Application of a multi-turn time-of-flight mass spectrometer with a vacuum ultraviolet photo ionization source with high light intensity

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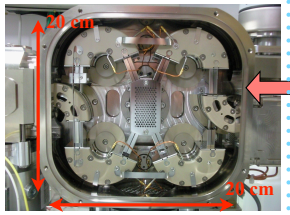
Introduction

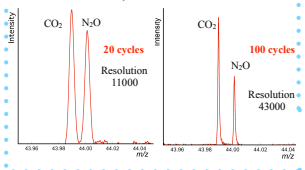
Photoionization with a **vacuum ultraviolet (VUV) light source** results in soft ionization with **minimal fragmentation** for compounds with ionization energies lower than the photon energy. Unlike electron ionization (EI), it is easy to interpret the mass spectrum of complex mixtures because overlapping peaks including molecular and fragment ion signals are eliminated. Recently, a newly developed **VUV photo ionization (PI) source with high light intensity** was combined with a **multi-turn time of flight mass spectrometer (MULTUM)** having **high resolving power and high mass accuracy**. This instrument (VUV-PI-MULTUM) may enable the **identification of individual components in complex mixtures**. In this research, the usefulness of VUV-PI-MULTUM for the analysis of individual components in complex mixtures is evaluated.

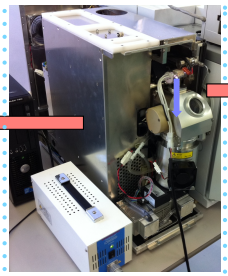
Instrumentation: VUV-MULTUM

MULTUM



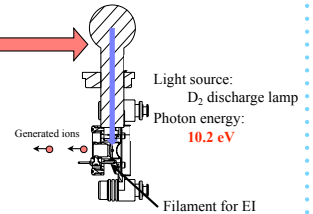
In our laboratory, **multi-turn time-of-flight mass spectrometer** was constructed and named "MULTUM"[1]. This instrument basically consists of four electric sectors and two additional electric sectors for purpose of ion injection/ejection. The size and weight of the system is 234 mm x 456 mm x 640 mm and 36 kg (including vacuum pump and electronic circuits).





Size: 234 x 456 x 640 mm^3
Weight: 36 kg
Roughing pump (x 2):
KNF Neuberger Inc.
N84.3ANDC
(5L/min, 500 Pa, 0.9 kg)
Turbomolecular pump (x 2):
Osaka Vacuum Ltd.
TG70FNRB
(70 L/s, Φ102x144.5, 3kg)

VUV light source



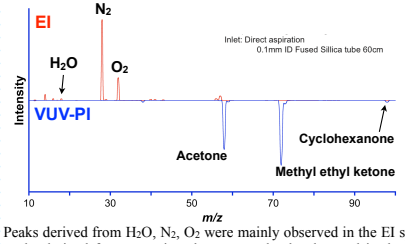
EI and **vacuum ultraviolet (VUV) photo ionization (VUV-PI) can be used in MULTUM.** The photon energy of the VUV-PI source is **10.2 eV**, which is sufficiently high to ionize most of many organic samples. Additionally, photoionization with a **vacuum ultraviolet (VUV) light source** results in soft ionization with minimal fragmentation[2] for compounds with ionization energies lower than the photon energy. Unlike EI, it is easy to interpret the mass spectrum of complex mixtures because overlapping peaks including molecular and fragment ion signals are eliminated.

In MULTUM, ions are stored in the orbit and traverse the same orbit many times. Accordingly, the flight path length can be extended infinitely. As a results, MULTUM offers **high mass resolution mass spectrometry** in a miniaturized/portable enclosure.

Results and discussion

★ Direct analysis of a mixture of organic solvents using EI and VUV-PI

(methyl ethyl ketone: 40~50%, acetone: 15~25%, cyclohexanone: 15~25%)

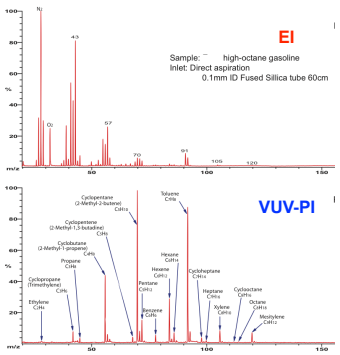


Ionization Potential (IP)
∗H_2O: 12.6 eV
∗N_2: 15.6 eV
∗O_2: 12.1 eV
∗Acetone: 9.7 eV
∗Methyl ethyl ketone: 9.5 eV
∗Cyclohexanone: 9.2 eV

Photon energy:10.2 eV
→H_2O, N_2, O_2 can not be ionized.

Peaks derived from H_2O, N_2, O_2 were mainly observed in the EI spectrum. On the other hands, three peaks derived form organic solvents are clearly observed in the VUV-PI spectrum. Therefore it is easy to **identify the components of the complex** in the VUV-PI spectrum.

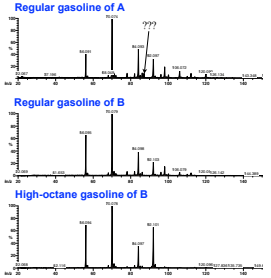
★ Direct analysis of gasoline using EI and PI



Many fragment ions with odd *m/z* values were present in the EI spectra. As a result, a **large number of peaks including molecular and fragment ion signals were overlapped** in the EI spectrum. **This made it difficult to distinguish the molecular ion peaks from the fragment ion peaks.** On the other hands, only molecular ion peaks such as C_4H_8, C_5H_{10} and C_7H_8 were clearly observed in the VUV-PI spectrum. All components could be identified by the *m/z* values due to the high mass resolution and high mass accuracy of the MULTUM. These results indicated that the **VUV-PI-MULTUM is useful for the analysis of individual components in complex mixtures** because VUV-PI can produce molecular ions of individual components with **minimal fragmentation**, and MULTUM can identify them from only the *m/z* values.

★ Direct analysis and identification of various gasoline using VUV-PI

(Regular gasoline of A- and B-company, High-octane gasoline of B-company)



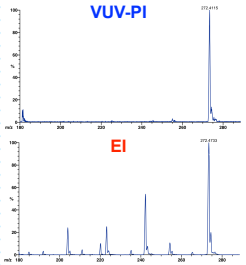
Three spectra were normalized by the peak intensity with *m/z* 70 values.

Regular gasoline (A-company vs B-company)
∗Relative intensities of each peaks such as *m/z* 56 and 84 values were slightly different.
∗Peak with *m/z* 87 values were observed in only the VUV-PI spectrum of A-company.

Regular gasoline vs High-octane gasoline
∗Relative intensities of each peaks such as *m/z* 92 values were largely different.

By using VUV-PI, subtle difference of the each components of the gasoline concentration could be identified.

★ Evaluation of sensitivity of VUV-PI ion source using GC-MS



In order to evaluate the sensitivity of VUV-PI ion source, GC-EI and GC-PI spectra of octafluoronaphthalene (OFN) were obtained. The concentration of OFN was 1000 ppm. Two spectra were normalized by the peak intensities with *m/z* 272 value. **In the VUV-PI spectrum, only the peak with *m/z* 272 values were observed.** On the other hand, the peak with many fragment ion peaks are clearly observed in the EI spectrum. The intensity with *m/z* 272 values of the EI spectrum were about 10 times higher than that of the VUV-PI spectrum. The sensitivity of VUV light source is sufficiently practical for the photoionization, although the size of the source is very small. A continuous improvement of the VUV-PI source would make **VUV-PI-MULTUM one of the most useful instruments in the analysis of individual component in complex mixtures such as mobile engine exhaust, cigarette smoke, and breath.**

References

1) S. Shimma, et al., Anal. Chem., **82** (2010), 8456-8463.
2) J. Wang, et al., Int. J. Mass Spectrom. **263** (2007), 30–37.