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Lithium ion attachment mass spectrometry for on-line analysis of trace components in air: direct introduction

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Abstract

Lithium ion attachment mass spectrometric method has been successfully applied for the real time, on-line continuous measurement of trace (ppb) organic compounds in air. The method is based upon the establishment of adducts with Li^+ ions, which attach to most organic compounds in air but do not react with any of the major components of air. This paper describes the application of on-line, continuous analysis of volatile organic compounds in air using strawberries as a source of organic volatiles. (Int J Mass Spectrom 209 (2001) 39–45) © 2001 Elsevier Science B.V.

Keywords: Li^+ ion attachment; Quadrupole mass spectrometry; Volatile organic compounds; Food chemistry; Strawberry

1. Introduction

The need for real-time trace analysis of air streams for environmental monitoring and process control has increased [1]. Hence, there is a real need for instrumentation for the continuous in situ analysis of process gases for process control and for meeting stringent regulations. Techniques such as mass spectrometry (MS) and Fourier transform infrared (FTIR) spectrometry are being used for on-line monitoring, and their features have been discussed [2,3]. Gas chromatography is attractive, especially when coupled with MS and FTIR [4].

A number of methods are capable of measuring chemical species in real time at or below the maximum permissible concentration in air. Mass spectrometric methods, such as atmospheric pressure ionization triple-quadrupole mass spectrometry [5,6] and direct sampling ion trap mass spectrometry [7], have the advantage of real-time or near-real-time detection and have become increasingly important tools for environmental monitoring.

Sciex developed the mobile low-pressure chemical ionization (LPCI) tandem mass spectrometer [8], which is useful for monitoring indoor ambient air for volatile organic compounds (VOCs). The LPCI source has a Townsend discharge electrode that emits energetic electrons by ionizing ambient air (nitrogen, oxygen, water vapor, and other components), which then forms reagent ions (N_2^+, O_2^+, H_3O^+, $[H_2O]^n$, $[H_3O{\cdot}n\,H_2O]^+$, and other species). These ions, in turn, ionize trace organic molecules by ion–molecule processes. Parent–daughter ion pairs are monitored to quantitate VOCs and to locate their possible source.

More recently, Lindinger et al. [9] developed proton-transfer reaction mass spectrometry for on-line

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monitoring of VOCs in medical applications, food control, and environmental research.

Membrane introduction mass spectrometry (MIMS) [10,11] can also address the challenges posed by ever decreasing regulatory limits for VOCs in air by providing on-line detection of VOCs at the part per trillion (v/v) level. Compared to air monitoring by mass spectrometric methodologies using high-pressure discharge sources, air monitoring by MIMS has the advantages of low cost and simplicity. Membrane air sampling inlets may potentially find widespread use in a number of applications, including stack monitoring, indoor air monitoring, breath analysis, and waste-site analysis. There is, however, the possibility that other compounds or fragments could interfere with quantitation.

Ion attachment mass spectrometry (IAMS) was developed [12] to obtain mass spectra consisting solely of quasimolecular ions formed by addition of Li^+ ions to sample molecules. This demonstrated that alkali metal ion attachment mass spectrometry was a useful addition to the field of analytical mass spectrometry. Potassium ion chemical ionization has also been used to ionize certain compounds selectively in a mass spectrometer source. We recently showed that IAMS has considerable advantages in the study of plasmas and polymerization processes when compared with traditional mass spectrometry [13]. Unlike traditional mass spectrometry, which uses high-energy electrons for ionization, IAMS preserves structure, allowing even free radical species and high polymers to be detected as adduct ions.

IAMS appears to be ideally suited to atmospheric monitoring. At reduced pressure, ion attachment may be shown to be especially sensitive for a variety of volatile organic molecules in air. The objective of this study was to apply an IAMS system for sampling ambient air at atmospheric pressure. This system is based on the establishment of an alkali metal ion attachment reaction in air in a region of reduced pressure. Here we report and discuss (1) the operation and characteristics of an optimized Li^+ source, (2) direct sampling into the mass spectrometer without prior sample preparation or preconcentration of individual sample components, and (3) possible applications to food control. The application in this work was limited in scope because this work was intended to serve as an initial feasibility study.

2. Experimental

2.1. Apparatus

All experiments were performed with a specially made ion attachment mass spectrometer (Anelva Corp., Fuchu, Japan). This apparatus, described in detail elsewhere [13], combines a quadrupole mass spectrometer (QMS) with a lithium ion emitter. Direct sampling at atmospheric pressure was accomplished with a laboratory-made gas sampling system (Fig. 1).

In the mass spectrometric setup, a stream of ambient air was directed through a sampling vessel into the IAMS reaction chamber (RC). The RC, which was fixed to the main vacuum envelope, housed a glass bead that contained lithium oxide in an aluminosilicate matrix. When this bead was heated, Li^+ ions were produced. These parent ions, in turn, attached to the sample species, forming charged adducts. Adduct complexes were formed by termolecular association reactions. Parent-daughter ion pairs were measured to detect and identify the sample compounds. The QMS could also be operated in the electron impact mode. The rods were biased below ground by connecting separate dc supplies to the dc rod driven circuit. The channeltron electron multiplier detector was operated for ion detection.

2.2. Gas sampling system

Benzene was used to characterize the gas sampling system. This system consisted of a Teflon sample line, a vessel (a stainless steel housing), and a variable-conductance valve and was directly connected to the IAMS reaction chamber.

Carrier gas was passed over a diffusion tube [D-10, D-20, or D-30 (2.5, 5, and 8 mm apertures, respectively; 10 cm length), Gastec, Tokyo, Japan] or Teflon, laboratory-made permeation tube to prepare various sample concentrations. The samples then

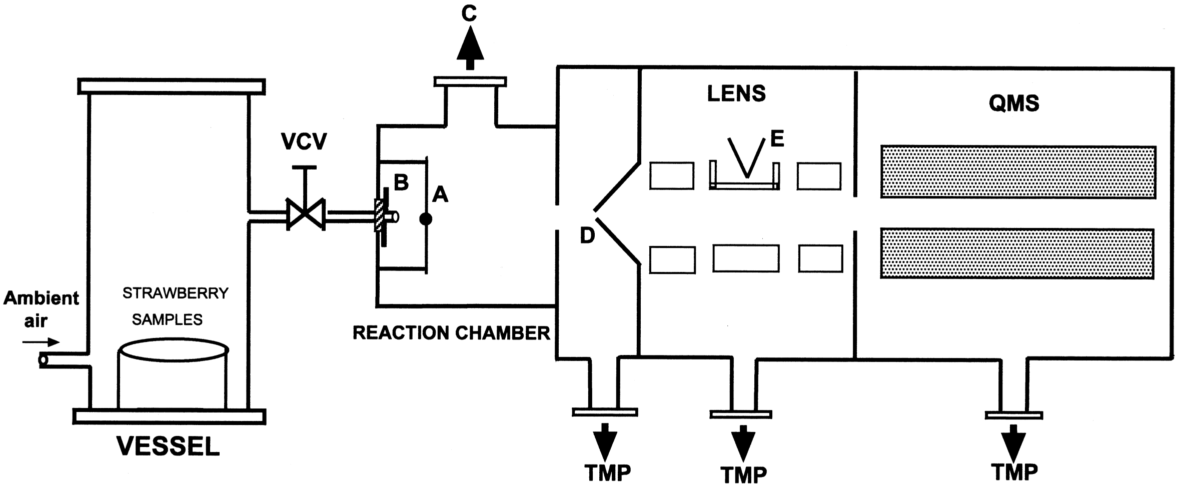

Fig. 1. Gas sampling system with a quadrupole mass spectrometer with a Li^+ ion attachment reaction chamber. A gas stream of headspace VOCs from a vessel is directed into the IAMS reaction chamber through a variable-conductance valve (VCV). Strawberry samples were placed in the vessel, which included a diffusion tube or permeation tube. (A) Li^+ ion emitter; (B) repeller; (C) 275 conductance gauge (Baratron); (D) skimmer; (E) electron impact source. TMP, turbomolecular pump; LENS, einzel lens system; QMS, quadrupole mass spectrometer.

passed through Teflon tubing into the IAMS system. Calibration curve data for benzene were obtained by the combined use of the diffusion and permeation tubes; a linear response was obtained over the chosen range of 3.0×10^{-8} g/s.

2.3. Sampling of headspace volatiles

Headspace volatiles were sampled as described by Olias et al. [14]. Strawberries were placed in the vessel (500 mL), housed within a thermostated water bath (25 °C). For sampling, a standard Teflon tube was attached to the outlet of the vessel. Extraction of the headspace volatiles was carried out with room air (6 mL/min). Fresh, greenhouse-grown strawberries (250 g), purchased at a supermarket, were used for direct mass spectrometric analysis of volatile compounds.

2.4. Data analysis

In the analysis of perfluoro compounds [13], the Li^+ adduct mass spectrum gives qualitative results; that is, the spectral data show pronounced trends. The reasons for this are twofold. First, species are modified by different Li^+ affinity values. Second, the QMS may have mass discrimination, because the mass resolution, $R = M/\Delta M$, is adjusted to the unit resolution ($M/\Delta M = 2M$). Consequently, the sensitivity, to some extent, is unavoidably lower at higher mass. Nevertheless, the present apparatus was able to sensitively and dynamically detect volatile species from strawberries.

3. Results and discussion

3.1. Performance and response characteristics

3.1.1. Sensitivity

Benzene was tested as a reference compound. The benzene sample, diluted by 10 mL/min of room air, was introduced at a rate of 4.5×10^{-9} g/s from the permeation tube at 25 °C. Measurement of the adduct ion yielded a value of 7.5×10^{-9} A, which was the output of the ion multiplier with the gain at 2×10^6. Thus, the sensitivity was 1.7 A/(g/s).

3.1.2. Minimum detectable amount

Taking the noise level of the system as the ultimate limitation on the minimum detectable amount (mda), we calculated the mda to be 3.5×10^{-14} g/s at a signal-to-noise ratio of 3, assuming the detection limit of the electrometer was around 2×10^{-14} A. Therefore, the mda of 3.5×10^{-14} g/s corresponds to a detection limit of 3.7 ppb (v/v) for benzene diluted by 10 mL/min of air.

3.1.3. Linear response range

Signal response was linear over the range 7×10^{-11} to 8.2×10^{-9} g/s for benzene. A plot of four introduction rates of benzene against their corresponding peak heights produced an essentially straight line up to 8.2×10^{-9} g/s, where more than 5% of the total Li^+ reactant ions are used for attachment. In a manner identical with that of the electron capture detector, the response follows Beer's law because the sample depletes the alkali metal ion density as it is cationized. Therefore, for a linear response, the sample size must be large enough to ensure a large excess of reactant ions in the cationizing chamber.

3.1.4. Background

When room air passed through the vessel cell to the mass spectrometer, the background mass spectrum generally showed an abundance of H_2OLi^+ ions as well as low-intensity ions at *m/z* 35, 51, 67, and 83. The mass spectrum was acquired over 5 s and a mass range of 5–150 amu. H_2OLi^+ was probably derived from the ever-present water in the nitrogen carrier gas. The *m/z* 35 and 51 peaks were assigned to N_2Li^+ and CO_2Li^+, respectively. The *m/z* 67 and 83 peaks were persistent, but were not assigned. Presumably, the limit of detectability is determined mainly [15] by the impurity content (Na^+, K^+, Rb^+, Cs^+) of the emitter bead.

The appearance of alkali metal ion contamination at *m/z* 23, 39, 41, 85, and 87 hinged on the heating condition. The distribution of these peaks depended primarily on the conditioning temperature and time. Interference from Na^+, K^+, and Rb^+ ions was negligible after weeks of heating.

The remaining peaks, *m/z* 35, 39, 51, 53, 65, 67, 79, 81, 83, 85, 91, 95, 99, 105, 109, 113, and 119, were due to major components in the laboratory air. Unfortunately, the limited resolution of the mass spectrometer and the lack of a reference spectrum did not allow a clear interpretation of the spectrum. However, some peaks can be assumed: *m/z* 35 (N_2Li^+), 39 (O_2Li^+), and 51 (CO_2Li^+) may be assigned as adduct ions due to the major components of ambient air.

The *m/z* 65 peak is due to Li^+ attached to acetone, a common solvent in our laboratory, while *m/z* 85, 99, and 113 may be $C_6H_6Li^+$, $C_7H_8Li^+$, and $C_8H_{10}Li^+$, respectively.

3.2. Analysis of strawberry headspace by direct introduction

Monitoring the emission of VOCs can be used in the control of food. Studying the constituents responsible for the aroma of fruits is useful for understanding the ripening/aging of fruit [16], and many automated inlet systems for MS have been developed for this purpose. The aroma of fruit, especially of raspberries [17,18] and strawberries [16,19,20], is well documented. The aroma of strawberries is mainly determined by a complex mixture of esters, aldehydes, alcohols, and sulfur compounds that have been extensively studied. Dirinck et al. [21] studied 30 Fragaria anannassa cultivars and concluded that esters were qualitatively and quantitatively the most important class of volatiles in strawberry flavor. The main components are esters formed from volatile organic acids with an even number of carbon atoms, such as acetic, butanoic, and hexanoic acids.

To evaluate our Li^+ IAMS direct sampling system for the on-line monitoring of VOCs for the control of aging or ripening of fruit, we preliminarily investigated emissions of various compounds from strawberries as a function of time.

The strawberries were purchased on August 16, 2000, and kept at 1 °C. From the afternoon of August 17 onward, the fruit was kept at room temperature (25 °C) and measurements of VOC emissions were performed over several days until the fruit began to decay. A mass spectrum of the VOCs from the dynamic headspace of ripe strawberries was recorded on the evening of August 18 (Fig. 2). Peak identification and relative amounts of flavor components in the dynamic headspace are presented in Table 1. The

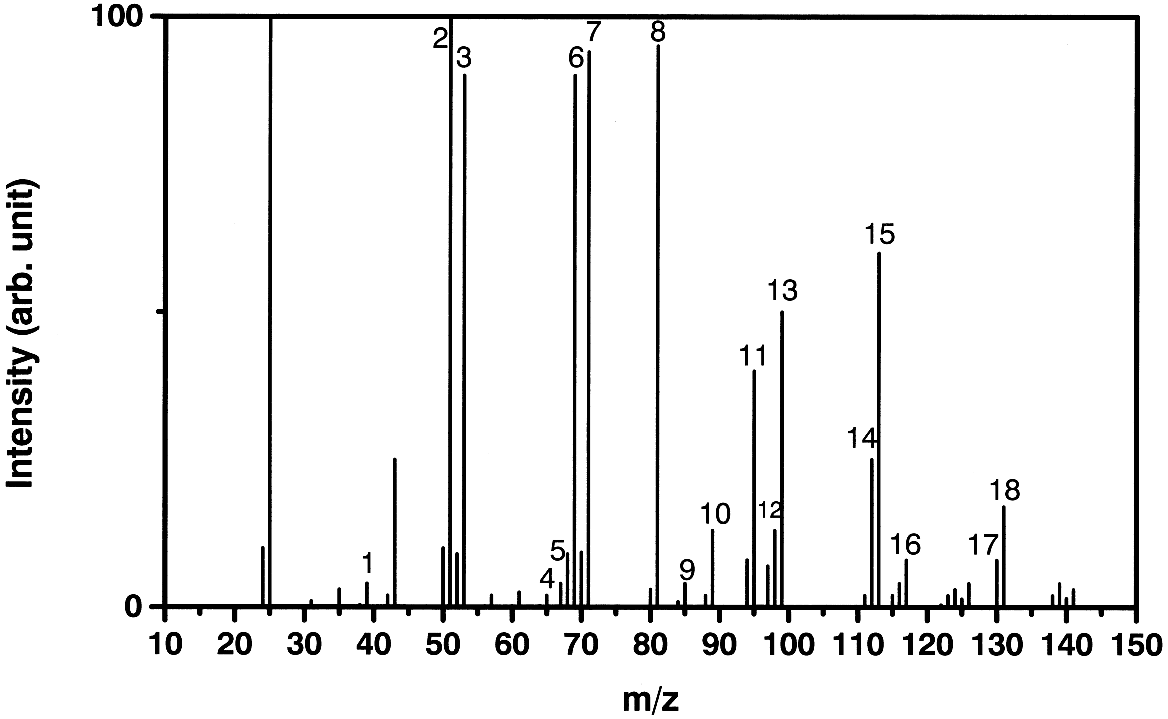

Fig. 2. Typical mass spectrum of headspace species from strawberries.

components are classified as esters, aldehydes, alcohols, acids, and others. Emissions due to water adducts of a few compounds were also observed.

Identification of the mass spectral peaks was based principally on mass number. Therefore, mass assignments for some species were uncertain. For example, the *m/z* 67 peak, which was assigned to $C_3H_7OHLi^+$ (propanol), may partially be due to $CH_3COOHLi^+$ (acetic acid). In accordance with the literature [22], we assume both were present.

Differences in emission intensities and patterns of primary aroma compounds can be studied as a function of time by dynamic headspace analysis. In our experiments, the emission intensities of ethanol, methylbutanol, and acetaldehyde increased until the measurements were terminated on August 21, but their pattern varied with time in a complicated way from species to species (Fig. 3). The emission intensity of ethanoic acid increased sharply, reaching a maximum, and then declined. In general, homologous

Table 1
Peak assignments, *m/z* ratios, and relative intensities of Li^+ adducts of species emitted from the strawberry headspace

No.	Substance	*m/z*	Relative intensity (%)
1	Methanol	39	4
2	Acetaldehyde	51	100
3	Ethanol	53	89
4	Acetone	65	3
5	Propanol (acetic acid)	67	4
6	Acetaldehyde + H_2O	69	90
7	Ethanol + H_2O	71	94
8	Methylpropanol (ethanoic acid)	81	95
9	Propanol (acetic acid) + H_2O	85	4
10	Ethanol + $(H_2O)_2$	89	13
11	Methylbutanol (ethyl acetate)	95	42
12	Ethyl nitrate (?)	98	13
13	Methylpropanol (ethanoic acid) + H_2O	99	51
14	Propyl nitrate (?)	112	25
15	Methylbutanol (ethyl acetate) + H_2O	113	62
16	Methylpropanol + $(H_2O)_2$	117	8
17	Propyl nitrate + H_2O (?)	130	8
18	Methylbutanol (ethyl acetate) + $(H_2O)_2$	131	17

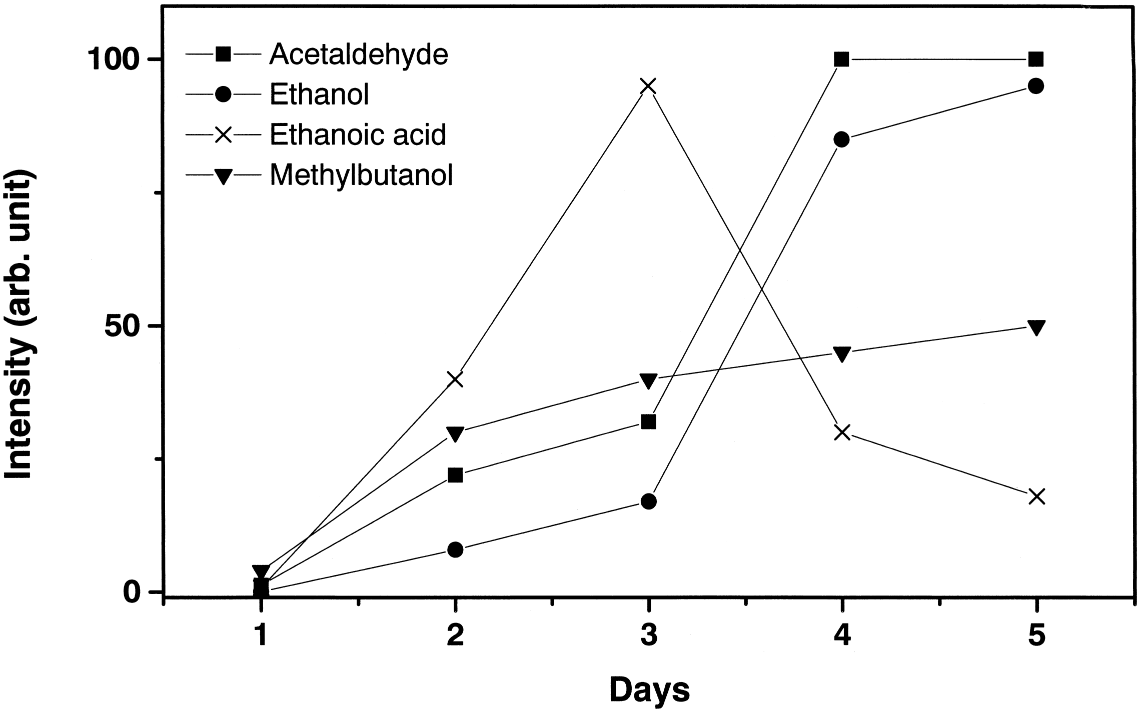

Fig. 3. Variation of the major species emitted from strawberries measured with the IAMS for a series of consecutive time intervals.

species showed similar behavior; as expected, water adducts behaved similarly to their parent compounds.

4. Concluding remarks

IAMS was successfully used for on-line measurements of trace constituents in air samples. The feasibility of measuring VOCs at the ppb level was demonstrated by the dynamic headspace analysis of the VOCs of strawberries.

The IAMS system described in this paper has the following features: (1) high-capacity, atmospheric pressure, direct sampling and easy coupling of various sample introduction sources to the mass spectrometer; (2) real-time detection of chemical species, possibly including radical intermediates; (3) easy compound identification due to analysis of ions that do not fragment; and (4) high chemical specificity, simplicity, and adaptability to any type of sample inlet system.

The efficiency of $(M + Li)^+$ ion formation strongly depends on the Li^+ affinity of the molecule, which ranges up to about 50 kcal/mol. Unfortunately, only a few molecules have been experimentally studied. However, theory is a powerful tool for determining accurate affinities [14], which are required for predicting which molecules can be detected at low concentrations.

In the near future, a large increase in the use of IAMS is likely in the areas of medicine, environmental research, and food chemistry, especially when direct air sampling is preferable. Further applications in breath analysis, emission control and monitoring of VOCs in urban and clean rural environments, emission control of VOCs from materials used for construction of buildings and furniture, and monitoring of VOC emissions from industrial plants and industrial fermentation and food production processes are feasible using this approach. Further applications may include monitoring catalytic processes, cigarette smoke, and material production in plasma reactors.

Thermogravimetry IAMS with a sampling inlet at atmospheric pressure seems promising for identifying and resolving complex coevolving products.

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