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A new method for thermal analysis

Ion-attachment mass spectrometry (IAMS)

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Abstract In this study, we developed the technique of Li^+ ion-attachment mass spectrometry (IAMS), a method that has shown promise in the fields of chemical analysis, plasma diagnostics, chemical process monitoring, and thermal analysis. The experimental setup is such that Li^+ ions get attached to chemical species (R) by means of intermolecular association reactions to produce $(R + Li)^+$ adduct ions, which are then transferred to a quadrupole mass spectrometer. Recently, an IAMS system became available commercially in a complete form from the Canon Anelva Corp. IAMS has several notable features. It provides only molecular ions, and it permits direct determination of unstable, intermediary, and/or reactive species. Also, it is highly sensitive because it involves ion-molecule reactions. With regard to its applications for thermal analysis, one of its greatest advantages is that it can be used to directly analyze gaseous compounds because it provides mass spectra only of the molecular ions formed by Li^+ ion attachment to any chemical species introduced into the spectrometer, including free radicals. Coupled with evolved gas analysis, IAMS works well for the analysis of nonvolatile, untreated, and complex samples because the simplicity of the ion-attachment spectrum permits the analysis of mixtures electron-impact spectra of which are difficult to interpret.

Keywords Ion attachment · Mass spectrometry · Thermal analysis · Evolved gas analysis

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Introduction

More than 20 years ago, Fujii developed a novel technique based on soft-ionization Li^+ ion attachment coupled with mass spectrometry (MS) [1]. This technique, referred to as Li^+ ion-attachment mass spectrometry (IAMS), has been extensively tested and optimized. The efficiency and sensitivity of the technique are moderately good, and the first commercially available IAMS system was recently developed by Canon Anelva Corp. IAMS has proven to be complementary to electron-impact ionization MS for the determination of components in, for example, microwave discharge plasma. Recently, some books have been published on the principles, instrumental techniques, unique characteristics, and applications of IAMS [1, 2].

One of the biggest advantages of IAMS is that it can be used to directly analyze gaseous compounds because it provides mass spectra only of the molecular ions formed by Li^+ ion attachment to any chemical species introduced into the spectrometer, including free radicals. The unique abilities of this system to detect intermediate free radicals, which is a challenging task, and novel molecular species produced in various plasmas have been explored [3, 4]. Therefore, it is interesting to apply these techniques to the identification and quantification of compounds and mixtures in chemical processes.

On the other hand, a number of analytic methods are used for thermal analysis [5], including thermogravimetry, differential thermal analysis, differential scanning calorimetry, pyrolysis (evolved gas analysis, EGA), combined with Fourier transform infrared spectroscopy, MS, and gas chromatography/mass spectrometry (GC/MS). In addition, EGA–MS, which can be considered a second generation of pyrolysis MS, has been developed [6] and found to be useful for thermal analysis, particularly in the characterization of

thermal decomposition processes. In addition to standard mass spectra, mass spectra obtained in total ion monitoring or selected ion monitoring mode as a function of temperature (spectra that are equivalent to a pyrogram or thermogram) can provide information for kinetic studies of thermal decomposition processes.

In almost all MS studies, electron-impact ionization [1] is used to analyze the degradation products. An electron-impact spectrum consists of the molecular and fragment ions produced by sample pyrolysis. Some difficulties occur: thermal decomposition products with energetic electrons cause further fragmentation, and fragmentation of the degradation products may depend strongly on the instrument conditions, especially in the ion source of the mass spectrometer. Therefore, the development of an efficient mass spectrometer for rapidly identifying species in chemical processes is needed.

For this purpose, we developed a system [7] that combines an ion-attachment quadrupole mass spectrometer with a direct inlet probe or an infrared image furnace (IIF) unit for EGA. EGA is most effectively performed by means of MS because of its specificity and sensitivity. The system enables us to introduce thermally decomposed analytes at atmospheric pressure directly into the Li^+IAMS system. In this article, we describe the technical details and operation of the EGA–IAMS system, as well as several advantages that this system has over conventional mass spectrometers. The EGA–IAMS system might work well for nonvolatile, untreated, and complex samples—such as lacquers—because the simplicity of the ion-attachment spectrum permits the analysis of mixtures electron-impact spectra of which are difficult to interpret. Finally, interesting applications for thermal analysis and possible future uses of this approach are reviewed.

Principles

Thermal ion-attachment (association) reactions are termolecular processes [8]:

$$A^+ + R + N \leftrightarrows [A - R]^+ + N \quad (1)$$

where A^+ denotes a positively charged alkali metal ion, R is a radical species, and N acts as a third body. The binding energy of the radical R to the alkali cation A^+ is defined by the enthalpy change for the reaction. Derived primarily from electrostatic forces, the binding energy of A^+ to R must be high enough to permit a significant number of adducts to be formed at the partial pressure used in the experiments. As indicated, most association reactions are reversible, although not necessarily appreciably so for all experimental conditions. The bonds between ions and neutral species are generally weak relative to normal chemical bonds: the energy of an A–M bond is typically 200 kJ mol^{-1} or less, often still lesser. The lithium ion affinity can be reviewed in the literatures [9, 10]. It seems likely that the A–M bond derives primarily from electrostatic forces such as ion–dipole attraction.

Instrumentation

Basics of instrument design

An overview of the Li^+ ion attachment mass spectrometer is shown in Figure 1 [1, 2, 11–13]. It is composed of four major functional parts: the sample inlet system (sample gas), the reaction chamber, the ion-focusing system (ion lens), and the quadrupole mass spectrometer chamber. Three vacuum pumps are generally employed to evacuate various sections of the system: The reaction chamber, ion-focusing system, and mass analyzer are held at approximately 100 Pa, less than 2×10^{-2} Pa, and approximately 5×10^{-5} Pa, respectively, by turbomolecular pumps (or diffusion pumps). These functional parts are discussed in more detail in the following sections.

Sample inlet system

Samples may be introduced into the MS system by several methods, such as leaks or insertion probes for EGA, and on-line combinations with chromatography. Because of the high-vacuum conditions, a controlled capillary leak is a simple method to introduce samples, but this method is restricted to samples with high vapor pressure. Solid and liquid samples can be introduced with a heated insertion probe via a vacuum lock into the high-vacuum region. Either gas chromatography or liquid column chromatography can easily be used as a sample inlet system. In principle, any gaseous sample components of which are to be identified can be introduced into the reaction chamber.

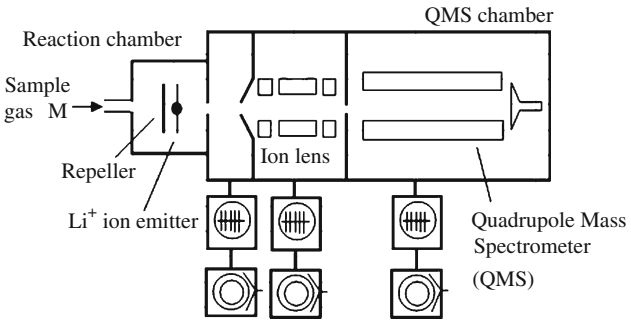

Fig. 1 Schematics of the lithium ion attachment mass spectrometer. Li^+ is supplied by a Li^+ emitter. Li^+ attaches to the sample gas (*M*) in the reaction chamber. The adduct ion $[M + Li]^+$ is then introduced to the QMS chamber (quadrupole mass spectrometer) after passing through focusing devices (ion lens)

Reaction chamber

The reaction chamber is a cylindrical tube with a Li^+ ion source centered along one side. The chamber can be evacuated through a cone aperture with a rotary pump and can be maintained at high pressure by altering the pumping speed or the carrier gas flow rate. The Li^+ ion source consists of a Li^+ ion emitter and a repeller electrode. The Li^+ ion emitter is a small mineral bead (about 0.2 cm in diameter) fused to a 0.25-mm-diameter Ir wire; the bead is prepared by thoroughly grinding a mixture of Li_2O:Al_2O_3:SiO_2 (1:1:1 molar ratio), and primary Li^+ ions are produced by heating the bead. The emission of contaminants along with the Li^+ ions is unavoidable as emission begins, but this ultimately decreases to less than 0.1% of the total emission. The repeller electrode, consisting of a stainless steel disk, is placed 1 cm behind the emitter bead; its voltage is maintained at the same potential as the emitter.

Ion-focusing system

Adduct ions from the reaction chamber pass through an aperture and are directed into the differentially pumped lens region through a 1-mm-diameter orifice drilled into the tip of a skimmer. The ion-focusing system is an electrostatic lens system.

Mass analyzer

The mass analysis chamber is equipped with a quadrupole mass spectrometer with rods biased below ground by connecting the DC rod-driven circuit to separate DC supplies. This type of mass spectrometer system has recently become available commercially in a complete form (Canon Anelva Corp, IA-Lab). It allows an easy linkup with a gas chromatograph and, hence, the acquisition of the mass spectra of molecular ions. The optimal use of direct measurements is facilitated by the IA-Lab, which includes a 5-port direct probe, a mass spectrometer operating to 1,000 *m*/*z*, and an easily maintained ion source.

Compact IAMS system

Unfortunately, the commercial apparatus is not practical for the study of atmospheric environments. Recently, we developed a new compact IAMS system that does not require a differential pumping stage (Fig. 2). The primary objective for this study was to develop a system that can be easily transported to the field and that can detect any chemical species at atmospheric pressure on a real-time basis. A single turbomolecular pump is employed as the vacuum system to fill the basic requirements for vacuum

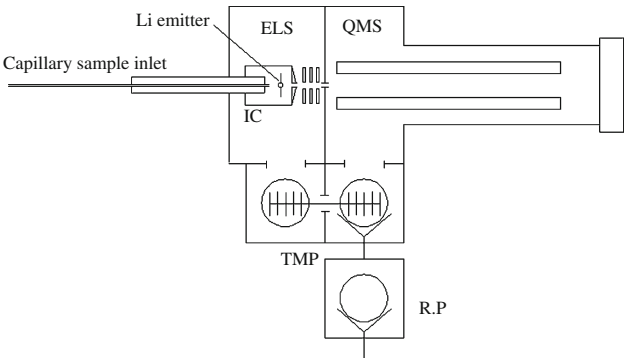

Fig. 2 A schematic drawing of new ion attachment mass spectrometer with the capillary sample inlet and a vacuum envelope with a wall separating ELS chamber from mass analyzer chamber. This capillary inlet is fixed on the front flange of the vacuum envelope. *IC* ionization chamber, *ELS* electrostatic lens system, *QMS* quadrupole mass spectrometer, *TMP* turbomolecular pump, *RP* rotary pump. The vacuum envelope is pumped by a single 230 L sec^{-1} turbomolecular pump with two ISO-100 inlet flanges (Pfeiffer-Vacuum TMH 261-250-010) plus a 250 mL min^{-1} rotary pump. Ionization chamber is closed-type, with a 1 mm φ aperture through which ionic species are passed. The typical operating conditions are: IC pressure with nitrogen gas used as a buffer gas, 40 Pa; pressure of ELS chamber, 8×10^{-2} Pa, pressure of the QMS chamber, 8×10^{-4} Pa

conditions; this is simple and cost effective. The system has been successfully used for online measurements of trace constituents in air samples in the field of food chemistry.

This system has the following features: (1) It has the ability to accept high-capacity direct introduction of samples, to operate at atmospheric pressure, and to allow easy coupling of various methods for sample introduction to the mass spectrometer. (2) It offers an opportunity for real-time detection of any chemical species, including radical intermediates. (3) It has the ability to identify compounds easily because the generated ions do not fragment, and (4) It has high chemical specificity, simplicity, and adaptability to any type of sample inlet system.

EGA–IAMS

When a mass spectrometer is used together with a temperature-programmed heating probe with total ion monitoring or selected ion monitoring, a thermogram can be obtained. The probe can also serve as an isothermal or temperature-programmed flow reactor for homogeneous, heterogeneous, or thermal decomposition kinetic studies. The non-isothermal method has the advantage of using only one sample for the entire experiment [5, 6].

We designed a simple EGA system to act as a sampler between solid samples at atmospheric pressure and the high vacuum inside a mass spectrometer [7]. The newly designed stainless steel EGA system is simple, small, and

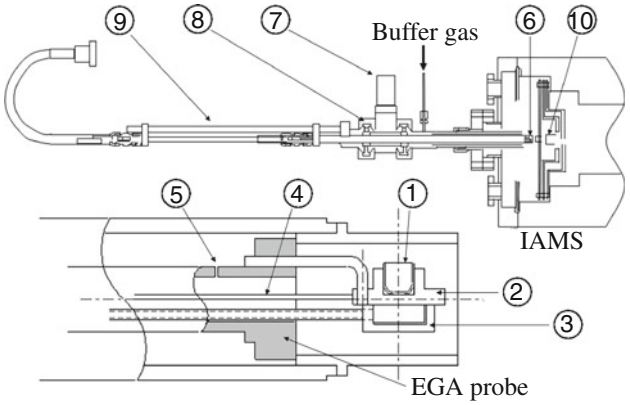

Fig. 3 General overview of the EGA probe attached to the lithium ion attachment mass spectrometer; extended view of EGA probe showing *1* sampler, *2* sampler holder, *3* heater, *4* thermocouple, *5* gas inlet, and the whole system of EGA probe and IAMS, showing *6* EGA probe, *7* isolation valve, *8* detachable flange, *9* slide guide, and *10* Li^+ emitter

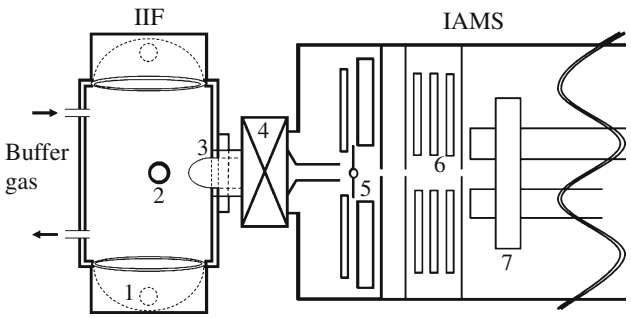

Fig. 4 A schematic drawing of infrared image furnace (IIF) inlet system coupled with IAMS, showing the IR lamp unit (*1*), the sample holder (*2*), the 70 μm orifice (*3*), the gate valve (*4*), the Li ion emitter bead fused onto the Ir wire (*5*), the focus lens (*6*), and the quadrupole MS (*7*)

rugged, and it fulfills all the basic requirements for EGA. Temperature parameters are programmable with a maximum heating rate of 60 °C min^{-1} and a maximum temperature of 600 °C. With this system coupled with Li^+IAMS, it is possible to study the temperature-programmed decomposition of a number of solid materials by detecting any chemical species on a real-time basis. Another advantage is the ability to directly analyze gaseous constituents; because the ion-attachment process is non-dissociative, it generates $(M + Li)^+$ that do not fragment. The fragment-free measurement of chemical species permits the analysis of mixtures with electron-impact spectra that are difficult to interpret.

Figure 3 is a schematic drawing of the cutaway side view of the EGA–probe inlet system fabricated in this study. The newly designed inlet system for the mass spectrometer consists of a gas inlet in the inner tube through which a buffer gas is introduced to carry the evolved gas. This arrangement ensures that the analyte flows in a constant stream from the sampler into the mass spectrometer. The EGA probe consists of two concentric stainless steel tubes (200 mm long with a 15.8 mm outer diameter, and 280 mm long with a 6.4 mm outer diameter). A holder with the sampler at its center is fastened to the end of this probe. The EGA probe is placed in front of the reaction (ionization) chamber of the mass spectrometer with a Conflat flange in such a way that the sampler is located 10 mm from the Li^+ emitter. This distance is adjustable, but 10 mm was found to be optimal in terms of sensitivity.

To permit thermal stability studies of a wide range of nonvolatile materials under atmospheric conditions or in a flowing stream, we designed an IAMS system coupled with an IIF (Fig. 4) [14]. We developed an orifice interface system to be placed between the sample IIF at atmospheric pressure and the high vacuum inside a mass spectrometer. With this system coupled with Li^+IAMS, it is possible to detect many chemical species at atmospheric pressure, including radical intermediates, on an EGA basis. The IIF used as the heat source consists of two tungsten lamps. The lamps are placed within gold-plated, parabolic reflecting surfaces, which can heat a sample up to 1100 °C at a heating rate of 10 °C sec^{-1}. The buffer gas, which also acts as the cooling gas, is drawn at a rate of 30 mL min^{-1} from the gas cylinder into the IIF. To ensure entry of the evolved gas into the IAMS, an orifice is set up as follows: The concentric quartz tube (100 mm long, with 20 mm outer diameter and 18 mm inner diameter) has an orifice with a 70 μm diameter at its center and a stainless steel exit tube; IIF is fixed to the flange of a gate valve with an O-ring system. The sample gas is carried to the Li^+ ion reaction chamber of the mass spectrometer through the gate valve in such a way that the outlet of the exit tube is located 15 mm from the Li^+ ion emitter. This arrangement ensures that the analyte flows in an unperturbed stream from the IIF into the IAMS. The sample cell is made of alumina (5 mm diameter) and is placed in the platinum holder of the IIF.

Features

The essential advantages and applications of the present Li^+IAMS system include the following:

No dissociative ionization takes place. There is no possibility of fragmentation of the adduct ions; Li^+IAMS provides only molecular ions and, hence, can be used for the determination of molecular weight and for the analysis of mixtures where no fragmentation is desired.

Mass spectra from a Li^+ ion-attachment mass spectrometer tend to be simple, and it is easy to determine which form of which radical species is reacting.

The sensitivity is high, especially for polar molecules, due to ion–molecule reactions.

Direct continuous measurements are feasible on a real-time basis for many radical species and stable molecules in a dynamic system. Because of the ability to identify and resolve complex coevolving products, IAMS enables the characterization of thermal processes via identification of any kind of reactive species, including neutral radical species.

The features described above can help us to expand the applications of MS into areas such as product analysis in plasma reactors, monitoring of catalytic processes, detection of cigarette smoke, detection of interstellar species, etc.

Applications

Li^+IAMS has already been used for several interesting thermal analyses, including the detection of free radicals produced from thermally irradiated polyethylene polymers, the temperature-programmed decomposition of polytetrafluoraethylene (PTFE), the detection of bisphenol A (BPA) from the thermal decomposition of polycarbonate, the mass spectral analysis and kinetic study of d-metal complex platinum anticancer agents (cisplatin), the thermal decomposition of vitamin C, the production of d-metal complex free radicals of $Mn(CO)_5$, and the thermal characterization of Japanese lacquers (urushi). Some of these studies are presented here.

Airborne free radicals

The widespread occurrence of free radical intermediates in gas-phase reactions has frequently been the subject of kinetics studies. Nevertheless, considerable experimental difficulties involved in detecting, identifying, and measuring the concentrations of intermediate species exist. Westerberg et al. detected the emission of airborne free radicals in air samples during the injection molding, extruding, seam welding, and wire cutting of polyethylene and polystyrene plastics [15]. On the basis of electron spin resonance spectroscopy on the resulting spin adducts, those investigators suggested a degradation mechanism based on free radical reactions.

Motivated by Westerberg's detection of various airborne free radicals in polyethylene processing fumes, our group investigated and identified the principal radical species produced in the pyrolysis of polyethylene by coupling an IIF with Li^+IAMS instrumentation [16]. All possible hydrocarbon products identified in the mass spectrum of polyethylene pyrolysis at 450 °C were classified by their formulas (Fig. 5). Identification was made under the assumption that the only products produced were hydrocarbons. Spectra of the thermal decomposition products, detected by means of Li^+IAMS, clearly showed that radicals—such as C_nH_{2n+1} ($n = 5$–12) and C_nH_{2n-1} ($n = 5$–11)—were the predominant species produced. Many of these species were identified for the first time by MS. Our results provided direct evidence that free radicals are formed in the pyrolysis environment and are detectable with mass spectrometric techniques.

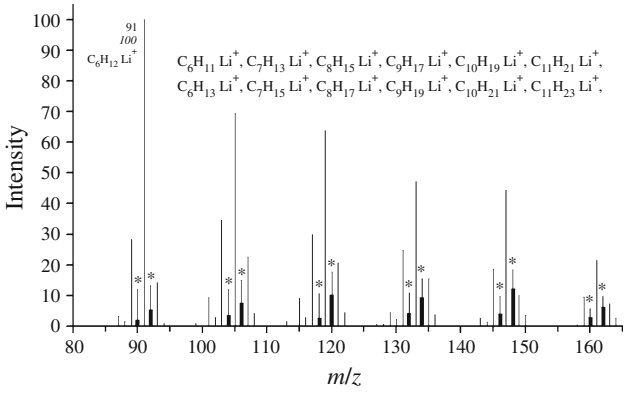

Fig. 5 Representative mass spectrum of the products produced from the thermal decomposition of polyethylene (PE) at 450 °C in a nitrogen environment. Free radicals observed are marked with an *asterisk*. The intensities of some peaks exceeded the scale, which was chosen for the purpose of demonstrating the adduct ion peaks, because of the free radicals. The peaks with the *asterisk* indicate that the *bold part of the line* is from the production of free radicals, while the *thin part* is the contributions from the ^{6}Li isotope adduct ions and ^{13}C isotope ions

Pyrolysis of PTFE

A number of methods are used for the thermal analysis of polymers: thermogravimetry, differential thermal analysis, and differential scanning calorimetry, pyrolysis (EGA) by Fourier transform infrared spectroscopy, MS, and gas chromatography. MS with EGA is superior to other conventional techniques in terms of high sensitivity, identification of unknown species, and real-time analysis. Online EGA quadrupole MS is designed and used as a valuable tool to study the kinetics and mechanisms of thermal degradation processes of many functional materials. [6, 17]

Mass spectral results on the temperature-programmed decomposition of PTFE demonstrate the capability of the system. A typical mass spectrum of the products of PTFE under oxidative conditions at 550 °C is shown in Fig. 6 [14]. Identification was made on the assumption that the only products were fluorocarbons and oxygenated fluorocarbons. The relative intensities of the mass peaks were normalized to 100 units for the $(CF_2)O$ peak among the C_nF_m species produced in the thermal process. The PTFE samples were heated in air, and so it is quite feasible for

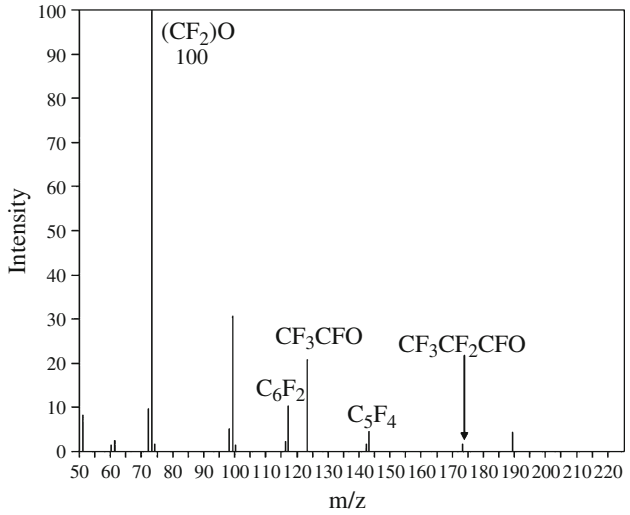

Fig. 6 A typical mass spectrum of the products of PTFE in the oxidative pyrolysis at 450 °C. The relative intensity is given as a percentage of the $(CF_2)O$ peak

oxygenated CF species to form. We detected abundant molecules with the general form $(CF_2)_nO$ ($n = 1$–3). In addition, the mass peaks at 117 and 143 can be assigned to C_6F_2 and C_5F_4, respectively. The remaining peaks at *m/z* 51, 99, and 189 are yet to be assigned.

BPA from polycarbonate

The accumulation of plastics in the environment is a matter of great concern [18]. One of the available solutions, waste recycling also known as incineration, can be used to transform waste plastics into energy. However, the combustion of plastics can produce many gaseous products, the nature of which depends mainly on external conditions, such as temperature and oxygen availability. Accordingly, a series of pyrolysis experiments were conducted with the EGA–IAMS system to mimic the reductive environment and conditions within incinerators [19]. Li^+ IAMS has considerable advantages for product monitoring in the gas phase in comparison with traditional electron-impact MS. Unlike traditional MS, which involves ionization by high-energy electrons, IAMS preserves the profiles of the product molecules much better, allowing their detection as adduct ions without any fragmentation.

Among the pyrolysis products of polycarbonates, BPA may be of most concern [20, 21]. BPA is an endocrine disruptor; although its acute toxicity is low, there is concern that long-term exposure to low doses of BPA may induce chronic toxicity in humans. Therefore, it is important to lower BPA emissions if possible.

Experiments were conducted with polycarbonate pyrolysis in nitrogen and air atmospheres (Fig. 7a, b, respectively). In air, a second BPA emission peak is observed at

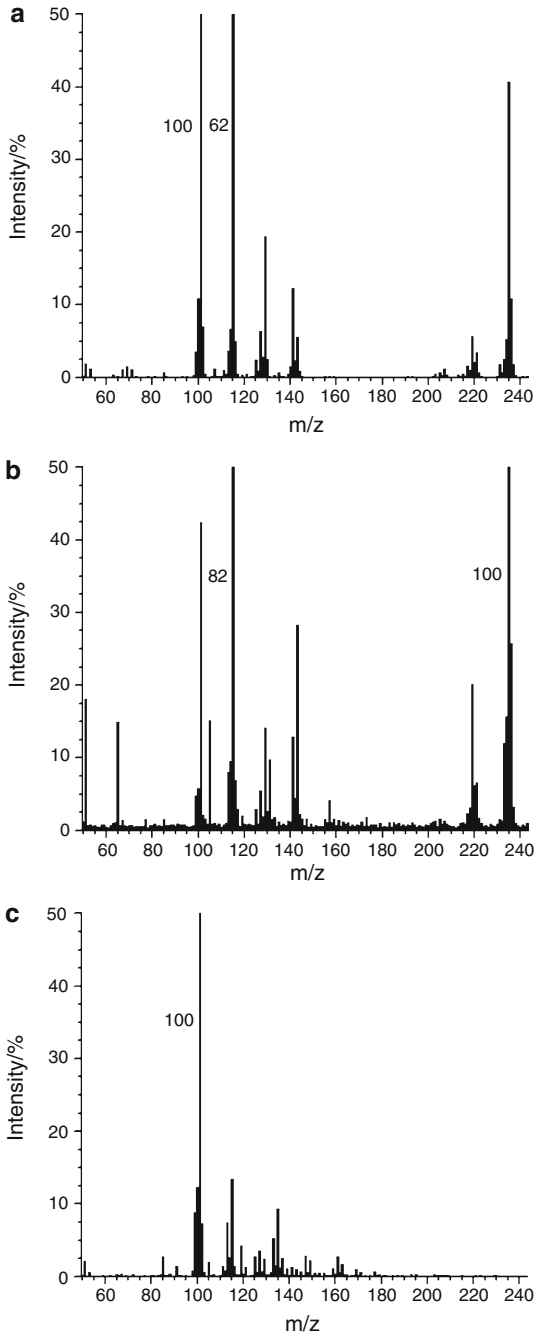

Fig. 7 Ion attachment mass spectra measured at 450 °C in N_2 atmosphere (**a**), air atmosphere (**b**), and with addition of $CuCl_2$ (ratio 1:3 in favor of $CuCl_2$) in N_2 atmosphere (**c**), respectively. The *peaks* at m/z 235 indicate the emission of BPA emitted

lower temperature than that observed in the nitrogen atmosphere. This clearly shows that there are two different mechanisms of BPA production, but the details are not yet known. In further experiments, a mixture of polycarbonate and $CuCl_2$ in a ratio of 1:3 was pyrolyzed (Fig. 7c). The amount of evolved BPA was almost 1/100 of that when no $CuCl_2$ was present. Thus, one can expect that BPA

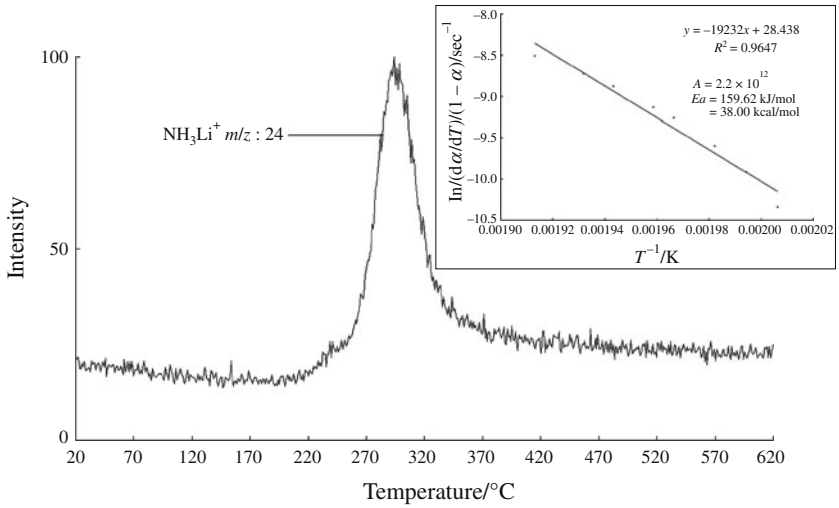

Fig. 8 An EGA curve (selected-ion monitoring) for cisplatin (sample weight, 1 mg; heating rate, 20 °C min^{-1}; atmosphere, nitrogen). Shown are the relative ion intensities for *m/z* 24 (NH_3Li^+) obtained during temperature-programmed heating of a cisplatin sample to 620 °C in the IIF. *Inset* an Arrhenius plot for NH_3 produced from cisplatin decomposition in the temperature range from 225 to 249 °C

emission can be successfully reduced not only by the addition of $CuCl_2$ but also by other metal salts.

Thermal characterization of cisplatin

Li^+IAMS was evaluated as an analytic methodology for the measurement of the thermally labile, nonvolatile, and insoluble compound cisplatin, which is used as an anticancer agent in the treatment of testicular and ovarian cancers. We aimed to develop an improved method for the mass spectrometric determination of cisplatin, particularly in its molecular ion form. A uniquely designed quadrupole MS system with a Li^+ ion-attachment technique and a direct inlet probe provided cisplatin molecular ions as Li^+ ion adducts; to our knowledge, this was the first reported instance of cisplatin Li^+ ion adducts. Full-scan spectra were obtained with ~10 μg samples. IIF combined with IAMS was also used to study the temperature-programmed decomposition of this drug [22]. The slope of the plot of signal intensity versus temperature for cisplatin decomposition from 225 to 249 °C was used to determine the apparent activation energy of 38.0 kcal/mol for the decomposition of cisplatin (Fig. 8). This value of decomposition parameter is useful for predicting drug stability (shelf life). In this study, we demonstrated that IAMS can be a valuable technique for the direct mass spectral analysis and kinetic study of d-metal complex platinum anticancer agents.

Vitamin C decomposition

EGA-IAMS was used to study the real-time, non-isothermal decomposition of vitamin C [23]. The results were compared with those obtained in a similar study on thermal decomposition of vitamin C using pyrolysis GC/MS. Significant differences were found between the two techniques, in terms of the nature and relative amounts of products formed. A major difference between the two techniques was in the transportation time of the pyrolysis products out of the pyrolysis chamber (or hot zone). This time was significantly shorter in EGA–IAMS than in pyrolysis GC/MS, which reduces the occurrence of secondary reactions of the primary pyrolysis products. Some decomposition products formed in the EGA–IAMS system were not detected in the previous pyrolysis GC/MS study and thus were detected here for the first time. The main degradation product detected by means of EGA–IAMS was dehydro-L-ascorbic acid (Fig. 9), which had not been detected from the decomposition of solid vitamin C before this study [24].

Analysis of d-metal complex radicals

The observation of coordinatively unsaturated d-metal radical intermediate species in a reaction provides a motivation to study the intrinsic role of 17-electron organometallic free radicals [25]. Because radical intermediates have short lifetimes and their steady-state concentrations in a reacting system are low, detecting and identifying such intermediates are always difficult tasks.

We used EGA–IAMS [26] to qualitatively analyze the d-metal radical products of the pyrolysis of $Mn_2(CO)_{10}$. The use of an atmospheric-pressure sampling inlet device to introduce the analytes, including radical intermediates, into the Li^+ attachment mass spectrometer permitted real-time, continuous monitoring of the pyrolysis products. Our results indicated that pyrolysis of $Mn_2(CO)_{10}$ produced two d-metal radicals as well as stable molecules, including $HMn(CO)_5$ (Fig. 10). These results are significant in two main respects: We were able to positively identify the free radicals by MS, and our results provide evidence that the reactions in the pyrolysis process involved neutral radicals. The radicals may have reacted with each other, with other

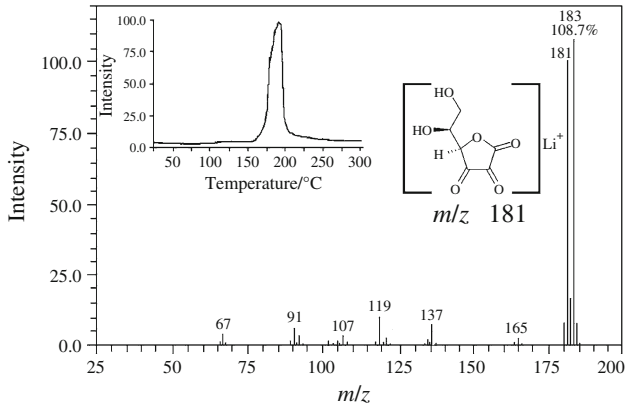

Fig. 9 Total ion chromatogram (TIC) of vitamin C obtained in total ion-monitoring mode at a heating rate of 128 °C min^{-1} in the temperature range of 25–300 °C (*Inset*). Mass spectrum of vitamin C heated to 150–230 °C at 128 °C min^{-1}. The intensities of the mass peaks were normalized to 100% for the peak representing the main thermal decomposition product (*m/z* 181, dehydro-L-ascorbic acid)

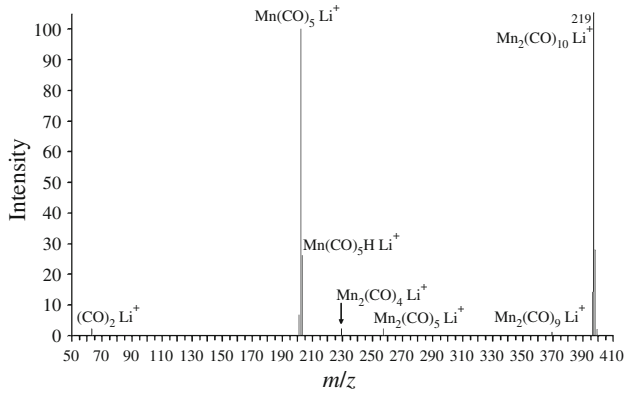

Fig. 10 Typical Li^+ adduct mass spectrum of the $Mn_2(CO)_{10}$ up to *m/z* 400 to show the production of free radicals $Mn(CO)_5$ and $Mn_2(CO)_9$ from $Mn_2(CO)_{10}$ thermal decomposition. This spectrum was acquired under N_2 with the conventional direct probe at 170 °C. The intensities were normalized to the $Mn(CO)_5Li^+$

pyrolysis products, or with the residual gases present in the IIF to form $HMn(CO)_5$ and other substituted products.

Thermal decomposition of Japanese lacquer films

The thermal decomposition of Japanese lacquer films (urushi)—nonvolatile complex natural materials—has been investigated by temperature-programmed heating (non-isothermally) and EGA–IAMS [27]. IAMS with a temperature-programmed direct probe offers the opportunity to study directly the thermal degradation processes occurring in complex natural materials, as well as the chance to determine the identity of a lacquer source by identification of different types of lacquer monomer.

A typical mass spectrum of the thermal products of a Japanese lacquer film was obtained by rapid heating up to

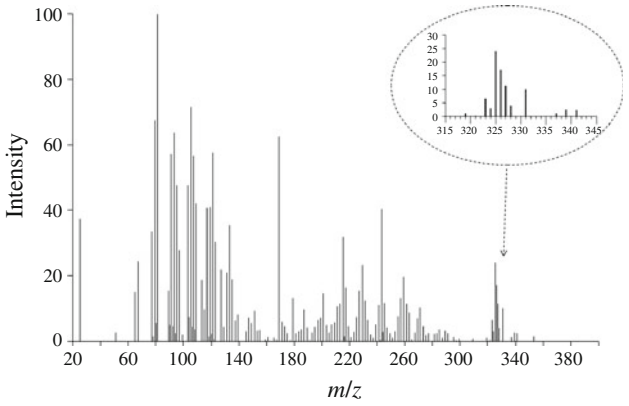

Fig. 11 A typical ion-attachment mass spectrum of the products from the pyrolysis of a Japanese lacquer film recorded as the furnace temperature increased from room temperature to 500 °C. Samples were placed in the EGA furnace and heated linearly in a N_2 atmosphere at a programmed rate of 128 °C min^{-1}. The relative intensity is given as a percentage of the intensity of the carboxylic acid peak at *m/z* 81 ($C_2H_5COOHLi^+$). *Inset* a partial mass spectrum from *m/z* 315 to 345. These *peak clusters* correspond to the urushiol monomer

500 °C in N_2 gas environment (Figure 11). Many peaks were found from *m/z* 315–345 (Fig. 11 inset). These peak clusters were identified as pure urushiol monomer molecules. Urushiol is a mixture of a catechol substituted with an alkyl chain of 15 or 17 carbon atoms; urushiol is a mixture of saturated and unsaturated molecules. Recent studies [28, 29] have revealed that lacquer can be roughly classified into three types: Japanese (or Chinese) lacquer (based on the urushiol monomer), Vietnamese lacquer (based on the laccol monomer), and Burmese lacquer (based on the thitsiol monomer). The mass spectral analysis of the urushiol monomer is interesting because identification of the type of lacquer monomer—urushiol, laccol, or thitsiol—can allow researchers to identify the source of ancient archeological lacquerware. Such identification is essential for conservation and restoration studies.

Future applications

The compatibility of thermogravimetry with Li^+IAMS may provide excellent temporal correspondence between thermogravimetry and mass spectral data, as well as the ability to identify and resolve complex co-evolving products. This method appears to hold great promise for the analysis of nonvolatile d-metal complexes, and thermally labile medicinal compounds should be explored extensively. Applications involving pyrolysis GC/IAMS are also promising analytically, in view of the simple mass spectra obtained where pseudo-molecular ions are predominant.

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