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Quantification of methylamine in the headspace of ethanol of agricultural origin by selected ion flow tube mass spectrometry

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ABSTRACT

Selected ion flow tube mass spectrometry, SIFT-MS, has been used to investigate if absolute levels of trace compounds in the headspace of ethanol/water vapour mixture can be quantified. This case study was directed towards the analysis of methylamine in distilled ethanol of agricultural origin because of its relevance to quality control legislation in the distillery industry. This has required a detailed study of the ion chemistry occurring – initiated by H_3O^+ precursor ions – when ethanol/water vapour mixtures are introduced into the H_3O^+/helium carrier gas swarm and has resulted in the construction of a full scheme of the complex ionic reactions that occur. It has been found that under the SIFT-MS flow reactor conditions (He pressure 130 Pa and temperature 299 K) the terminating ions of the several parallel and sequential reactions that occur are the proton bound ethanol clusters ions, $C_2H_5OH_2^+(C_2H_5OH)_n$, with $n = 1,2,3$, proton bound trimer ($n = 2$) being the dominant species. These ethanol cluster ions can be used as precursor (reagent) ions for the chemical ionisation of the methylamine present in the ethanol/water vapour, which produces two characteristic product ions $CH_3NH_2H^+(C_2H_5OH)_{1,2}$ that are used for the methylamine analysis. The ratio of the product ion count rate to the precursor ion count rate is used in an analogous way to the routinely used for SIFT-MS analyses to quantify the methylamine concentration. The results of calibration experiments show that using SIFT-MS it is possible to quantify methylamine in liquid ethanol/water mixtures at levels of 0.1 mg/L or greater.

1. Introduction

Quantification of methylamine in distilled ethanol of biological origin and in spirit drinks is of interests and importance in the various phases of production and quality control in the distillery industry. The primary purpose of the present study was to test whether or not selected ion flow tube mass spectrometry (SIFT-MS) can be used to reliably quantify the concentration of methylamine in both drinks-grade refined ethanol produced by the distillation of fermented agricultural products and in spirit drinks. Methylamine, CH_3NH_2, is the simplest primary biogenic aliphatic amine. Such amines, many of which are known to be hazardous to human health, are found, for example, in (waste) water [1], decaying foodstuffs such as fish [2] and in the fermentation broths used for ethanol production [3]. Methylamine and other toxic aliphatic amines are able to readily access the brain and spinal tissues and interfere with neurological function [4]. Considerable amounts of these compounds can be produced during food fermentation processes or in food storage, especially if amino acid-decarboxylase positive microorganisms are present. Several different amines, including methylamine, have been identified in wine using high-performance liquid chromatography (HPLC) following the indirect process of derivatization [5,6]. Analyses of biogenic amines in foods, including methylamine and larger amines like histamine, putrescine, cadaverine and spermine, have received considerable attention recently and the methods used for their analyses are reviewed in [7].

Because of the potentially serious hazard to health, the production of ethanol by the distillation of fermented agricultural products is closely regulated. The levels of volatile bases containing nitrogen in the ethanol, including amines, must be known and these are usually expressed in grams of nitrogen per hectolitre of alcohol at 100 vol%. [8]. The raw material that is fermented to produce the ethanol must also be given. Because of the toxicity of methylamine, a legal limit is imposed on its concentration in spirit in some countries and regions. In the Czech Republic this limit is legislated as 1 mg/L of 100% ethanol [9]. Currently, the amount of nitrogen-containing bases is determined as the content of methylamine by

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titration with 0.005 mol/L solution of sulphuric acid using a colour change as an indicator or by gas chromatography [9].

It would be very advantageous if the methylamine content was more quickly assayed than is currently possible using the techniques mentioned above. In this respect, our pilot experiments have suggested that SIFT-MS is a more rapid analytical method. SIFT-MS quantification is based on chemical ionisation using selected precursor (reagent) ions (H_3O^+, NO^+ and $O_2{}^+$ are available) that are injected into a flow tube where they selectively react rapidly with trace gases present in air, breath or liquid headspace samples that are introduced into the helium carrier gas (but react only slowly with the major components of air and water vapour) resulting in characteristic product ions [10]. Thus, extensive studies of exhaled breath, urine and cell culture headspace and other systems have been carried that demonstrate well the value and potential of this analytical technique; the results of these studies have been reviewed in recent papers [10,11,12].

Previous work has revealed that the analysis of trace amounts of alcohols and amines in air or exhaled breath is best carried out using H_3O^+ precursor ions [13]. However, when the headspace of liquid ethanol or concentrated ethanol/water mixtures is applied directly to the input port of the SIFT-MS instrument, the flow rate of ethanol (headspace) vapour is such that the injected H_3O^+ precursor ions are totally consumed and protonated ethanol clusters dominate the product ions formed, as can be seen in the spectra shown in Section 3. Obviously, under such sample conditions the conventional mode of analysis using H_3O^+ ions to analyse trace amounts of compounds in the ethanol vapour cannot be achieved. However, all is not lost because the ethanol cluster ions can themselves be used as precursor ions for the analysis of trace compounds with which they react, amines being prime examples. But to achieve this it is essential to understand the complex ion chemistry occurring and to describe the detailed reaction scheme if accurate analyses are to be realised of the trace gases present in the ethanol/water vapour mixtures such as headspace of distilled ethanol and of spirit drinks. Such an approach has been previously attempted using proton transfer reaction mass spectrometry to obtain characteristic mass spectral fingerprints of the volatile compounds emitted by several different wine varieties [14]. However, neither the identification of the product ions nor the quantification of the trace compounds in the wine headspace was obtained.

Thus, the objective of the present study was first to understand the ion chemistry occurring in the SIFT-MS flow tube reactor in the presence of excess concentrations of ethanol vapour and from these gas phase analyses to quantify methylamine in liquid ethanol, validating these analyses using standard mixtures of methylamine in ethanol over a range of concentrations relevant to the limits imposed by current legislation.

2. Experimental

A *Profile 3* SIFT-MS instrument (manufactured by Instrument Science Limited, Crewe, UK) was used for these studies. Its principle of operation and its special features have been outlined in previous papers [10,15]. Using this generation of SIFT-MS instruments, concentrations of trace gases can be determined down to the parts-per-billion, ppb, level in just a few seconds of data acquisition time, which allows the time profiles of some metabolites in single breath exhalations to be described. A special feature of these SIFT-MS instruments is that calibration is unnecessary to obtain absolute quantification [16]. This method has been described thoroughly in previous papers [10,16] so only some particular details are required here. The helium carrier gas was at a pressure of typically 1 Torr at the ambient temperature, which was 26 °C, and both pressure and temperature were recorded during every measurement. For headspace analyses, the liquid samples were contained in vials of volume 25 mL sealed with septa and the headspace volatiles were introduced into the helium carrier gas of the SIFT-MS instrument via a calibrated capillary, as illustrated in Fig. 1. A PEEK capillary was used with internal diameter of 0.25 mm providing a sample flow rate of 0.3 Torr L/s (24 sccm), which is routinely used for analyses of air samples containing water vapour at pressure equivalent to the saturation vapour pressure of water at 37 °C as pertains to exhaled breath or liquid headspace.

The first experiments involved the introduction of the headspace vapour from mixtures of ethanol in water at varying dilutions up to 97% ethanol. Distilled ethanol of biological origin, strength 97%,

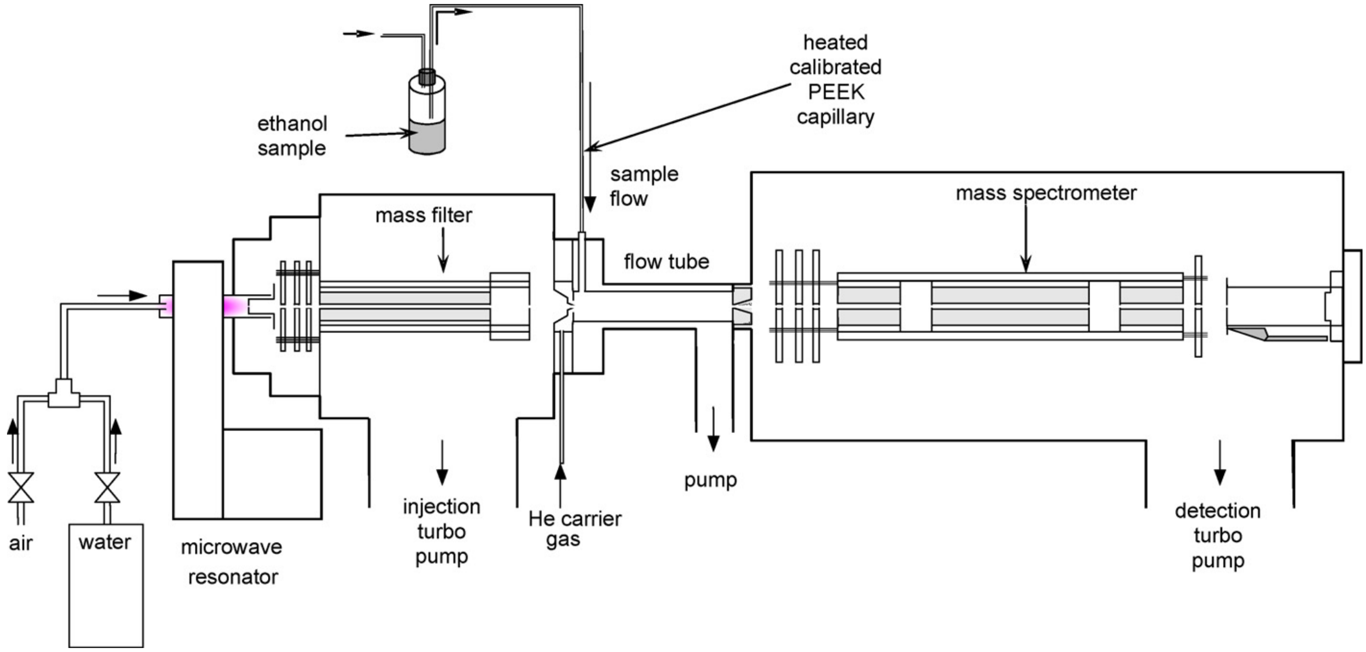

Fig. 1. Schematic diagram of SIFT-MS configured for headspace analyses of ethanol/water vapour/trace compound samples.