

# Design and Performance of an Atmospheric Pressure Inlet System for Lithium Ion Attachment Mass Spectrometry

P. Christopher Selvin,<sup>†</sup> Keiichiro Iwase, and Toshihiro Fujii\*

National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-0053, Japan

**We designed a simple and efficient inlet system to act as an interface between samples at atmospheric pressure and the high vacuum inside a mass spectrometer. The newly designed stainless steel orifice leak sample inlet system is simple and rugged and fulfills all the basic requirements. With this inlet system coupled with a lithium ion attachment mass spectrometer, it is possible to detect any chemical species at atmospheric pressure, including radical intermediates, on a real-time basis. For illustrative purposes, the sampling efficiency of the inlet probe coupled with a lithium ion attachment mass spectrometer is discussed for laboratory air and polyethylene pyrolysis.**

Recent years have seen a rapidly growing number of mass spectrometers (MS) employed for a variety of analytical applications in physics and chemistry laboratories. However, identification and quantification of compounds and mixtures in the environment still provide challenges to scientists. In particular, the identification of intermediate free radicals and species in chemical reactions is a hectic task due to many interfering factors such as fragmentation. Being motivated to develop an efficient mass spectrometer to rapidly identify species in the chemical processes, Fujii<sup>1</sup> proposed and developed a novel technique based on a soft ionization Li<sup>+</sup> ion attachment process coupled with a mass spectrometer (Li<sup>+</sup>MS). The performance of this equipment has been extensively tested and optimized, and experimental tests show that the efficiency and sensitivity of the instrument are moderately high. One of the greatest advantages of Li<sup>+</sup>MS is the ability to directly analyze gaseous compounds. Fujii and co-workers<sup>2–4</sup> explored the unique features of this system to detect intermediate free radicals and novel molecular species produced in microwave discharges. However, the analytes could not be introduced directly into this apparatus at atmospheric pressure. Hence, to extend our investigations, we developed a new atmospheric pressure sampling inlet system that does not require a differential pumping stage. Our primary objective was to convey the analytes directly at atmospheric pressure quickly and efficiently into the mass spectrometer.

We developed a stainless steel sample inlet to introduce the smallest possible amount of analytes at atmospheric pressure directly into the lithium ion attachment mass spectrometer. When designing the inlet system, we considered the following properties:<sup>5</sup> The inlet surface should be as chemically inert as possible and be able to withstand temperatures up to ~1000 K for long periods and higher temperatures for shorter periods; the response time should be less than 0.1 s; and the gas sampling should be spatially local and introduce a minimum of perturbation to the gas flow into the mass spectrometer.

Sample inlet systems based on leak<sup>5,6</sup> were found to be suitable for introducing analytes from atmospheric pressure into the Torr range in a mass spectrometer. A simple orifice leak as proposed in the literature<sup>6</sup> seemed appropriate for the present Li<sup>+</sup>MS.

In this article, we describe the details and operation of the unique features of the atmospheric pressure inlet with respect to technical points together with some preliminary experimental results.

## EXPERIMENTAL SECTION

**Atmospheric Pressure Inlet. Design Considerations.** A schematic drawing of the cutaway side view of the atmospheric pressure sample inlet system and part of the lithium ion attachment mass spectrometer developed by Anelva Corp. (Fuchu, Japan) is shown in Figure 1. The newly designed atmospheric pressure inlet for the mass spectrometer consists of an orifice leak set up as follows to ensure a consistent and streamlined entry of analytes into the mass spectrometer. The sample inlet consists of two concentric stainless steel tubes 145 mm long (9-mm outer diameter, 6-mm inner diameter); a stainless steel disk with a 30- $\mu$ m orifice at its center is fastened to the end of this probe with a nut system. There is an outlet in the outer tube to which a vacuum pump (model 5A-DS, Ulvac, Chigasaki, Japan) with a pumping speed of 5 L/min is connected to extract the excess sample gas. The inlet is connected to the reaction chamber of the mass spectrometer with a Conflat flange in such a way that the orifice is located 5 mm from the Li<sup>+</sup> emitter. This arrangement ensures that the analyte leaks in a constant, unperturbed stream of excellent consistency from the atmosphere into the mass spectrometer.

**Reaction Ionization Chamber.** The reaction chamber consists of a lithium ion emitter, a repeller, and a reaction ionization

\* Corresponding author. E-mail: t-fujii@nies.go.jp.

<sup>†</sup> On leave from N.G.M. College, Pollachi 642 001, India.

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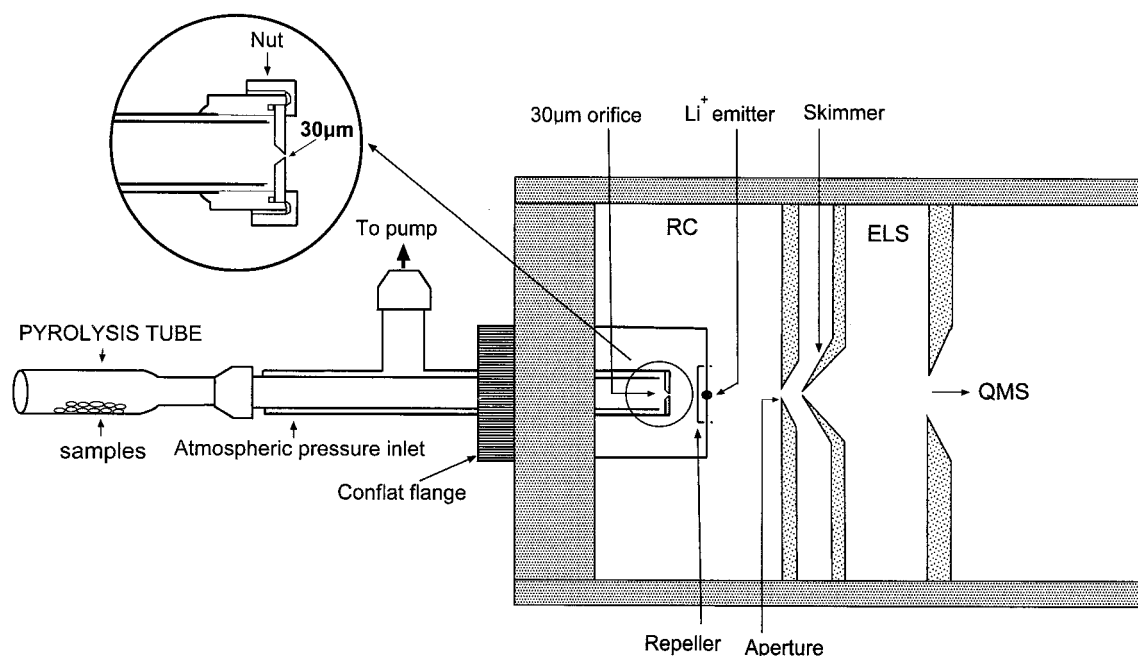


Figure 1. General overview of the atmospheric pressure inlet system attached to the lithium ion attachment mass spectrometer. RC, reaction chamber; ELS, electrostatic lens system; QMS, quadrupole mass spectrometer.

region. The  $\text{Li}^+$  emitter is lithium aluminosilicate mounted on a filament, and by heating it, lithium ions are produced. The experimental setup is such that, in a process of intermolecular association reactions,  $\text{Li}^+$  ions are attached to the chemical species (M) with the help of a third body (e.g.,  $\text{N}_2$ ) existing in the environment; consequently, the species becomes ionic as a whole ( $\text{MLi}^+$ ). The dc electrostatic field, which is produced by the emitter, the repeller, and the first aperture, transports these adduct ions to the next chamber.

**Interface.** These  $\text{Li}^+$  adducts, referred to as cationized molecules from the reaction chamber are directed into the differentially pumped lens region through a 1-mm-diameter orifice drilled into the tip of a skimmer. No potential was applied to the skimmer. The adduct ions are focused by ion lenses (ELS) installed in the chamber and transferred to the mass-analyzing chamber.

**Mass Analyzer and Detector.** The mass-analyzing chamber is equipped with a commercial quadrupole mass spectrometer (Anelva Corp., M-QA400-M) from which the standard EI ion source was removed. The analog signal is detected by the electrometer associated with the secondary electron multiplier, and the spectrum is recorded with a real-time response and high sample throughput capability. Thus, the formation and involvement of species produced in any chemical process at atmospheric pressure can be directly confirmed by the  $\text{Li}^+$  ion attachment to them.

**Procedure.** While introducing the analytes directly into the mass spectrometer, the pressure of the RC is maintained between 60 and 133 Pa, which is the optimum pressure for the formation of  $\text{Li}^+$  adducts through a termolecular association reaction. The analysis of the mass spectra is made by identifying the mass, determining the peak height, and normalizing each peak considered. The relative abundance of the mass peaks represents the monoisotopic intensity (including contributions from all the

isotopes for a given ion) with the relative intensities normalized to 100 units for a selected peak.

## RESULTS AND DISCUSSION

Here we briefly describe the operational characteristics of the inlet. We tested the compatibility of the  $\text{Li}^+$ MS and the atmospheric pressure inlet by introducing laboratory air and products from thermal decomposition (pyrolysis) of polyethylene samples carried out in air at atmospheric pressure.

**Operational Characteristics.** When an analyte at atmospheric pressure is introduced through the 30- $\mu\text{m}$  orifice in the sample inlet, the pressure in the reaction chamber reaches 100 Pa (measured with a model 722A11TCD 2FK Baratron gauge). No deterioration or marked changes in the leak rate have been noticed over a long period of use. However, sometimes the leak rate of the probe suddenly decreased by  $\sim 1$  order of magnitude. Such changes occurred only when the probe had been used without dust filtering of the gas admitted into the reaction chamber or when the probe had been contaminated. In such cases, the function of the probe could be regenerated by dipping the orifice disk in hydrofluoric acid for 30 min, washing in distilled water, and drying in a flame. The orifice leak inlet system appears to withstand much higher temperatures for longer periods than conventional Pyrex or quartz inlets.

**Laboratory Air.** We tested the performance of the atmospheric pressure inlet by introducing air from our laboratory into the reaction chamber of the mass spectrometer. Figure 2 shows a typical mass spectrum of our laboratory air. The appearance of contamination by alkali metal ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ) at  $m/z$  23, 39, and 85 is dependent on the heating condition. Their distribution primarily depends on the conditioning temperature and time. Practically, contamination by  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Rb}^+$  becomes negligible after many weeks of heating. Mass peaks at  $m/z$  25, 43, 61, 79, and 97 are due to  $\text{Li}^+$  adducts of water clusters,  $(\text{H}_2\text{O})_n\text{Li}^+$  (where

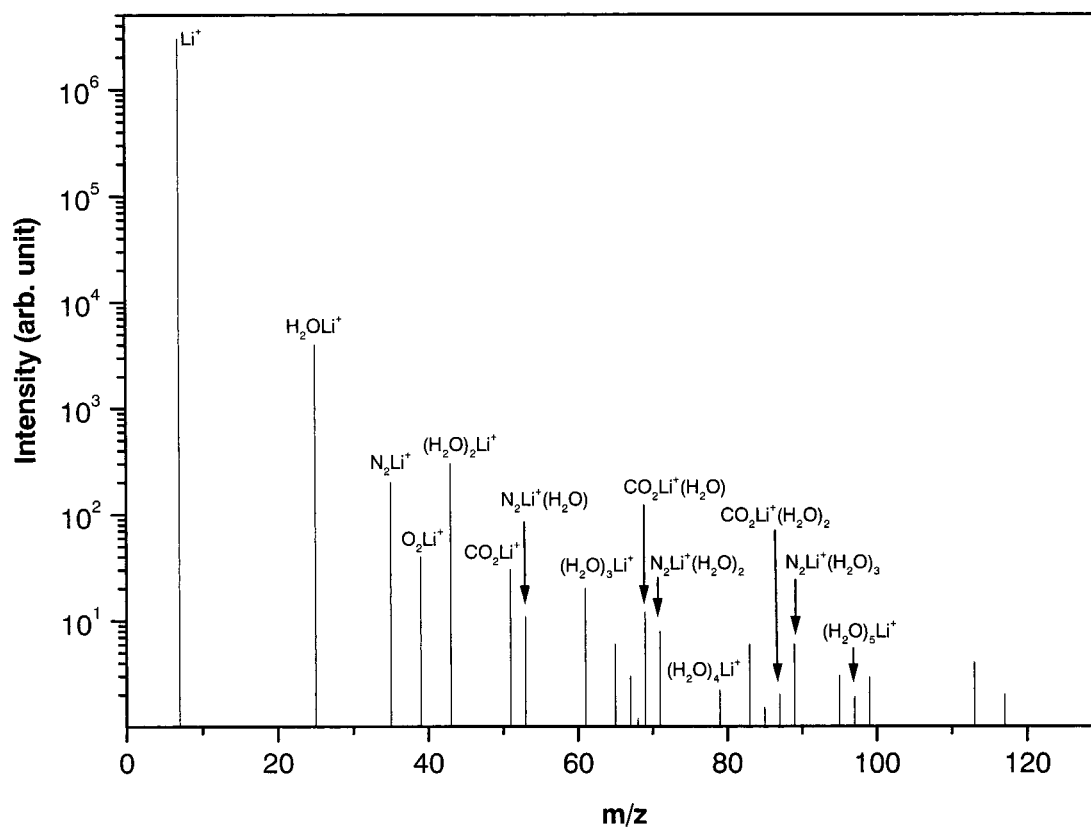


Figure 2. Typical mass spectrum of laboratory air.

$n = 1-5$ ), respectively. The distribution of these ions varies with relative humidity. The other peaks at  $m/z$  35, 39, 51, 53, 65, 67, 69, 71, 83, 85, 89, 91, 95, 99, 101, 113, and 117 are caused by major components in our laboratory air.<sup>7</sup> A few well-known components of air,  $N_2$ ,  $O_2$ , and  $CO_2$ , were identified by the presence of  $Li^+$  adduct mass peaks at  $m/z$  35, 39, and 51, respectively. The mass peaks at  $m/z$  53, 71, and 89 can be assigned to  $N_2Li^+H_2O$ ,  $N_2Li^+(H_2O)_2$ , and  $N_2Li^+(H_2O)_3$ , respectively,  $Li^+$  adducts of complex molecules containing both nitrogen and water clusters. Similarly, the mass peaks at  $m/z$  69 and 87 can be assigned to lithium adducts of  $CO_2$  with water,  $CO_2Li^+H_2O$ , and  $CO_2Li^+(H_2O)_2$ , respectively. The mass peak at  $m/z$  65 is due to  $Li^+$  attached to acetone, attributable to the presence of acetone used as a solvent in the room, while the mass peaks at  $m/z$  85, 99, and 113 may be due to  $C_6H_6Li^+$ ,  $C_7H_8Li^+$ , and  $C_8H_{10}Li^+$ , respectively. The remaining persistent peaks at  $m/z$  67, 83, 95, and 117 are yet to be assigned.

**Pyrolysis of Polyethylene.** The thermal decomposition of polyethylene (PE) is usually a sequence of complicated physical and chemical processes. The sample inlet system coupled with the lithium ion attachment mass spectrometer was highly efficient in acquiring many products produced during pyrolysis at atmospheric pressure. For pyrolysis of PE, we placed high-density PE (Aldrich) samples (5–15 mg) in a cylindrical quartz tube attached to the above-mentioned inlet system (Figure 1). The pyrolysis products were introduced into the reaction chamber of the lithium ion attachment mass spectrometer for direct analysis.

Figure 3 shows a typical mass spectrum of products of PE pyrolysis at 450 °C. All possible hydrocarbon (HC) compounds

from that particular experiment are classified in Table 1 by their formulas along with the relative intensities of their spectral data. Identification was made under the assumption that, except for water and simple carbon oxides, the only products were HCs. The relative intensities of the mass peaks were normalized to 100 units for the highest peak among the HC species produced in the pyrolysis process ( $C_5H_2Li^+$ ,  $m/z$  69). Some small (unidentifiable) peaks also appeared in the spectrum, but these are not included in Table 1. Although a quantitative assessment and rigorous analysis of the product species are beyond the scope of this paper, a brief description of the acquisition and detection of various HC species produced during pyrolysis is given below.

Since the PE pyrolysis process was carried out in the open atmosphere, we were unable to distinguish between the mass peaks due to components of air and those due to pyrolysis products. The mass peaks at  $m/z$  25, 35, 43, 51, 53, and 61 might be assigned to components of atmospheric air such as  $H_2OLi^+$ ,  $N_2Li^+$ ,  $(H_2O)_2Li^+$ ,  $N_2Li^+H_2O$ ,  $CO_2Li^+$ , and  $(H_2O)_3Li^+$ , respectively. All the other adduct mass peaks could be unambiguously assigned to HCs from the PE pyrolysis process. Since the quantitative evaluation and assignment of all these peaks were based on mass number only, some uncertainty prevails due to the overlapping of species with the components of air or other HC products. For example, the cyclobutene ( $C_4H_6$ ) lithium adduct mass peak at  $m/z$  61 is also assigned to the adduct of the water trimer,  $(H_2O)_3Li^+$ . Similarly, the  $m/z$  127 peak, which can be assigned to polycarbon ( $C_{10}Li^+$ ), may also overlap with the production of  $C_9H_{12}Li^+$ .

Many research groups have analyzed the thermal decomposition of plastic wastes including PE.<sup>8-13</sup> In those studies, all the

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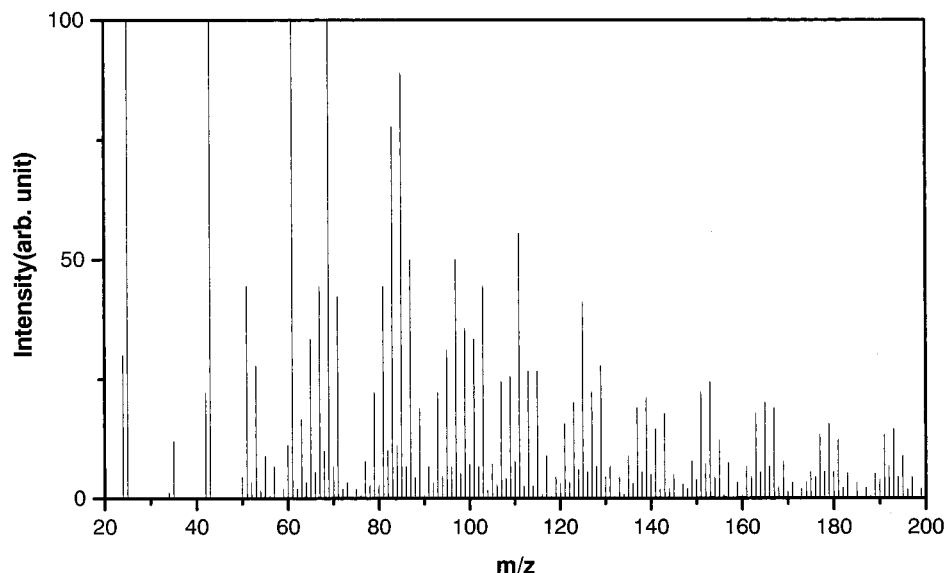


Figure 3. Typical mass spectrum of the products from the pyrolysis of polyethylene.

Table 1. Analysis of the Neutral Products from the Pyrolysis of Polyethylene: Classification by Their Formulas, and the Relative Intensities (Percent Values) of Their Adducts

type	chemical species													
$C_n$	$C_4$ (9)	$C_5$ (44)	$C_6$ (22)	$C_7$ (7)	$C_8$ (44)	$C_9$ (27)	$C_{10}$ (22)	$C_{11}$ (21)	$C_{12}$ (22)	$C_{13}$ (18)	$C_{14}$ (6)	$C_{15}$ (2)	$C_{16}$ (2)	
$C_nH_2$	$C_4H_2$ (6)	$C_5H_2$ (100)	$C_6H_2$ (45)	$C_7H_2$ (22)	$C_8H_2$ (8)	$C_9H_2$ (9)	$C_{10}H_2$ (28)	$C_{11}H_2$ (14)	$C_{12}H_2$ (24)	$C_{13}H_2$ (20)	$C_{14}H_2$ (13)	$C_{15}H_2$ (5)		
$C_nH_4$	$C_4H_4$ (2)	$C_5H_4$ (42)	$C_6H_4$ (78)	$C_7H_4$ (31)	$C_8H_4$ (24)	$C_9H_4$ (4)	$C_{10}H_4$ (7)	$C_{11}H_4$ (18)	$C_{12}H_4$ (12)	$C_{13}H_4$ (19)	$C_{14}H_4$ (16)	$C_{15}H_4$ (13)		
$C_nH_6$	$C_4H_6$ (111)	$C_5H_6$ (3)	$C_6H_6$ (89)	$C_7H_6$ (49)	$C_8H_6$ (26)	$C_9H_6$ (15)	$C_{10}H_6$ (4)	$C_{11}H_6$ (6)	$C_{12}H_6$ (8)	$C_{13}H_6$ (8)	$C_{14}H_6$ (12)	$C_{15}H_6$ (14)		
$C_nH_8$	$C_4H_8$ (17)	$C_5H_8$ (2)	$C_6H_8$ (50)	$C_7H_8$ (35)	$C_8H_8$ (56)	$C_9H_8$ (20)	$C_{10}H_8$ (9)	$C_{11}H_8$ (3)	$C_{12}H_8$ (3)	$C_{13}H_8$ (3)	$C_{14}H_8$ (5)	$C_{15}H_8$ (9)		
$C_nH_{10}$	$C_4H_{10}$ (33)	$C_5H_{10}$ (8)	$C_6H_{10}$ (19)	$C_7H_{10}$ (33)	$C_8H_{10}$ (26)	$C_9H_{10}$ (41)	$C_{10}H_{10}$ (18)	$C_{11}H_{10}$ (8)	$C_{12}H_{10}$ (7)	$C_{13}H_{10}$ (2)	$C_{14}H_{10}$ (3)	$C_{15}H_{10}$ (4)		
$C_nH_{12}^a$	$C_4H_{12}$ (44)	$C_5H_{12}$ (22)	$C_6H_{12}$ (7)	$C_7H_{12}$ (44)	$C_8H_{12}$ (27)	$C_9H_{12}$ (22)	$C_{10}H_{12}$ (21)	$C_{11}H_{12}$ (22)	$C_{12}H_{12}$ (18)	$C_{13}H_{12}$ (6)	$C_{14}H_{12}$ (2)	$C_{15}H_{12}$ (2)		

<sup>a</sup>  $C_nH_{12}$  species may also be assigned to  $C_{n+1}$  (polycarbon) species.

product species were broadly classified into alkanes, alkenes, and aromatics. In the present study also, we observed the same tendency with respect to the nature of the products. Nevertheless, there were some exceptions. We detected many pure carbon molecules, sometimes referred to as polycarbon species ( $C_n$ , where  $n = 4-16$ ), and  $C_nH_2$  species (polyacetylenes) with  $n = 4-15$ , with  $C_5H_2$  being more plentiful than the others. In addition, we detected many new species with the general formulas  $C_nH_4$ ,  $C_nH_6$ ,  $C_nH_8$ ,  $C_nH_{10}$ , and  $C_nH_{12}$  (where  $n = 4-15$ ) as products of the pyrolysis. Some of them, such as  $C_6H_6$ ,  $C_7H_8$ , and  $C_8H_{10}$ , may be species with an aromatic ring. These molecular species, including aromatics, may be obtained from the cracking of the polymeric structure. This appears to lead to intermediate species with several carbon atoms, which are then stabilized probably by hydrogen also obtained from the cracking of the polymeric structure.<sup>11</sup>

Fujii examined ethylene ( $H_2C=CH_2$ ) microwave discharge plasmas with the  $Li^+$ MS technique and detected polymer species,

such as  $C_n$  ( $n = 2-8$ ),  $C_nH_2$  ( $n = 2, 3, 4, 6, 8, 10$ ), and  $C_nH_4$  ( $n = 2, 4, 6, 8, 10$ ), and other free-radical species, such as  $C_nH_3$  and  $C_nH_5$  ( $n = 1-6$ ), along with a few aromatic compounds.<sup>4</sup> Therefore, it is reasonable that similar HC species and HC species with higher carbon numbers should be produced by pyrolysis of polyethylene ( $[-H_2C-CH_2-]_n$ ). The detection of these species was made possible with the help of the sample inlet coupled with the  $Li^+$ MS system.

Westerberg et al.<sup>14</sup> detected many free radicals in PE processing fumes and suggested a degradation mechanism based on the reaction of free radicals. Although the  $Li^+$ MS method was successfully employed to detect many short-lived free radicals produced in plasma processes,<sup>3,4</sup> we detected hardly any free radicals in the present PE pyrolysis process. Hence, it is possible that, due to the open atmospheric air environment, free radicals were not produced in the present study.

An unsatisfactory result is that molecules with low polarizability, such as methane, ethane, and propane, were not detected in the present pyrolysis process. These molecules possess weak lithium affinities and  $Li^+$  ions do not easily attach to them. Therefore, although these alkanes are abundantly produced during PE pyrolysis,<sup>11</sup> they were hardly detected with the present method.

Because the pyrolysis of the PE samples was carried out in the open atmospheric air, the formation of oxygenated HC species

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is quite feasible.<sup>9,10</sup> For example, the mass peak at  $m/z$  65, which was assigned to  $C_4H_{10}Li^+$ , may also belong to  $C_2H_4O_2Li^+$  or  $C_3H_6OLi^+$ , which are known byproducts of the pyrolysis process.

## CONCLUSIONS

An atmospheric sampling inlet device to introduce analytes, including radical intermediates, into a lithium ion attachment mass spectrometer is presented. The inlet system is relatively maintenance free and is able to introduce high volumes of sample gas into the mass spectrometer. These characteristics, combined with the elimination of long chromatographic separations, result in near-real-time sample analysis. The sample inlet in combination with  $Li^+$ MS has a number of features that make it useful as an extremely sensitive instrument for continuous monitoring of trace

organic species and small quantities of environmentally important analytes, such as radical intermediates including toxic radicals present in ambient air. We anticipate a wide range of practical applications that will employ this inlet coupled with  $Li^+$ MS.

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