Rapid analysis of trace pollutants using laser mass spectrometry

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Abstract Organic pollution has been gaining more and more attention. Yet, at present the determination of virtually all of them, including polycyclic aromatic carbons (PAHs), the largest single class of chemical carcinogens known today, is made via pre-purification and pre-concentration. The major problems are complexity and time-consuming, thus, no ideal real-time on-line monitoring can be done. Laser mass spectrometry combines UV spectroscopy and time-of-flight mass spectrometry (TOF-MS) through resonance-enhanced multiphoton ionization (REMPI). It is characteristic of high sensitivity, high selectivity and rapidity. In this paper, after its principles, a small mobile laser mass spectrometer, in which a mini-excimer (KrF, 248 nm) laser was used, is introduced. Real-time analysis of vehicle exhaust gas was made using this instrument, and the results showed some advantages over traditional methods: multicomponent detection, including benzene, toluene, xylene, C2-benzene, naphthalene, and methyl-naphthalene; high sensitivity (100 ppb); high time-resolution (0.1 s); and no need for pre-purification or pre-concentration of samples.

Keywords: laser mass spectrometry, pollutant detection, aromatic hydrocarbons, REMPI, TOF-MS.

In order to reduce pollution, attention has been paid to developing efficient methods to clean up exhausted gases or to deal with the remaining residues. The ideal pollutants monitoring method, also the prerequisites for development of new low emission devices through optimizing processes by primary pollutants monitoring, is the reliable real-time analytical techniques. Such techniques are significant for reducing pollution and for increasing technical benefits.

Polycyclic aromatic carbons (PAHs) are the largest single class of chemical carcinogens known today. The organic pollutants from burning of woods and fossil fuels that are harmful to human health are mainly due to them. At present, virtually all PAHs determinations are made via the "pre-concentration" method. In this approach, gases bearing PAHs first pass through a variety of organic adsorbents for long enough time, so that enough PAHs are adsorbed. The PAHs captured are then extracted using suitable solvents and are detected using gas chromatography/mass spectrometry or liquid chromatography/fluorescence. The major problems for such analytical processes are complexity and time-consuming. "Pre-concentration" of samples makes real-time monitoring impossible and leads to considerable uncertainties.

One of the promising methods for trace pollutants analysis is resonant laser mass spectrometry. It is a two-dimensional analysis method, including UV spectroscopy and TOF mass...
spectrometry. It combines selectivity, sensitivity and rapidity of measurement.

The fourth harmonic radiation from a Nd:YAG laser (266 nm) has been used to detect pollutants in vehicle exhaust gases in our laboratory. In this paper, a newly built mobile laser mass spectrometer will be introduced. This new instrument can be moved to make in situ analysis, and in addition, equipped with fast sampling and inlet apparatus, it can make real-time measurements that could not been done before.

1 Principle of laser mass spectrometry

Laser mass spectrometry is the combination of two different analytical approaches: UV spectroscopy and TOF mass spectrometry. The link is REMPI.

For different molecular species, their electronic transition absorption bands spread over a wide range of wavelengths from vacuum-UV (< 190 nm) to the visible (> 450 nm). For a general introduction to analytical UV spectroscopy, see ref. [11]. For benzene molecules, one-electron transitions from the highest filled molecular orbital (1e_{1g}) to the lowest empty molecular orbital (1a_{2u}) lead to three excited singlet states \( S_1(1B_{2u}) \), \( S_2(1B_{1u}) \) and \( S_3(1E_{1u}) \), which have been located in the vicinities of 40000, 48000 and 57000 cm^{-1} [12]. The transition from ground state to \( S_1(1B_{2u}-1A_{1g}) \) is electronically forbidden, and only can occur through electron-vibration interaction. Its 0-0 band is at 38089 cm^{-1} [13]. Above the three valence states are Rydberg series. The effects of alkyl groups on the benzene spectrum are not large, so that in almost every case, the pattern of \( S_1(1B_{2u}) \), \( S_2(1B_{1u}) \) and \( S_3(1E_{1u}) \) valence shell states followed by Rydberg transitions can be readily discerned [12]. In general, the effects of added alkyl groups are to shift the benzene bands to lower frequencies, and to broaden the bands.

In laser mass spectrometry, REMPI is the link between UV spectroscopy and mass spectrometry. The characteristic processes of REMPI are that: molecules firstly absorb m-photon energy to their intermediate excited states, then the excited molecules further absorb another n-photon energy and get ionized. Thus, the selective UV-excitation of the first absorption step is transferred to a selective resonant ionization. In laser mass spectrometry, \((1 + 1)\) REMPI is usually used. This is the most efficient multiphoton ionization way, with the ionizing efficiency up to 20% [14]. In addition, it may avoid molecular fragmentation due to further photon absorption of parent molecular ions in a highly intensive laser spot that is necessary for higher order multiphoton processes [15]. Using a KrF excimer laser (248 nm, one photon energy 40322 cm^{-1}), aromatic hydrocarbons may be ionized through \((1 + 1)\) REMPI process with \( S_1 \) being the intermediate state [14]. “Soft ionization” may be realized because the surplus energy may not lead to molecular fragmentation. Even so, laser intensity should be controlled in case a strong laser intensity may cause further radiation absorption and fragmentation of molecular ions. The ideal light sources are wavelength tunable lasers, as a fixed wavelength laser cannot excite different molecular species, neither can it excite a molecule at its strongest absorption peak and thus to reach highest detection limit. Yet, at present, only fixed wavelength lasers work stably after long transportation and for in situ detection under poor circumstances of pollution sources.

TOF-MS is one of the simplest ways to perform mass analysis. The main advantages of TOF-MS is its high speed and its high ion transmission efficiency. For every single laser pulse a total mass spectrum is obtained. With repetition rates of the ionization process of 100 Hz (limited by the pulsed laser specifications), time resolution of 10 ms would be achieved. Pulsed lasers are an