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# EVOLVED GAS ANALYSIS-MASS SPECTROMETRY USING SKIMMER INTERFACE AND ION ATTACHMENT MASS SPECTROMETRY

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A new EGA-MS instrument consisted of a combination of skimmer interface with no change of evolved gaseous species and IAMS (Ion Attachment Mass Spectrometry) with no fragmentation during the ionization has been developed successfully. As its application of evolved gaseous species from PVA as firing process of alumina ceramics binder, the method has indicated detection of gaseous species which have not been detected with Py-GC-MS.

***Keywords:*** *binder, EGA-MS, GC-MS, IAMS, skimmer interface*

## Introduction

EGA-MS that is well-known as TG-MS has generally used a quadrupole mass spectrometer to detect various gaseous species evolved from a sample and carried via capillary interface between the MS and the furnace. The capillary interface has a problem of adsorption of the evolved gaseous species. Thus the skimmer interface which is useful to infrared image furnace has been developed [1]. In the case of an electric resistance furnace, the coupling with skimmer interface between a furnace and a mass spectrometer was reported [2, 3].

However, the fragmentation due to the ionization for MS obstructs to identify the gaseous species in a furnace. Furthermore capillary which is a separation device of GC and an interface between TG and MS has a problem to generate some species in addition to pyrolized species. Therefore a combination of skimmer interface with no change of evolved gaseous species and IAMS (ion attachment mass spectrometry) with no fragmentation during the ionization has been expected the accurate characterization of gaseous species in the furnace. For this purpose, a prototype instrument of IAMS and infrared furnace connected with skimmer interface based on the principle of a jet separator has been build up.

The IAMS is a new technique using ion attachment for ionization to mass spectrometry [4–6]. To ionize gaseous species, $Li^+$ attachment has been used. At this time, the $Li^+$ ion has energy of less than a few eV. Thus no fragmentation has occurred because the energy of $Li^+$ is less than the binding energy in the gaseous species. It means that the detected fragments in the mass spectra are only due to the thermal decomposition and not due to the ionization.

## Experimental

The EGA-IAMS instrument was constructed with a gold image furnace based on TPD type R (Rigaku Corporation) and L-241G-IA (ANELVA Technix Corporation) which is a process monitor type IAMS instrument. The schematic diagram of the prototype apparatus is shown in Fig. 1. The skimmer-interface consists of two conic quartz tubes with orifice to connect the two devices as atmospheric pressure and vac-

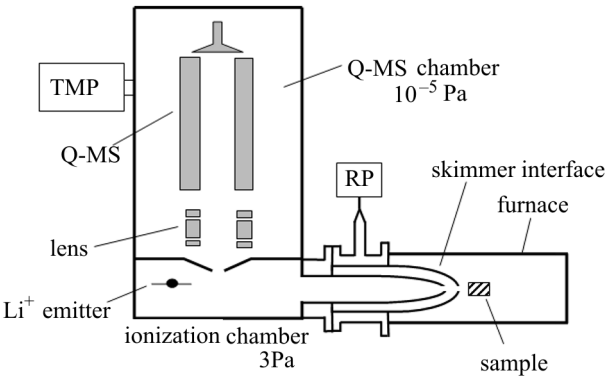


**Fig. 1** Schematic diagram of the prototype instrument TIAS-254 with IAMS and skimmer interface

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**Table 1** Comparison of detected evolved gaseous species with Py-GC-MS and IAMS with skimmer interface

| M.W. | GC | Characterized by GC-MS | IAMS |
|---|---|---|---|
| 18 | N.D. | | + |
| 30 | N.D. | | + |
| 44 | N.D. | | + |
| 58 | N.D. | | + |
| 60 | + | acetic acid | + |
| 66 | N.D. | | + |
| 70 | + | crotonaldehyde | + |
| 74 | N.D. | | + |
| 78 | + | benzene | + |
| 84 | N.D. | | + |
| 88 | N.D. | | + |
| 96 | + | 2,4-hexadienal | + |
| 96 | + | vinylcyclopentane | + |
| 96 | + | 2-ethylfuran | + |
| 100 | N.D. | | + |
| 106 | + | benzaldehyde | + |
| 110 | + | 2,5-dimethyl-2,4-hexadiene | + |
| 110 | + | 1,3-dimethyl-cyclohexene | + |
| 114 | N.D. | | + |
| 120 | + | 2-methyl-benzaldehyde | + |
| 120 | + | 4-methyl-benzaldehyde | + |
| 122 | + | 2,5-dimethyl-3-methylene-hexadiene | + |
| 122 | + | 2,4,6-octatrienal | + |
| 125 | + | benzylalcohol+OH | + |
| 126 | N.D. | | + |
| 134 | + | *p*-methylanisole+12 | + |
| 136 | + | $\alpha$-terpinene | + |
| 140 | N.D. | | + |
| 148 | + | 2-methoxy-1,4-dimethyl-benzene+12 | + |
| 148 | + | 4-isopropylbenzaldehyde | + |
| 158 | N.D. | | + |
| 162 | N.D. | | + |
| 166 | N.D. | | + |
| 174 | N.D. | | + |
| 178 | + | undecatetraene | + |
| 187 | N.D. | | + |
| 199 | N.D. | | + |

uum as same as the previous report [1]. Since the carrier gas we used is also high-purity helium, the evolved gaseous species that have higher mass enriched after the second orifice, consequently as a principle of a jet separator. The quartz tube was without any special heating, except infrared from the furnace lamp and radiant heat from a sample. The carried gaseous species evolved from the sample by thermal decomposition without any transformation were ionized by $Li^+$ attachment in the ionization chamber and analyzed by a quadrupole mass spectrometer.

For comparison of the qualitative results, Py-GC-MS were carried out with 5989B (Agilent) using a pyrolyser 2010 (Frontier Lab.).

As sample preparation, we used simple way to prepare a raw material of alumina ceramic as an example. That is just mixing of alumina powder and polyvinyl alcohol (PVA) granule. The procedure is as

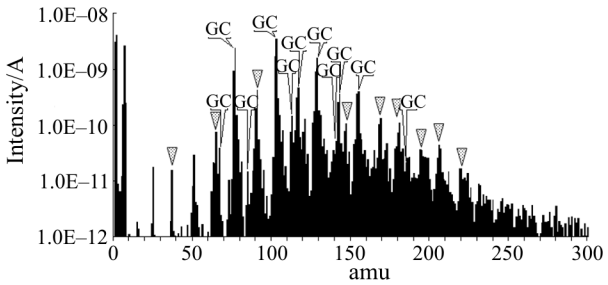


**Fig. 2** IAMS spectrum obtained from alumina/PVA at 289°C. The peaks marked with 'GC' were also detected with Py-GC-MS. The other peaks marked with wedge were major peaks detected only by IAMS

follows; the 10 mass% PVA was added to $Al_2O_3$ powder. The mixture was milled with addition of distilled water in a mortar, and dried.

## Results and discussion

Figure 2 shows a mass spectrum obtained from the mixture specimen of alumina and PVA at 289°C which temperature is on the peak top of thermal decomposition of PVA. Some peaks corresponded to the results of Py-GC-MS as on the molecular mass. However some peaks marked were not identified from the result of Py-GC-MS. On the principles, skimmer interface has less adsorption and touch of the gaseous species to the wall of the device. Further IAMS has a potential of detection of all gaseous species even if it is radical species. Thus there is a possibility of that our instrument can detect some gaseous species which were disappeared in the Py-GC-MS measurement due to, e.g., adsorption or some reaction. Table 1 shows the comparison of the detected species as molecular mass between Py-GC-MS and IAMS with skimmer interface. The species which were detected and characterized by Py-GC-MS were detected also by IAMS. The other species were detected by IAMS only. The problem of identification is still remained because IAMS spectrum can offer molecular mass only of gaseous species without any information of the chemical structure.

## Conclusions

It is confirmed that new instrument with skimmer interface and IAMS has been developed successfully. This technique can offer unique data of the evolved gas due to pyrolysis. Gaseous species which is not detected with Py-GC-MS, have been detected with IAMS via skimmer interface. However the interpretation problem is still remained.

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