RESEARCH ARTICLE

Design and Performance of a Compact Li⁺ Ion Attachment Mass Spectrometry System with an Atmospheric Sampling Device

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Abstract

This report describes the development of a compact ion attachment mass spectrometry system. A single turbomolecular pump was employed to fill the basic requirements for vacuum conditions simply and cost-effectively, without the need for a differential pumping stage. A Li⁺ ion source was placed in the first of two vacuum chambers; a 0.4 mm aperture allowed the product ions to enter the second chamber for mass analysis. With the present system, any chemical species, including radical intermediates, can be detected at atmospheric pressure in real-time. The minimum detectable amount (at $S/N=3$) of toluene was around 1.3×10^{-12} g/s with a linearity greater than 10^4 . For illustrative purposes, we tested the system on laboratory air and on aroma compounds in the headspace of the Yuzu plant, *Citrus junos*.

Keywords: Ion Attachment Mass Spectrometry(IAMS), Capillary leak inlet, Citrus junos, Laboratory Air, Soft ionization, Direct Introduction

Introduction

More than 20 years ago, Fujii [1] proposed and developed a novel technique combining soft-ionization Li⁺ ion attachment with mass spectrometry. This technique has been extensively tested and optimized. Experimental tests indicated a moderately high efficiency and sensitivity, and the first commercially available Li⁺ ion attachment mass spectrometer was produced by Canon Anelva Corporation in 2002.

Ion attachment mass spectrometry (IAMS) has proven to be a unique method that complements electron-impact ionization mass spectrometry for the determination of components in chemical processes and environments, such as microwave discharge plasma. Recently, a book was

published on the principles, instrumental techniques, unique characteristics, and applications of IAMS [2]. The identification of intermediate free radicals and other species in chemical reactions is particularly challenging. One of the greatest advantages of IAMS is that it can be used to directly analyze gaseous compounds. The features that allow this system to detect the intermediate free radicals and novel molecular species produced in various plasmas have been extensively explored [3–5], and IAMS techniques can be used to identify and quantify compounds and mixtures under plasma [6, 7] and pyrolysis [8, 9] conditions. To extend the ion attachment technique to ion trap mass spectrometry [10] or time of flight mass spectrometry [11] has been realized.

However, the commercial IAMS apparatus is too cumbersome for use in field analysis of air samples. Therefore, we aimed to develop a new, compact IAMS system by eliminating the differential pumping stage. Our primary purpose was to design a system that could be easily and quickly transported to the field.

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In this study, we had four goals: to design and construct a new, compact IAMS system, to describe the optimal operation parameters for its use, to describe the details and operation of the capillary leak inlet, and to demonstrate the system's analytical power in some preliminary applications.

Experimental

We designed a compact ion attachment mass spectrometer that is simple and small and fulfills all the basic requirements for IAMS: the system can be used to obtain only molecular ions by detecting any chemical species in real-time. This custom-made apparatus (Figure 1) consists of a Li⁺ ion attachment ion source (IS) into which a stream of gas from a capillary leak inlet is directed, an electrostatic lens system (ELS), and a quadrupole mass spectrometer and detector, all of which are installed in a vacuum-separated envelope. The system employs a single turbomolecular pump on the vacuum envelope instead of a differential pumping system.

Ion Source

The IS constructed for this work is a modification of the previously reported IS for Li⁺ IAMS [1]. A stainless steel wall enclosing a 1.5-cm³ volume forms the IS. A tight seal is made between the IS and the capillary inlet assembly. Most of the sample gas entering the IS from the capillary leak inlet is vented into the first vacuum region via a 0.4-mm-diameter aperture in the center of the IS, through which ionic species pass to the mass spectrometer.

The IS contains a Li⁺ ion emitter (isotopically pure Li -7) and an ion attachment reaction region. Li⁺ ions are emitted from a small mineral bead (about 2 mm in diameter) fused to an

Ir filament wire (0.127 mm in diameter). The bead, prepared from a thoroughly ground mixture of Li₂O:Al₂O₃:O₂ in a 1:1:1 molar ratio for Li⁺, is situated 10 mm from the aperture. Primary ions are produced in the buffer gas by heating the bead. The measured emission current of Li⁺ ions is about 6×10^{-7} A at an emitter current of 4.0 A, with a N₂ gas flow of 8 mL/min passing through the IS at 40 Pa and an ion multiplier gain of 3×10^3 . At a fixed pressure, the Li⁺ ion current increases approximately linearly with the emitter current.

The reaction region is a cylindrical tube (inner diameter, 1.5 mm) with the Li⁺ ion emitter centered within the IS. Within the IS, ion attachment reaction conditions are maintained by changing the pumping speed or changing the diameter of the aperture. To reduce the pumping speed, a valve is situated in the line to the pump, allowing the pressure in the IS to be increased. For instance, when an aperture with a 0.4 mm diameter is used, the ambient air is sampled at a rate of roughly 7 mL/min. Under these conditions, the pressure in the IS is 40 Pa, as measured with a Baratron gauge (model 722A11TCD 2FK; MKS Corporation, MA, USA). The accessible pressure range is determined by the ability to sustain the ion attachment reaction.

The adduct ions of sample gas (cationized molecules) from the reaction region are directed into the second vacuum region through a 1-mm-diameter hole drilled through the partition wall. The adduct ions are focused by the ELS and transferred to the mass analyzer chamber (the second vacuum region). The ELS consists of an extractor, deflectors, and four sets of coaxial sequential cylinders, each biased at a particular direct current voltage. The mass analyzer chamber is equipped with a commercial quadrupole mass spectrometer (M-QA400-M; Canon Anelva, Kawasaki, Japan) from which the standard IS was removed. A Channeltron electron multiplier detector is used for ion detection.

Figure 1. A schematic of an ion attachment mass spectrometer with a capillary leak inlet and a vacuum envelope with a wall separating the first vacuum region (ion source region) from the second vacuum region (mass analyzer region). The capillary leak inlet is fixed on the front flange of the vacuum envelope. The typical operating conditions are as follows: IS pressure with nitrogen used as a buffer gas, 40 Pa; pressure in the ELS chamber, 8×10^{-2} Pa; pressure in the QMS chamber, 8×10^{-4} Pa. ELS=electrostatic lens system; IS=ion source; QMS=quadrupole mass spectrometer; TMP=turbomolecular pump

Vacuum System

The vacuum envelope is separated into the two regions by means of a fabricated partition (Figure 1). A single SplitFlow turbomolecular pump (Pfeiffer-Vacuum TMH 261-250-010; Ideal Vacuum Products, Tokyo, Japan) is installed on the vacuum envelope (which has two high-pressure pumping ports) in order to create a significant pressure differential between the first and second vacuum regions of the vacuum envelope. The 230 L/s turbomolecular pump is pumped by a single diaphragm pump (Pfeiffer-Vacuum, MVP 055-3; Hakuto Co. Ltd., Tokyo, Japan) to around 2×10^{-1} Pa as the ultimate pressure. The pressure is monitored by an ionization gauge in each region (MG-1I, control unit M-430HG-J; Canon Anelva, Kawasaki, Japan).

Sampling

A capillary leak inlet system is used for the introduction of gaseous samples [12]. One end of a 1-m-long fused-silica capillary tube (0.04 mm inner diameter, internally inert) is open to the atmosphere, and the other end is fixed on the flange of the vacuum envelope. This inlet makes it possible to effectively introduce gases while maintaining the vacuum required for IAMS. The inset of Figure 2 shows a schematic of the assembly that allows the sample gas from the diffusion cell into the capillary leak inlet.

The present system was characterized with reference compounds through a standard gas generator—that is, by means of the diffusion cell method [13, 14]. Diffusion tubes

(D-10, D-20, D-30; Gastec, Tokyo, Japan) with apertures of 2.5, 5, and 8 mm and a length of 10 cm were used to create concentration samples by flowing buffer gas over a diffusion tube enclosed in a diffusion cell (a stainless steel housing). The prepared samples passed through the exit tubing of the diffusion cell system into the capillary leak inlet system.

The Yuzu Plant

The Yuzu was purchased on February 12, 2011, and kept at 5 °C. From the afternoon of February 17 onwards, the fruits were kept at room temperature (25 °C) as measurements on volatile emissions were performed. Yuzu was placed in the diffusion cell (500 mL) housed within a temperature-controlled laboratory (25 °C) after the diffusion tube used for the specification studies was removed. For sampling, a stream of volatile gas from the Yuzu was directed into the IAMS via a capillary leak inlet inserted into the outlet of the diffusion cell. Headspace volatiles were extracted with room air (30 mL/min).

Results and Discussion

We tested the compatibility of the IAMS system and the atmospheric-pressure capillary leak inlet by sampling toluene from a diffusion cell and by introducing laboratory air and gaseous compounds from Yuzu (*Citrus junos*) plant samples placed in air at atmospheric pressure.

Performance Characteristics

A test sample of toluene was used to assess the system's linear response range, sensitivity, and minimum detectable amount. Toluene was chosen because it is the most ubiquitous volatile organic compound in the urban atmosphere [15].

Sensitivity

The toluene sample, diluted by 30 mL/min of N_2 gas, was introduced at a rate of 8.2×10^{-9} g/s from the gas flow tube at 25 °C. The measurement of the adduct ion yielded a value of 2.8×10^{-9} A, which is the output of the ion multiplier with the gain at 2×10^5 . Thus, the sensitivity is 3.4×10^{-1} A/(g/s).

Linear Response Range

The signal response for toluene was linear over the chosen range of 7×10^{-11} g/s to 8×10^{-8} g/s. A plot of four introduction rates of toluene against their corresponding peak heights produced an essentially straight line up to 8×10^{-8} g/s, where more than 5% of the total Li^+ reactant ions were used for the attachment.

Figure 2. The spectrum obtained from toluene samples in the diffusion tube shows $\text{C}_7\text{H}_8\text{Li}^+$ ($m/z=99$). The inset shows that a gas stream of toluene from a diffusion cell is directed into the IAMS through a capillary leak inlet. Sample streams were introduced to the capillary leak inlet through the diffusion cell at the rate of 8.2×10^{-9} g/s

Figure 3. Typical ion attachment mass spectrum of laboratory air. A stream of laboratory air was directed into the IAMS through a capillary leak inlet

Minimum Detectable Amount

Taking the actual noise level (1.5×10^{-13} A, see Figure 2) of the system as the ultimate limit on detection, the minimum detectable amount was calculated to be 1.3×10^{-12} g/s, on the assumption that the capability of the ion detection system in the electrometer is 4.5×10^{-13} A, at the signal-to-noise ratio of 3. Therefore, the minimum detectable amount of 1.3×10^{-12} g/s corresponds to a minimum detectable concentration of 2.1 ppb (vol/vol) if the reference compound enters the IAMS diluted by 30 mL/min of N₂ gas. Although we did not perform a rigorous or precise comparison of the performance characteristics in this study, a brief comparison reveals that our present results are essentially the same to the previous

conventional IAMS system [2] in terms of sensitivity, linear response range, and minimum detectable amount.

Lab Air Spectrum

We introduced air from our laboratory into the reaction chamber of the mass spectrometer. A typical mass spectrum of the air showed a mass peak at m/z 43 due to Li⁺ ion adducts of water clusters, the intensity of which varies with relative humidity (Figure 3). The other peaks—at m/z 35, 39, 51, 53, and 65—correspond to the major components of the air. The major components of the air—N₂, O₂, and CO₂—were identified by the presence of Li⁺ ion adduct mass peaks at m/z

Figure 4. Ion attachment mass spectrum of headspace species from Yuzu plants. The Yuzu sample was placed in the diffusion cell. The intensities of the mass peaks were normalized to 100% for the peak representing the main aroma product (m/z 143, C₁₀H₁₆Li⁺). Peak assignments are as follows: (1) C₁₀H₁₆, monoterpene; (2) C₁₀H₁₈O, monoterpene alcohol; (3) C₁₁H₂₀O, alkene aldehyde; (4) C₁₁H₂₂O, alkane aldehyde; (5) C₁₅H₂₄, sesquiterpene; and (6) C₁₅H₂₆O, sesquiterpene alcohol

35, 39, and 51, respectively. The mass peak at m/z 53 was assigned to $\text{N}_2\text{Li}^+\text{H}_2\text{O}$. The mass peak at m/z 65 is due to Li^+ ion attached to acetone, which can be attributed to the presence of acetone (used as a solvent) in the room, and the mass peaks at m/z 85, 99, and 113 may be due to $\text{C}_6\text{H}_6\text{Li}^+$, $\text{C}_7\text{H}_8\text{Li}^+$, and $\text{C}_8\text{H}_{10}\text{Li}^+$, respectively. The remaining persistent peaks at m/z 81, 95, 154, 155, and 158 have not yet been assigned.

Aroma in the Headspace of Yuzu Plants

The newly developed system appears to be distinctly suited for atmospheric monitoring. We aimed here to test this use, as well as potential food control applications, by the direct introduction and on-line monitoring of volatile organic compounds from Yuzu fruits without prior sample preparation or preconcentration of individual sample components. The aroma compounds of many plants, including Yuzu, are well documented. The Yuzu aroma is mainly determined by a complex mixture of monoterpenes, monoterpene alcohols, and sesquiterpenes [16–20]. We report here our preliminary investigations on the emissions of various aroma compounds from Yuzu. This study was limited in scope, however, and is intended to serve as an initial feasibility study.

A typical mass spectrum of the components from the dynamic headspace of the Yuzu fruits shows six peaks and their relative intensities (Figure 4). In the identification of mass spectral peaks, the validity is based principally on the mass number. Therefore, some species cannot be assigned unambiguously. For example, the m/z 143 and 161 peaks, which were assigned to $\text{C}_{10}\text{H}_{16}\text{Li}^+$ and $\text{C}_{10}\text{H}_{18}\text{OLi}^+$, may consist of assortments of monoterpenes and monoterpene alcohols, respectively. Therefore, the peak assignments in the present study were confirmed by referring to a previous study on volatile products detected by gas chromatography-mass spectroscopy in the headspace of Yuzu fruits [16–20].

Our results are in good agreement with those from the Sawamura group's studies on the aroma components of *Citrus junos* [16, 18, 20]. These investigators concluded that limonene (a monoterpene) was the major hydrocarbon in the Yuzu aroma, and that linalool (a terpene alcohol) and sesquiterpenes were responsible for the characteristic aroma. The present results suggest that dynamic headspace analysis allows the study of differences in the emission intensity and pattern of primary aroma compounds over time. The study of the aroma compounds of fruits is useful for understanding the fruit ripening and aging, and monitoring the emission of volatile organic compounds could be useful in food quality control.

Conclusions

IAMS can be used for on-line measurement of trace constituents in air samples in the field of food chemistry. The present study demonstrated the feasibility of measuring volatile organic compounds in the headspace air of a plant via direct introduction into the IAMS instrument. It is noted,

however, that using the turbo pump may not be satisfactorily good enough toward the in-fields system.

The instrument constructed for this study has several important features. It accepts high-capacity direct introduction of samples, operates with the atmospheric sampling device, and allows easy coupling of various sample introduction sources to the mass spectrometer. It permits real-time detection of chemical species—possibly including radical intermediates—and easy identification of compounds via the generation of ions that do not fragment. In addition, the capillary leak inlet system is simple and adaptable.

In the near future, we expect a large increase in the use of IAMS for environmental and food chemistry research, especially in cases where direct air sample introduction is preferable. Potential applications include emission control and monitoring of volatile organic compounds in urban and rural environments, emissions from construction material and furniture, and emissions from industrial facilities and industrial fermentation and food production processes. Further uses could also include the monitoring of catalytic processes, cigarette smoke, and breath.

Acknowledgments

The authors thank Mr. H. Hino of Canon Anelva Corporation for his contribution to the development of the compact IAMS. This work was supported in part by a grant from the France–Japan Sasakawa Foundation (code 11-PT/14) and from the JSPS (code 21–09706).

References

1. Fujii, T., Ogura, M., Jimba, H.: Chemical Ionization Mass Spectrometry with Use of Alkali Ion Attachment to Molecule. *Anal. Chem.* **61**, 1026–1029 (1989)
2. Fujii, T.: Encyclopedia of Mass Spectrometry, Vo. 6: Ionization Methods; Gross, M. (ed.) American Society for Mass Spectrometry, pp 327–334. Elsevier (2007)
3. Fujii, T.: Alkali-Metal Ion/Molecule Association Reactions and their Applications to Mass Spectrometry. *Mass Spectrom. Rev.* **19**, 111–138 (2000)
4. Sablier, M., Fujii, T.: Mass Spectrometry of Free Radicals. *Chem. Rev.* **102**, 2855–2924 (2002)
5. Fujii, T.: A novel method for detection of radical species in the gas phase: Usage of Lithium ion attachment to chemical species. *Chem. Phys. Lett.* **191**, 162–168 (1992)
6. Fujii, T., Kareev, M.: Mass spectrometric studies of a CH_4/H_2 Microwave Plasma Under Diamond Deposition Conditions. *J. Appl. Phys.* **89**, 2543–2546 (2001)
7. Fujii, T.: Diagnostics of Microwave Plasmas of C_2H_2 : Mass Spectrometric investigations of ionic and neutral species. *Phys. Rev. E* **58**, 6495–6502 (1998)
8. Kitahara, Y., Takahashi, S., Kuramoto, N., Sala, M., Tsugoshi, T., Sablier, M., Fujii, T.: Ion Attachment Mass Spectrometry Combined with Infrared Image Furnace for Thermal Analysis: Evolved Gas Analysis Studies. *Anal. Chem.* **81**, 3155–3158 (2009)
9. Takahashi, S., Kitahara, Y., Nakamura, M., Shiokawa, Y., Fujii, T.: Temperature-Resolved Thermal Analysis of Cisplatin by means of Li^+ Ion Attachment Mass Spectrometry. *Phys. Chem., Chem. Phys.* **12**, 3910–3913 (2010)
10. Faye, T., Brunot, A., Sablier, M., Tabet, J.C., Fujii, T.: Sodium Ion Attachment Reactions in an Ion Trap Mass Spectrometer. *Rapid Commun. Mass Spectrom.* **14**, 1066–1073 (2000)
11. Saito, N., Nanjyo, J., Taneda, Y., Shiokawa, Y., Tanimoto, M.: *Rapid Commun. Mass Spectrom.* **21**, 2654–2662 (2007)

12. Bach, H.T., Meyer, B.A., Tuggle, D.G.: Role of Molecular Diffusion in the Theory of Gas Flow Through Crimped-Capillary Leaks. *J. Vac. Sci. Tech. A* **21**, 806–813 (2003)
13. Miguel, A.H., Natusch, D.F.S.: Diffusion Cell for the Preparation of Dilute Vapor Concentrations. *Anal. Chem.* **47**, 1705–1707 (1975)
14. Altshuller, A.P., Cohen, I.R.: Application of Diffusion Cells to the Production of Known Concentrations of Gaseous Hydrocarbons. *Anal. Chem.* **32**, 802–810 (1960)
15. Yamamoto, N., Okayasu, H., Murayama, S., Mori, S., Hunahashi, K., Suzuki, K.: Measurement of Volatile Organic Compounds in the Urban Atmosphere of Yokohama, Japan, by an Automated Gas Chromatographic System. *Atmos. Environ.* **34**, 4441–4446 (2000)
16. Nguyen, T.L.-P., Shimamura, T., Ukeda, H., Sawamura, M.: Chemical and Aroma Profiles of Yuzu (*Citrus junos*) Peel Oils of Different Cultivars. *Food Chem.* **115**, 1042–1047 (2009)
17. Akakabe, Y., Sakamoto, M., Ikeda, Y., Tanaka, M.: Identification and Characterization of Volatile Components of the Japanese Sour Citrus Fruit *Citrus nagato-yuzukichi* Tanaka. *Biosci. Biotechnol. Biochem.* **72**, 1965–1968 (2008)
18. Song, H.S., Sawamura, M., Ito, T., Kawashimo, K., Ukeda, H.: Quantitative Determination and Characteristic Flavor of *Citrus junos* (Yuzu) Peel Oil. *Flavor Fragrance J.* **15**, 245–250 (2000)
19. Njoroge, S.M., Ukeda, H., Sawamura, M.: Changes in the Volatile Composition of Yuzu (*Citrus junos* Tanaka) Cold-Pressed Oil during Storage. *J. Agric. Food Chem.* **44**, 550–556 (1996)
20. Song, H.S., Sawamura, M., Ito, T., Ukeda, H.: Chemical Compositions of the Volatile Part of Yuzu (*Citrus junos* Tanaka) peel cold-pressed oils from Japan and Korea. *Flavor Fragrance J.* **14**, 383–389 (1999)