the sample. DART and DESI are mainly

* Corresponding author. Tel.: +34 976 761873.
 E-mail address: cnerin@unizar.es (C. Nerín).

qualitative techniques where the main purpose is to identify the presence of specific compounds present at the surface of the sample, i.e. targeted analysis. The development of these techniques creates an awareness of the power of Ambient MS and a new sub-field in mass spectrometry. DART and DESI techniques usually coupled to time of flight (TOF) detectors have been widely applied as direct screening techniques to a wide variety of samples [5–10].

Atmospheric-pressure solid-analysis probe (ASAP) was developed in 2005 [11]. The sample, usually introduced into the ionization chamber with a glass rod dipped either in the powdered or liquid sample or rubbing the surface, is vaporized and ionized at atmospheric pressure inside a small chamber, thus providing the ions, which arrive at the MS detector [12–13]. The major difference between DART and ASAP is the ionization mode. While DART is open to the environment allowing for water to be part of the chemical ionization process, ASAP takes place in dry atmosphere. DESI, DART and ASAP can be considered as screening techniques to take rapid decision about the further analysis in depth. Their major advantages are the absence of sample treatment, which is usually a tedious, expensive and time consuming step. None of them have a chromatographic separation before detection. This means that all the analytes present in the sample matrix, or formed during the ionization step, reach the source and all of them can be analyzed, thus minimizing any analyte losses. Thus, these techniques are mainly focused on target analysis and constitute powerful tools for screening the absence or presence of target compounds. In a few minutes the sample is injected and processed.

In ASAP, several key parameters, such as corona current, sample cone voltage and gas desolvation temperature need optimization, because they condition the total number of ions arriving at the detector. Important features, like the temperature of the ion source chamber where the sample is volatilized, remain constant (120 °C) to ensure the maximum volatilization. This technique can be applied to volatile or semi-volatile compounds in solid or liquid complex matrices, without previous sample treatment. The presence or absence of specific compounds at low concentration, and in some cases the order of magnitude of their concentration in the sample, are shown as very interesting characteristics of this technique. However, it is not possible to estimate toxicity from the presence of single compounds by using this method, because too similar compounds in environmental samples superimpose. Using ASAP for screening and semi-quantitative simultaneous analysis of several pollutants, such as polycyclic aromatic hydrocarbons (PAHs) and their nitro and oxo derivatives in complex matrices, can be very useful in health and environmental areas. This is the main purpose of the present paper.

PAHs, nitro-PAHs and oxo-PAHs derivatives are organic compounds listed as priority pollutants by international environmental protection agencies due to their carcinogenic, mutagenic, and toxic effects [14–20]. There are a few applications of Ambient MS methods for direct analysis of PAHs and related compounds [21–26]. However, the possibility of having a semi-quantitative approach using ASAP has not been explored yet. For this reason, the main objective of this work is to evaluate the performance of ASAP-Q-TOF-MS as a screening tool and semi-quantitative approach for PAHs, nitro-PAHs and oxo-PAHs in several liquid and solid complex samples, such as car exhaust, oil, atmospheric dust, urine and saliva. As far as we know, this article represents the first study using direct analysis in one single run through ASAP-Q-TOF-MS for this large series of priority organic pollutants. It is also the first time that a semi-quantitative approach has been proposed using a direct ASAP-MS-Q-TOF in very different complex matrices. A solid certified reference material (CRM) for PAHs was run in parallel with the samples, in order to check the method performance and the semi-quantitative data. The results obtained are shown and discussed.

2. Materials and methods

2.1. Chemicals and reagents

Certified standards of PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene, cyclopenta[cd]pyrene, benzo[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene and benzo[ghi]perylene), Nitro-PAHs (1-nitronaphthalene, 2-methyl-1-nitronaphthalene, 1,5-dinitronaphthalene, 2-nitrofluorene, 9-nitroanthracene, 2-nitrofluoranthene, 1-nitropyrene and 6-nitrocrysene) and Oxo-PAHs (1,4-naphthalenedione, benzophenone, 9-fluorenone, anthrone, 9,10-anthracenedione, 7H-benz[de]anthracen-7-one, benzo[a]anthracene-7,12-dione and naphthacene-5,12-dione) were supplied by Sigma-Aldrich (Madrid, Spain). Acenaphthene-d10 (99 atom% D) and benzo[a]pyrene-7,8-d2 (98 atom% D) for being used as internal standards were purchased from Sigma-Aldrich (Madrid, Spain). Detailed information about the molecular weight, chemical formula, CAS number and molecular structure for each of the analyzed compounds of the three families can be found in Table 1 and Figs. S1, S2 and S3 in the Supplementary information material. All the standard solutions were prepared in methanol reagent grade purchased from Scharlab (Barcelona, Spain). Combined solutions of the three families (PAHs, nitro-PAHs and oxo-PAHs) containing different concentrations of each standard were also used to check the performance of the mixtures in ASAP. A sediment as certified reference material (RTC-CRM104-50G, RT-Corp, WY, USA) containing PAHs was supplied by Sigma-Aldrich (Madrid, Spain). The amount of deuterated compounds added to both the standard mixture solution and the samples was in each case in the required final concentration of 10 ng/g IS in the sample. All standards were under gravimetric control and all concentrations are expressed as w/w basis.

2.2. ASAP-Q-TOF-MS instrument

The atmospheric solids analysis probe (ASAP) was coupled to a quadrupole-time of flight-mass spectrometer (QToF-MS), Xevo G2 QTOF (Waters Corporation, Manchester, UK). The instrument has a mass range up to m/z 100 000 and a resolving power of > 22,500 full width at half maximum (FWHM). In the ion source atmospheric pressure chemical ionization was used and the chamber temperature is constant at 120 °C. The key ion source parameters to be optimized were: corona current (μA), sample cone voltage (V) and desolvation gas temperature (°C). Acquisition mode used was MS full-scan data from 70 to 800 amu. Nitrogen was used as desolvation gas at 400 Lh⁻¹ flow. Cone flow was not needed for this technique. Currently, ASAP requires manual injection and can neither be processed unattended nor automatically.

2.3. ASAP-Q-TOF-MS analysis

As this technique is for target analysis, the first step is to analyze the individual compounds under the optimal experimental conditions. Variables such as cone voltage, desolvation gas temperature and corona current were optimized using standard solutions of pure compounds. Voltage of sampling cone was varied from 20 V to 80 V and voltage of the extraction cone was fixed at 0.1 V. The parameters of acquisition were as follows: a scan time of 1 s and mass range of m/z 70–800 to cover all PAH, nitro-PAH and oxo-PAH standards [27]. For each MS spectrum, the characteristic masses were selected and this information was used for searching the presence or absence of each compound in the real samples. Positive identification of the compounds was done using pure standards for all analyzed compounds, using several ions for each compound.

Download English Version:

<https://daneshyari.com/en/article/7679141>

Download Persian Version:

<https://daneshyari.com/article/7679141>

[Daneshyari.com](https://daneshyari.com)