



Biogenic aldehyde determination by reactive paper spray ionization mass spectrometry



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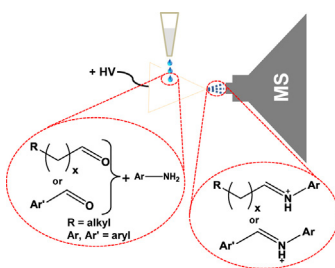
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HIGHLIGHTS

- *In-situ* derivatization and simultaneous ionization used to detect aldehydes.
- Biogenic aliphatic and aromatic aldehydes reacted with 4-aminophenol.
- Derivatized products yield structurally characteristic fragment ions.
- This measurement demonstrated using a miniaturized portable mass spectrometer.

GRAPHICAL ABSTRACT



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ABSTRACT

Ionization of aliphatic and aromatic aldehydes is improved by performing simultaneous chemical derivatization using 4-aminophenol to produce charged iminium ions during paper spray ionization. Accelerated reactions occur in the microdroplets generated during the paper spray ionization event for the tested aldehydes (formaldehyde, *n*-pentanaldehyde, *n*-nonanaldehyde, *n*-decanaldehyde, *n*-dodecanaldehyde, benzaldehyde, *m*-anisaldehyde, and *p*-hydroxybenzaldehyde). Tandem mass spectrometric analysis of the iminium ions using collision-induced dissociation demonstrated that straight chain aldehydes give a characteristic fragment at *m/z* 122 (shown to correspond to protonated 4-(methyleamino)phenol), while the aromatic aldehyde iminium ions fragment to give a characteristic product ion at *m/z* 120. These features allow straightforward identification of linear and aromatic aldehydes. Quantitative analysis of *n*-nonanaldehyde using a benchtop mass spectrometer demonstrated a linear response over 3 orders of magnitude from 2.5 ng to 5 μg of aldehyde loaded on the filter paper emitter. The limit of detection was determined to be 2.2 ng for this aldehyde. The method had a precision of 22%, relative standard deviation. The experiment was also implemented using a portable ion trap mass spectrometer.

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1. Introduction

Trace organic analysis [1–3] is commonly performed by combining a chromatographic method [4] with mass spectrometry (MS) [5]. Ambient ionization [6–14] is a relatively recent approach

to MS analysis which avoids chromatography and is characterized by the absence of any requirement for sample preparation. Paper spray ionization [15–20] is a particularly simple ambient ionization technique which can be employed to study reactions and identify intermediates as well as to measure trace constituents of complex mixtures. Like other spray ionization methods, paper spray is least successful for non-polar or weakly polar compounds. Aldehydes fall into this group and for this reason a reactive version of paper spray is examined here as way to generate an aldehyde

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derivative during the ionization process. The reaction chosen was that of the aldehyde with a primary amine to generate an iminium ion under the ambient ionization conditions. The generation of a charged product is expected to improve ionization efficiency in a process once known as 'reverse derivatization' [21]. The combined derivatization/ionization process is tested in this study for the analysis of simple aldehydes.

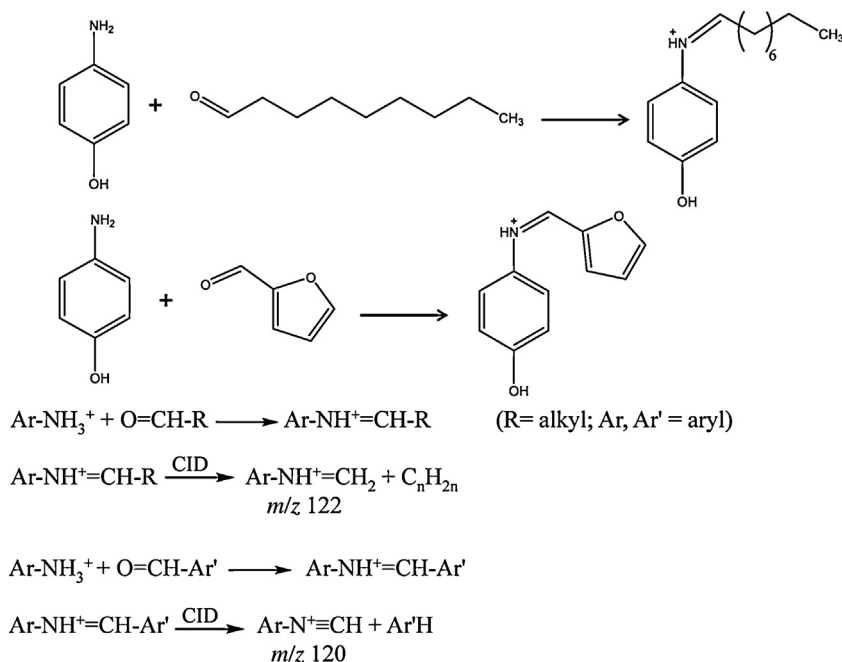
A miniature portable mass spectrometer (Mini 10/12) [22–24] designed to be used in a field setting [25] was also used in this study. The Mini MS/paper spray ionization combination has been successfully demonstrated for the analysis of surface active tetraalkylammonium halides in an oil matrix [26] to simulate oil transmission pipeline monitoring. The closely related ambient ionization method of leaf spray [27] also has been used *in-situ* with a miniature mass spectrometer to follow the time dependent removal of herbicides from grass leaves [25]. Because of the low pumping speed of the Mini mass spectrometer, the flow of air and ionized sample into the instrument is regulated by a discontinuous atmospheric pressure interface (DAPI) valve [28]. Positioning the paper spray ionization source in front of the DAPI valve allows ions formed by paper spray to be transported into the rectilinear ion trap for tandem mass spectrometric analysis.

This method is particularly advantageous for the analysis of traces of compounds like aldehydes which have low proton affinities and are present in complex mixtures. Chemical reactions have been shown to proceed at greatly elevated rates in thin drop-cast layers [29] and in electrosprayed microdroplets [30] enabling derivatization to be completed during ionization and keeping total sample analysis times to a few seconds. Both ionization efficiency and molecular selectivity can be improved by chemical derivatization. In addition, the use of an ion trap allows tandem mass spectrometry experiments to be performed in a small and simple instrument. By using what is in effect selected reaction monitoring (SRM) [31] a high degree of confidence is achieved in measuring only the analyte of interest. This approach to the analysis of aldehydes can be contrasted with the more traditional method of gas chromatography–mass spectrometry (GC–MS) [32,33].

One of the driving forces for this study is the fact that the presence of straight chain aldehydes in breath has been linked to the lung cancer [34]. Therefore, easy rapid methods of identification of straight chain aldehydes could be important in diagnosis. In this context, mass spectrometry, especially small, portable, mass spectrometers might be of future interest to allow the measurement in a clinical environment. This is one reason to test the reactive paper spray method of analyzing aldehydes with both benchtop and portable mass spectrometers. Breath analysis by mass spectrometry is an area of increasing interest due to its capability for making non-invasive measurements [35–37] which can be used to monitor metabolic state and potentially detecting disease biomarkers [38–40]. It is in this context that we describe a fast, direct and reactive paper spray approach to determine aldehydes using *in-situ* derivatization with 4-aminophenol to produce iminium ions.

2. Experimental

In-situ derivatization of aldehydes was carried out using 4-aminophenol as the reagent in 80:20 acetonitrile:water. Separate reactions of 4-aminophenol with 1-nonanal and furfural are shown in Scheme 1. The product of this reaction (iminium ion) carries a formal charge on the nitrogen atom which gives it a strong mass spectrometric response. Aldehyde standards and the 4-aminophenol reagent were prepared as solutions in the acetonitrile:water (80:20) solvent mixture. All the aldehydes as well as the 4-aminophenol were purchased from Aldrich Chemical Company (Milwaukee, WI). *In-situ* derivatization was performed by first applying 5 μL of the 4-aminophenol reagent (1000 $\mu\text{g mL}^{-1}$) followed by 5 μL of the aldehyde standard (formaldehyde, *n*-pentanaldehyde, *n*-nonanaldehyde, *n*-decanaldehyde, *n*-dodecanaldehyde, benzaldehyde, *m*-anisaldehyde or *p*-hydroxybenzaldehyde in the range 100 ng mL^{-1} to 100 $\mu\text{g mL}^{-1}$) to the paper spray emitter. Paper spray emitters were isosceles triangles of Whatman no. 1 grade filter paper (Maidstone, UK) with typical dimensions of 10 mm in length and with a width at base of 5 mm.



Scheme 1. Reaction schemes showing formation of iminium ions using 4-aminophenol in the cases of a typical aliphatic and a typical unsaturated aldehydes (1-nonanal and furfural, respectively). The scheme also shows the CID dissociation of the iminium ions to give the characteristic fragment ions m/z 122 and m/z 120 for aliphatic and aromatic aldehydes, respectively.

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