A New Laser Mass Spectrometry for Chemical Ultratrace Analysis Enhanced with Multi-Mirror System (RIMMPA)

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A new laser mass spectrometry RIMMPA has been proposed and developed for on-site and real-time ultratrace analysis of air pollutants such as dioxin and the endocrine disruptors. The advantageous features are described from the theoretical aspect of MMS effects. The proof of principle experiment has successfully been carried out with use of diluted benzene gas and an UV tunable laser. The experimental results have proven the high ionization efficiency of the ion source and the sensitivity and resolution of RIMMPA, comparing with the case of laser one-pass irradiation such as in Jet-REMPI. The higher sensitivity and resolution can be expected by combining a new TOF/MS such as of Jet-REMPI

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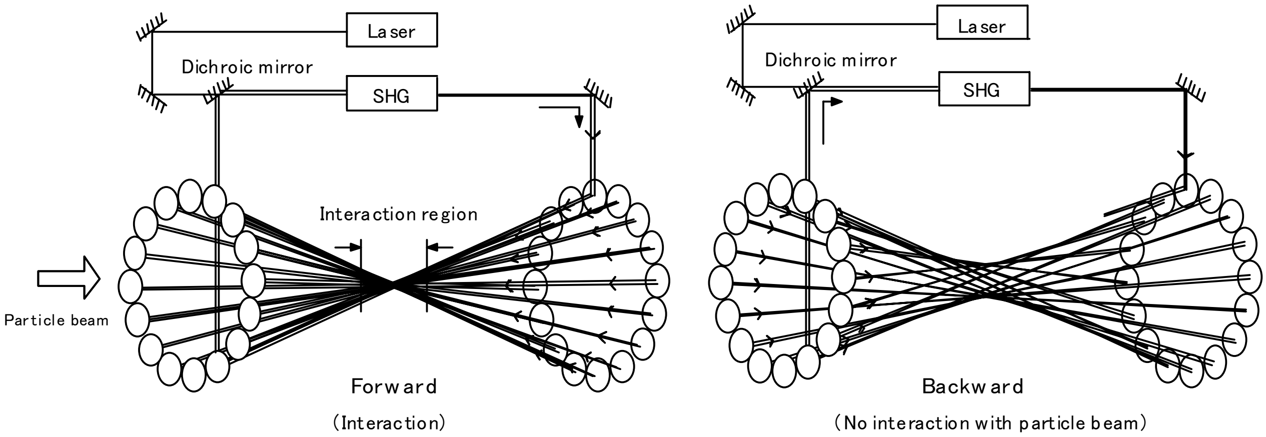
A photon-efficient-use device, RIMMPA

A new laser mass spectrometry (RIMMPA: Resonance Ionization with MMS Photon Accumulation) has been proposed and developed by IDX Technologies for on-site and real time ultratrace analysis of air pollutants such as dioxin and the endocrine disruptors. RIMMPA is featured by use of MMS (Multi-Mirror System), which is a kind of an optical image relay system and can store the photon beam in the system with the high efficiency, and irradiates the injected gas with multiple times. By adding MMS to on so-called, the ionization part of Jet REMPI (Jet-Resonance Enhance Multi-Photon Ionization)[1,2,3)], we can expect the better efficiency of photons to ionize the ultratraces. Consequently, RIMMPA[4)] will show the exceeding performance on the ultratrace detection and it gives rise to the identification and quantitative data of extremely low concentration of chemical species. The photon-efficiency factor enhanced by MMS[5)] on resonance multi-photon ionization is theoretically studied in detail. The proof of principle experiment has successfully been carried out in the cooperative research program with Ibaraki University and proven the high ionization efficiency and the high sensitivity and resolution.

Multi-mirror system (MMS)

Multi-mirror system is a kind of multiple image relay system. It is composed of two flat circular discs that have halls respectively at the center. The many concave mirrors are located on the discs that are placed facing each other as shown in Fig. 1.

In order to utilize a laser power effectively, this MMS was developed in Japan Atomic Energy Research Institute (JAERI) as a new charge exchange device for the high-energy physics project. Figure 1 shows ray paths in the multi-mirror system and there, the forward rays (right to left) at the left hand side and the backward ones (left to right) at the right hand are illustrated separately. The focal length of the mirrors is selected at half of the distance L between the mirrors. In the optics, this image-relay is designed to minimize profile distortion and loss of laser beam by aberration at the reflection. If the properly diverging laser beam is injected at the first reflection mirror, the reflected laser beam becomes a constant cross-section beam in the forward beam and then travels to the next mirror passing through the central region of the MMS. The laser beam reflected at the next mirror becomes the backward beam, and focuses at the off-center point. All the forward flight paths of constant cross-section cross altogether at the central part of the system and so the photon beam can interact multiply with gas injected there in the RIMMPA's scheme. There, the cold gas is injected by the fast pulse valve and flows into the interaction space. As the cross-sectional area of the beam is controllable by the optical expander placed at the external optical circuit of MMS, the volume of the interaction space formed at the central part, is also controllable whether to make larger or smaller. MMS cannot only increase the irradiation time of laser beam



Forward
(Interaction)

Backward
(No interaction with particle beam)

Fig.1 Ray traces in the multi-mirror system and of light accumulation system

with the round-trip of the light but also can make the larger interaction volume at the center of the system. The beneficial effects of MMS on the multi-photon ionization scheme are: The first is the ability to prolong the irradiation time on the gas. The second is the multiple-folding effect of the laser beam when the length of laser light is longer than the round-trip distance, The third is the volume controllability of the interaction (ionization) region mentioned above. The last is the power feedback ability and re-entrance capability of laser power by using dichroic mirror as shown in Fig.1, though the last two effects are not applied in the present RIMMPA scheme.

MMS effects on RIMMPA

The MMS effects on RIMMPA are theoretically studied in detail. Are considered the relations among the number or the current of detected ions (hereafter we call this as signal intensity), laser power, the volume of ionization space, the ionization cross-section and characteristic parameters of MMS.

	L	M	g	β	gβ	$(g\beta)^2$
1	45	8	5	2	10	100
2	45	12	7	2	14	200
3	30	8	3.7	3	11	120
4	30	12	5	3	15	225
5	20	8	2.8	4.5	12.5	156
6	20	12	3.7	4.5	16.5	277
7	20	16	4.7	4.5	21.2	477

Table 1 Enhance factor :$(g\beta)^2 = (M + \beta)^2$, where M is number of mirrors on disc, $\beta = cT / 2LM$, and $g = 2LM / ct + 1$. The laser pulse length is 180 cm (6 nsec)

Let's consider the simple model of one color 2-photon resonance ionization scheme neglecting the lifetime of the excited level. The rate equations of the model become in unit interaction volume:

Equation of excitation : $\delta N^* = (n / 2)\, n_p\, \sigma{:}{*}c\, \delta t$、

Equation of ionization: $\delta N^+ = (\delta N^*)\, n_p\, \sigma^{+.}\, c\, \delta t$

Here, δN^*, δN^+ n_p, $\sigma*$, $\sigma+$, n, c and δt are increments of excited particles and ionized ones, photon density, the cross-section of excitation and ionization, density of seeded molecular, light velocity and irradiation time of laser light, respectively. Inserting the relation between laser power I and photon density: $I = S_p h\nu n_p c$ and assuming $h\nu = 3$ eV, that is, $n_p\, c = 2 \times 10^{18} (I / S_p)$ and integrating it over the interaction volume V, then we obtain

$\delta N = 2\alpha \times 10^{36}\, n\, V(\beta I/Sp)^2 \sigma (gT)^2, = 2\alpha \times 10^{36}\, n\, V\, r^2 E^2\, (g\beta)^2$,

where δN, α,S_p, T and E are number of detected ion, transport efficiency of ions to the detector, cross-section of laser light, pulse duration of laser light, and laser power / shot, that is, IT. One of the MMS parameters r is the loss rate of laser power including the mirror loss and absorption by the gas during traveling in MMS, and so rE means the average power of the laser beam during the time. The other MMS parameters g and β, are expressed by irradiation prolongation factor: $g = \delta t / T = 2LM / cT + 1$ where M is the number of mirrors placed on one side of the disc. The multiple folding factor $\beta = cT / 2L$ where cT means the pulse length of laser light and 2L does the twice distance between mirrors in the MMS, respectively. In the 2-photon ionization cross-section: σ becomes $\sigma^* \sigma^+$, and the irradiation duration δt can be replaced by $2LM / c + T$. Here we can define the enhancement factor of MMS: $(g\beta)^2$ on the 2-photon resonance ionization.

Briefly summarizing MMS effects from above consideration, the number of detected ions δN is proportioned to n, V, $(g\beta E)^2$, and r^2. About photon efficiency, the factor $(rg\beta E)^2$ is important for MMS consideration.

Three beneficial effects on RIMMPA can be picked up as follows: One is the prolongation ratio g of the irradiation time, that is, staying time of laser light in MMS (long time irradiation effect). The other is the folding factor β (multiply irradiation effect) which is the ratio of laser-light length to the round-trip distance 2L. In our present device, we adopt the parameters of the first column in Table 1 and β = 2 means that photon density is doubled. The other is the volume controllability, V, of the interaction space (volume effect) and lastly the power re-circulation effect as illustrated in Fig. 1. The enhancement factor $(g\beta)^2$ which couples the benefits of long time irradiation effect and multiply irradiation effect mentioned above, are listed in Table 1 where we calculate the parameters in the cases of various L (the distance between mirrors) and M (mirrors number placed on each disc) under the condition of the laser pulse length 180 cm (6ns).

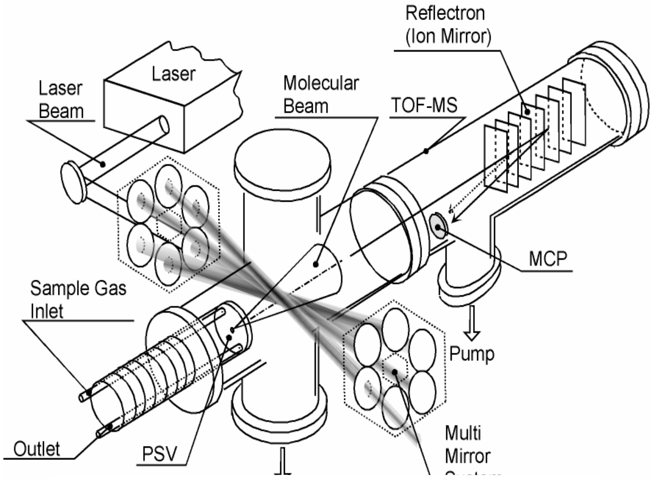


Fig. 2 Conceptual drawing of RIMMPA

Outline of the proof of principle experiment

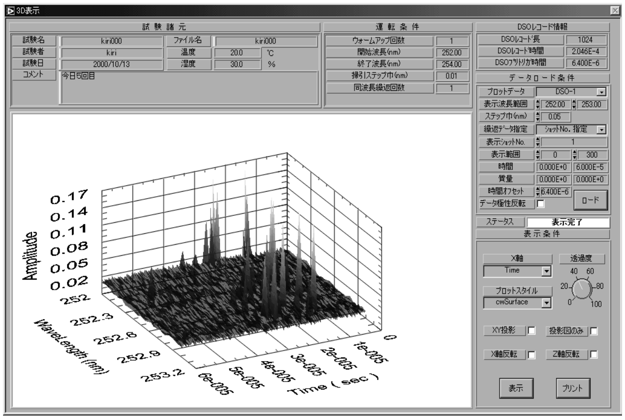
The concept of RIMMPA device is illustrated in Fig. 2. The sample gas of Benzene seeded in N_2, which is calibrated with GC/MS beforehand and diluted down to a certain density with He gas, is prepared in the sample gas supplier. It includes PSV, the dilution chamber, the connecting pipes and a kind of gas circulator. The sample gas supplier is baked up uniformly to 100^o C. By providing a circulator and the baking, the gas flows constantly, avoiding local condensation of Benzene. By this method, the reproducible and steady condensation of measurements is obtained in the experiment.

The sample gas is injected into the evacuated MMS chamber by activating the fast pulse valve PSV (opening duration: about 50μs) and in the space interacting with laser light, that is, in the central part of MMS chamber.

The injected gas is cooled down to a few degree in absolute temperature by adiabatic expansion flow out of the nozzle of PSV and is ready to be selectively soft-ionized in the multi-photon resonance excitation / ionization process. And then, laser light is injected and stored in the MMS. A tunable laser (Nd:YAG+OPO) is used and of which the specifications are: The tunable range is 250 nm to 300 nm, 1 to 10 mJ, 10Hz and 6 ns duration. Only particular molecules are selected and ionized due to the specific resonance character of the molecular structure by the laser wave-length, and the ionized molecules are brought over into the time of flight mass spectrometer (TOF/MS: Reflectron and the resolution 1500) by the electric charge of ions. The ionization efficiency is enhanced by use of

MMS as mentioned above.

The cooling effect of gas is checked first of all by changing the PSV position and by looking for the optimum position, where the signal intensity is at the maximum in the neighborhood. TOF analyses the mass spectra by the fact that the mass difference causes the different arrival time on the detector (micro-channel plate: MCP) from the ion source. Thereby, by scanning the wavelength of the tuning laser, RIMMPA gives rise to the two-dimensional spectra of molecular structure and mass. An example of the experimental data is shown in Fig. 3: It represents three dimensional on-line spectrum data about the wavelength (252 to 253.2 nm) and the mass (flight time: 0 to 60 μsec). Before the experiment, however, plenty of the basic data had to be obtained, such as the sensitivity dependency of MCP on the applied voltage, the output signal dependency on the laser power, the wavelength, and the signal to noise ratio S/N.



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プロットスタイル cwSurface
透過度 0 20 40 60 80 100
XY投影 ☐
投影図のみ ☐
X軸反転 ☐
Z軸反転 ☐

Fig.3 Three dimensional graph of TOF mass spectrum by scanning the wave-length of laser light

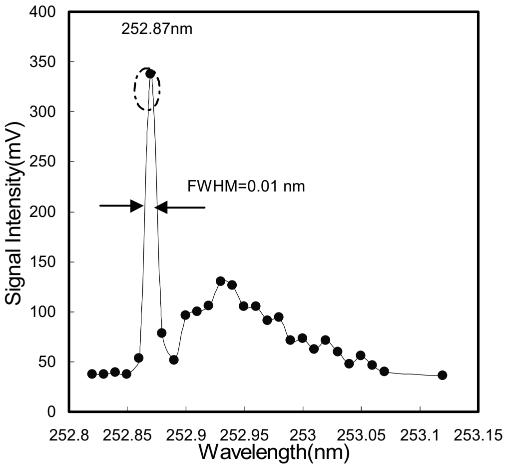

Fig.4 Tuning curve for Benzene ionization

The signal intensity of detected ions shows experimentally to depend on the square of the laser power that suggests the two-2 photon resonance ionization scheme. Figure 4 shows the resonance ionization of Benzene at 252.87 nm and the half width of the spectrum is less than 0.01 nm. This fact means also that the sharp resonance ionization occurs at the cooled gas of a few degree in absolute temperature. The cooling effect by the jet action is also confirmed experimentally by getting the signal intensity of the detected ions as a function of PSV position, that is, the distance between PSV and the interaction space. Optimum position of PSV is around the transition region from the continuum flow to the molecular one of the injected gas as reported in reference[1)]. The optimum position of PSV is experimentally determined so that molecular beam may intersect with the laser light at the best condition. The best position of PSV is less than 28mm in this experiment. However it is impossible for PSV to approach nearer, because it interferes with one of the extraction electrodes of TOF/ MS.

MMS benefits are proven as follows: The enhancement factor of MMS is studied experimentally by changing the number of mirrors M, that is, g and β, by masking the laser light in front of mirrors and increasing the laser power E. We can change $(g\beta)$ from 1 to 10 and E from 1 mJ to 5 mJ. Totally we can change the parameter $(g\beta E)$ from 1 to 50 as shown in Fig. 5. The signal intensity changes from 0.3 to 300 at signal intensity within this parameter range. These result shows that the signal intensity in case of 8 mirrors and 5 mJ, is 1000 times larger than the case of one pass and 1 mJ (Jet-REMPI case). In other words, in the case of present RIMMPA, $\beta = 2$ and $M = 8$ and $E = 5$ mJ (the laser power /pulse is 5 times larger than that of Jet-REMPI) are used and then the signal intensity is obtained 1000 times larger in this MMS effects. From this data, we can deduce that the enhancement factor of MMS is 100 and r^2 is 0.4.

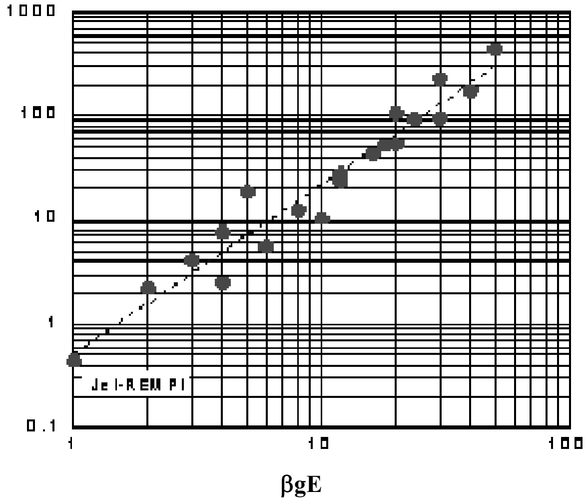

Fig. 5 MMS effect: Comparison of signal intensity of sigle pass & 1mJ with 8 passes & 5 mJ. Signal intensity of 1000 times larger is obtained.

From this data, we can report that RIMMPA has the exceeding performance on the efficiency of the laser irradiation by use of the MMS for the multi-photon resonance ionization. That is, the signal amplification is obtained up to about 1000 times higher than that of the 1 pass and 1 mJ case (Jet-REMPI) which has so far shown the best performance in the world, though in the former, the laser power is 5 times larger than the latter. The enhancement factor of photon density $(g\beta)^2$ becomes to 100 as calculated in the previous session and $(Erg\beta)^2$ becomes more than about 1000 in comparison with that of one pass case of Jet-PEMPI.

The controllability of the volume of interaction space is one of the RIMMPA's features. In the RIMMPA, as the cross-section area of laser light is controllable, the volume of interaction space V is also controllable by changing the distance between the optical expander lens. The figure 6 indicates the tendency between the volume and the signal intensity: The irradiation volume becomes larger, the larger signal intensity is obtained. If we obtain the extra photon density or extra ionization probability by this highly enhanced factor of MMS effect, it is also useful efficiently to extend the volume V of interaction space keeping the photon density less than the critical one which means the value of 100 % ionization probability.

The result and discussion

The sample gas of Benzene diluted by He was used as the test gas in the experiment and the MMS effects was studied. We got the results that MMS effects can intensify the signal intensity up to three orders of magnitude though laser power was used 5 times larger than 1 mJ. In other word, MMS is useful to make a powerful intense ion source. Though we have succeeded to get the high signal intensity with MMS effects, it does not mean that the uppermost detection ability is obtained. It is because the noise by non-resonance ionization becomes larger according to the rich photon density by photon-efficient use of MMS and the signal to noise ratio becomes worse. In this experiment, large non-resonantly ionized N_2^+ disturbs the detected signal. It may be owe to the structure of extraction electrodes of our TOF/MS (parallel plates), where the particle-induced noise can not be avoidable. In order to make the S/N ratio larger, we should use noiseless new extraction electrodes such as one reported in Reference1).

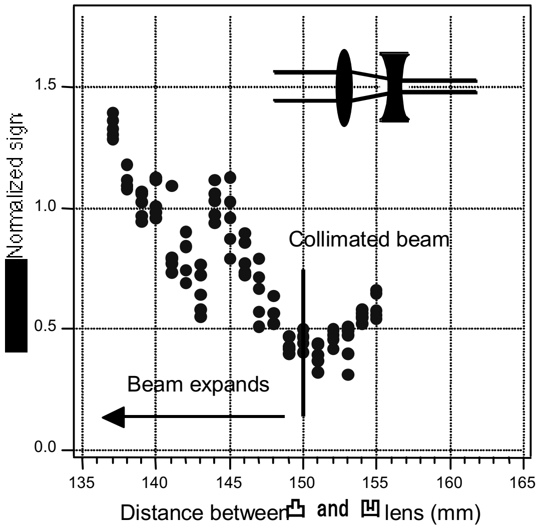

Fig. 6 Signal intensity vs. the cross-section area of laser beam

The detectable sensitivity limit is pursuit. Figure 7 represents the proportionality between the signal intensity and the dilution degree or concentration. The detectable limit is about 1ppt as far as we can study and measure in the experiment using our sample gas supplier. We could not produce the sample gas ensuring the exact concentration. Moreover we could not produce the concentration below 1 ppt because the dilution gas He included itself the Benzene about 1ppt or so.

We tried the various methods and processes of the dilution and endeavored to develop the better performance of the gas intake device. The gas circulation circuit and the uniform baking to 100 degree C, were provided so that the exactly diluted sample gas could be produced and the reproducible data might be obtained. We tried the purification of He gas and application of Argon gas but both the trials were not successful. In conclusion, we could decide that the producible and steady data might be the real value of the ultratrace concentration.

The proof of principle of experiment was successfully carried out for not only the enhancement factor but also the volume effect, which was suggested in the Fig. 6. Increasing the cross-section of laser beam, the signal intensity increases proportionally according to enlargement of irradiation volume. This means the possibility of getting the higher sensitivity. MMS effects can locally produce over-irradiated volume where the calculated ionization probability becomes over 100 %.. By increasing the cross-section of laser light beam that is, flattening the ionization probability under 100%, we can produce the large irradiation volume of appropriate photon density up to the allowable resolution limit of the mass analyzer. This effect may be indispensable for the detection of the ultratraces because of the extremely low density of the seeded molecules.

In conclusion, the experimental results using Benzene show the prominent efficiency of the MMS. The signal intensity is proportional with the square of power density and enhancement factor, and the irradiated volume. RIMMPA utilizes multi-irradiation effect of MMS and so the sensitivity grows up extremely in comparison with one pass ionization.

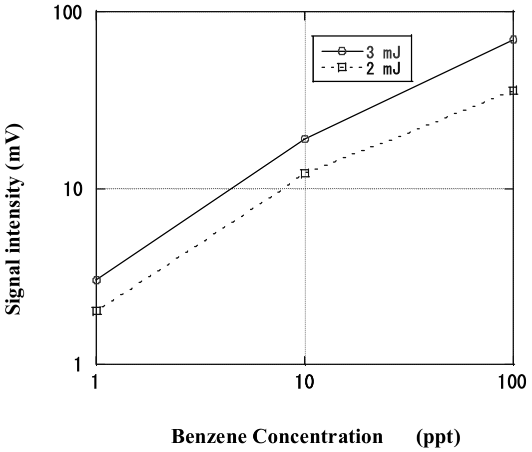

Fig.7 The minimum detectable ability of RIMMPA

We have built a new laboratory to be able to treat toxic material and will expand the kind of sample gas to PCB, Dioxin and so on. At the same time, a new small and robust laser for 2-color resonance ionization and new extraction electrodes of TOF/MS, which includes the DLR type, should be studied and developed.

Acknowledgement

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