Resonance-Enhanced Multiphoton Ionization Mass Spectrometry (REMPI-MS): Applications for Process Analysis

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Annu. Rev. Anal. Chem. 2014. 7:361–81

The *Annual Review of Analytical Chemistry* is online at anchem.annualreviews.org

This article's doi:
10.1146/annurev-anchem-062012-092648

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Keywords

photoionization, time-of-flight mass spectrometry, lasers, combustion, online analysis, exhaust gas

Abstract

Process analysis is an emerging discipline in analytical sciences that poses special requirements on analytical techniques, especially when conducted in an online manner. Mass spectrometric methods seem exceedingly suitable for this task, particularly if a soft ionization method is applied. Resonance-enhanced multiphoton ionization (REMPI) in combination with time-of-flight mass spectrometry (TOFMS) provides a selective and sensitive means for monitoring (poly)aromatic compounds in process flows. The properties of REMPI and various variations of the ionization process are presented. The potential of REMPI for process analysis is highlighted with several examples, and drawbacks of the method are also noted. Applications of REMPI-TOFMS for the detection and monitoring of aromatic species in a large variety of combustion processes comprising flames, vehicle exhaust, and incinerators are discussed. New trends in technical development and combination with other analytical methods are brought forward.

1. PROCESS ANALYSIS

Process analysis as an autonomous discipline in analytical sciences has attracted growing interest in recent years (1–3). The term process analysis, often used to describe the multiplicity of all actions and measures to control industrial processes, comprises a variety of different concepts. Hence, it includes the measurement of species concentrations for monitoring purposes and the utilization of this information for controlling, regulating, and steering a process. In more recent years, terms such as knowledge-based systems, smart systems, fuzzy logic, sensors, neuronal nets, and even artificial intelligence are drawn on to describe measures for process analysis and control. As a matter of course, this transcends the mere conception and execution of an analytical method to determine concentration values of key components in a process; it broadens to the concept of a comprehensive measurement and control system, utilizing conventional analytical chemistry as well as modern microsystem technology. The overall purpose may be twofold: On the one hand, the acquired information could be utilized to detect and correct errors in the production process (feedback approach), if for example it is realized that the contents of some intermediate or product species are deviating from the norm values. On the other hand, one can also opt for the frequently desired alternative approach, the so-called feedforward procedure (4). Here, correcting measures are taken before problems, and perturbances arise by detecting small deviations from normality and with this information predicting dysfunctions beforehand. This requires a deepened knowledge about the process and the behavior of its parameters.

Process analysis, however, is not restricted to the detection and prevention of disruptions in the production procedures but can also be applied for quality control. This is indeed its main application area at the moment. For instance, in a chemical production process, this could mean the monitoring of the yield and the verification of the purity of a desired product. In a power plant or combustion facility for energy and heat generation, the focus would be on the optimized energy output or the prevention of inefficiency during the energy-generating process. In biotechnology, information about cell activity and morphology in conjunction with external parameters such as temperature, pressure, and oxygen content is of importance to ensure a satisfying conversion. The latter example illustrates that often more than one parameter or measured variable is needed to reach the desired result. This encompasses pure process parameters such as temperature as well as chemical analysis of feedstock, intermediate, or product species. For this, sensor arrays could be employed to gather as much simultaneous information as possible. An inevitable drawback of the much diverse information is the ever increasing data analysis capacity that has to be provided. Moreover, data evaluation and the derived information, with which the process or quality control will be achieved, rely heavily on statistical treatment. This means that complex analytical information is gathered, which often requires an even more complex chemometrical evaluation or data mining. Several different methods have been developed in this field, for example, principal component analysis, cluster analysis, and other multivariate data analysis tools. However, a more intense discussion of this aspect would go beyond the scope of this review.

2. ANALYTICAL CHEMISTRY FOR PROCESS AND QUALITY CONTROL

Irrespective of the ultimate purpose and goals of process analytical procedures, the analytical method itself provides the initial basis for all subsequent steps. The information obtained from analytical data helps to control and steer production processes and ensures product quality. For this, several prerequisites have to be met by the analytical method. On the one hand, the measurement has to be representative of the procedure and it must be reliable with respect to precision and accuracy, including when carried out under field conditions; that is, the measurement will almost always be conducted in a rough industrial environment. On the other hand, one factor is often of even greater importance. The results of the analytical process should be available in as short a time as possible. It is often crucial, for process and quality control as well as steering, to learn about problems quickly and to take countermeasures in sufficient time.

However, to meet especially this latter requirement it is not mandatory that the analytical measurement is conducted in real time or even continuously. It may be sufficient to take samples from a product flow and subsequently investigate them in the laboratory. As a matter of fact, an across-the-board system of rules for carrying out process analysis is not feasible. It depends too much on the individual characteristics of a process and the definite goals one wants to achieve with the process analysis step. Despite this, a method usually is more in demand the more closely to the actual process it can be operated. Roughly, process analytical methods can be classified in four different groups depending on their manner of performance and their closeness to the process. These groups are labeled as offline, atline, inline, and online analysis, in ascending order of their closeness to the process.

Offline analysis includes instrumental analysis of samples after their transport to the laboratory. The inherent drawback of this type of process analysis is that it is time consuming and does not allow direct reactions or process control changing steps. Moreover, the process has to be considered exceptionally good to devise a time scheme for taking each sample. However, offline analyses are relatively inexpensive, and there is no need for robust and rugged equipment onsite.

Atline analyses fall somewhere between offline and online techniques. They still preserve the character of offline methods in that samples are taken discontinuously. However, the subsequent analytical investigation takes place in the immediate vicinity of the process flow and the sampling position. Hence, the response time is faster compared to offline methods; however, more specialized equipment is needed, which in addition has to be more robust.

In contrast to these two briefly described process analysis types, online methods provide continuous monitoring of a process. The preferential targets thereby are those parameters or chemical species that change, and variations throughout the process are the most significant with respect to dysfunctions of the process or impairment of product quality. The faster the measurement signal can be obtained and the information transmitted to a central data station, the better an analytical method is suited as an online process control detector. As a matter of course, the drawbacks of online methods, unlike offline methods, are the requirements for frequently expensive and robust measurement devices to perform an adequate process analysis.

Before moving on to specific analytical techniques applied under the generic term online process analysis, the fourth type of process analysis should be addressed. Inline analysis can be regarded as a special subspecies of online methods. Whereas conducting an online analysis invariably requires some kind of sampling train, either directly from the flow or by utilizing a bypass, inline analysis takes place inside the process flow with no sidelining installed. Hence, all sources of error caused by the sampling train are avoided. However, there is no possibility to preprocess the analytes by, for example, filtering, which often enhances the quality of the online analyses. All variations taking place in the product flow are captured by the measurement probe, even those that may interfere with the desired measurement. To offset these detriments, the demands for statistical evaluation and chemometry are sometimes considerably higher for inline process analysis. One way to overcome this problem would be to use a measurement application, which requires no direct contact with the process flow (noninvasive analysis). As a matter of course, this would also reduce the number of possible analytical methods to be implemented, given that techniques such as chromatography, mass spectrometry, and most spectroscopic methods cannot be inserted into the product flow.

3. METHODS FOR ONLINE PROCESS ANALYSIS

Spectroscopic methods still comprise the majority of online techniques applied in process analysis due to their cost efficiency and ruggedness (4, 5). There are many subspecies of spectroscopic measurement methods, namely ultraviolet/visible spectroscopy and infrared spectroscopy (6), which itself may be subdivided into several types such as near-infrared spectroscopy, Raman spectroscopy (5, 7–9), and fluorescence spectroscopy (10). Even nuclear magnetic resonance spectroscopy can be utilized in a real-time manner (11, 12).

Chromatography, a versatile analytical technique advantageous in that it is a separation method, also seems a logical choice for process analysis. However, one would consider chromatography primarily as an offline method. Nevertheless, process gas chromatography (GC) and process liquid chromatography have been applied as online tools (13–15). For this, separation time has to be minimized while guaranteeing a sufficient resolution. This is helped by reducing the number of target compounds to be separated (which is often small anyway) with the use of short capillaries with optimized separation power for the specified target species. With liquid chromatography, ultrahigh performance liquid chromatography provides short analysis times without losing resolution.

Given its very nature, mass spectrometry would seem a natural choice for an online process analysis method. Therefore, the crucial factor is the sampling from the product flow, normally at atmospheric pressure, to the vacuum of the ion source of the mass spectrometer without losing any information on the way; that is, the incoming sample should properly reflect the proportions at the sampling point. The second important factor to be considered is the means of ionization.

The classical method of ionization in mass spectrometry is electron ionization (EI), which is indeed also applied in online measurements (16, 17). Ionization involves electrons (normally with energies of 70 eV). The advantage of EI is its high stability and easy application. In addition, interpretation of obtained mass spectra is aided by an extensive spectra library. However, EI is a hard ionization method, causing intense fragmentation of the ionized molecules. This may lead to serious problems for the monitoring of process gases containing hundreds of species.

Another widely employed method is chemical ionization (CI) (16, 17), wherein a primary ion acting as reagent gas ionizes analyte molecules by means of charge or proton transfer. The latter is known as proton-transfer-reaction mass spectrometry (PTR-MS) (18–21). Ionization is carried out by primary ions derived from water or ammonia such as H_3O^+ or NH_4^+. PTR-MS exhibits certain selectivity in the shape of their proton affinity. Combined with time-of-flight mass spectrometry (TOFMS), PTR-MS is a sensitive method with limits of detection down to the parts-per-trillion level. CI is in most cases a soft ionization method leading to less fragmentation. Ionization may also take place under atmospheric conditions (atmospheric pressure chemical ionization) (22–24).

Photoionization techniques compose a further group of soft ionization methods. Ionization is carried out by absorption of one or more photons, in most cases UV or vacuum-UV photons. The softness of photoionization is a result of the energy of the irradiating photons being similar to the ionization energies of most molecules (5–12 eV). As a consequence, only a small amount of excess energy is transmitted to the molecules. Therefore, the application of photoionization is especially advantageous for the investigation of even complex process flow mixtures, as it maintains high sensitivity and in some cases also high selectivity.

One photoionization method with increasing employment in process analysis is single-photon ionization (SPI) with vacuum-UV photons. SPI exhibits threshold selectivity in that all molecules with ionization energies below the photon energy are ionized, in principle regardless of their chemical structure. Bulk gases such as nitrogen, oxygen, water, or carbon dioxide are not ionized, because the applied photons are between 8.4 and 10.5 eV, i.e., below their respective ionization energies. This facilitates the monitoring of selected target compounds in process flows due to the lack of interfering strong signals from these bulk gases. Several applications are reported, whereby vacuum-UV radiation is generated by either lasers (25–29) or compact rare gas excimer lamps (30–32).

4. RESONANCE-ENHANCED MULTIPHOTON IONIZATION

The REMPI ionization method is a unique soft photoionization technique, in that at least two photons have to be absorbed by a molecule to get ionized. Predominantly UV photons generated by a laser are applied for this purpose, categorizing REMPI as a subspecies of laser-based ionization methods. Utilizing absorption properties of molecules and taking advantage of resonant intermediate states provide aspects of UV spectroscopy within the REMPI process. As a matter of fact, the introduction of REMPI was primarily meant as a new tool for spectroscopic investigations and not as an ionization method for mass spectrometry (33, 34). However, it was not long before REMPI was combined with mass spectrometric devices. In these first studies of REMPI with mass spectrometry, fixed-frequency lasers were applied for the ionization of aromatic compounds (35), as well as tunable dye lasers that were tuned to a resonant transition of the benzene molecule (36, 37). Further fundamental studies followed in rapid succession to investigate numerous polyatomic molecules from various compound classes (38–45).

Figure 1 shows some basic ionization schemes for REMPI. One-color, two-photon REMPI (1 + 1 REMPI) is the applied ionization scheme in most cases (**Figure 1*a***). For this, ionization is carried out by subsequent absorption of two photons of the same wavelength. The first photon excites the molecule to a higher energetic transition state. If the lifetime of the transition state is sufficiently long, a second photon is absorbed and elevates the molecule above the ionization threshold. In addition to the lifetime of the excited state, it is important to provide a high photon density to enhance the probability of absorbing a second photon during the lifetime of the excited state. The latter prerequisite can be fulfilled by using lasers as beam sources. The first step provides the selectivity of the REMPI process, given that only those molecules can be ionized, which exhibits suitable transition states at a given wavelength. This is the reason why by utilizing UV photons, REMPI becomes substance class selective for (poly)aromatic compounds. Moreover, these spectroscopic properties of REMPI can also be exploited to further enhance selectivity. Because each molecule exhibits a characteristic UV spectrum with unique resonance frequencies, it is possible, by applying a distinct laser wavelength, to achieve the selective ionization of a single molecule. For this, a tunable laser is employed, the frequency of which is tuned such that only the desired molecule absorbs the photons, or the ionization efficiency of that molecule is considerably enhanced by going over the resonant state. This enables even the differentiation of various isomers, which could be interesting for those process analyses for which it is deemed important to know the concentration trend of one specified compound. Generally, this increase in ionization efficiency has the added advantage of better sensitivity, leading to lower limits of detection when the resonance enhancement is utilized.

However, 1 + 1 REMPI is not always possible as an ionization scheme. Sometimes, the transition state is at an unfavorably high energy for the available laser wavelengths (as is the case with aliphatic hydrocarbons or alcohols) and thus could be reached only by absorbing two or even three photons; ionization, subsequently, must be completed by absorbing an additional photon (2 + 1 and 3 + 1 REMPI, respectively; see **Figure 1*b*** for the 2 + 1 REMPI case). This requires high photon fluxes to ensure the absorption of all photons during the short lifetime of the transition state, thus causing more fragmentation compared to the very soft 1 + 1 scheme. Therefore, the schemes applying more than two photons may prove unsuitable for process analysis of a complex product mixture.

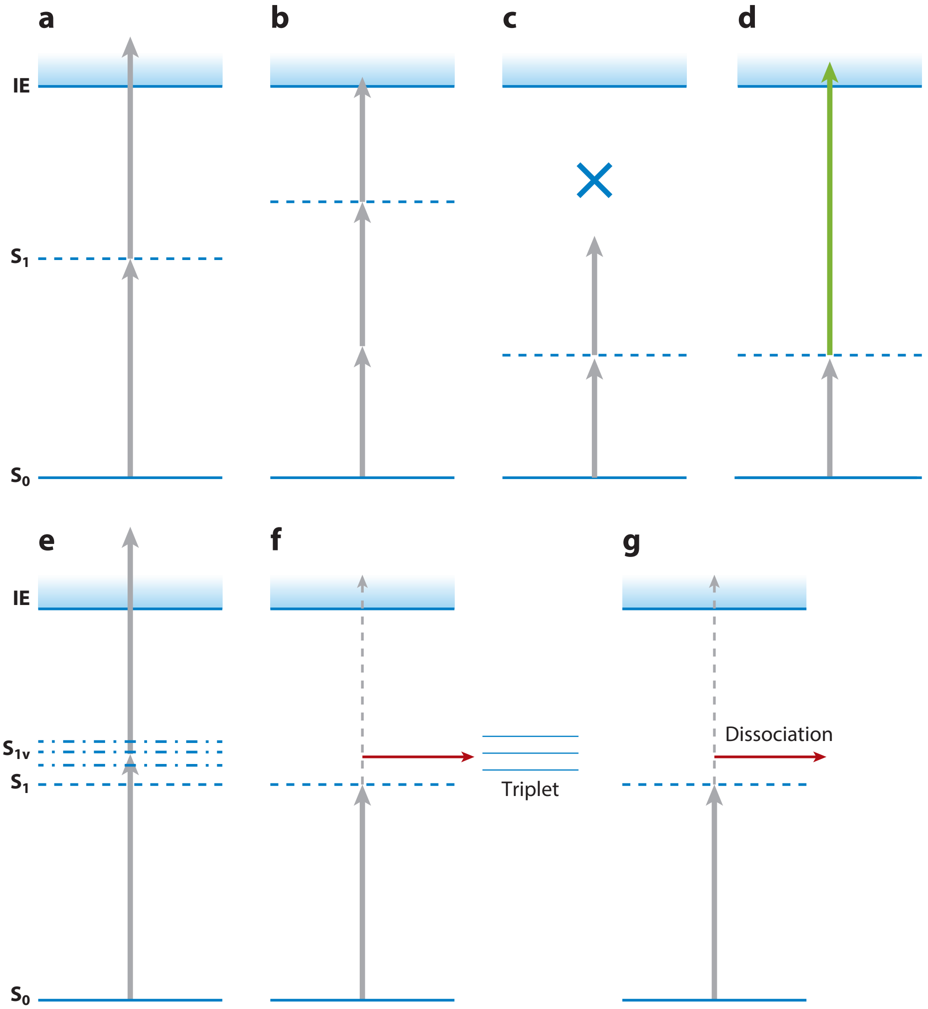

Figure 1

Schemes for ionization by resonance-enhanced multiphoton ionization (REMPI). (*a*) One-color, two-photon (1 + 1) REMPI, the variant applied in most process analyses. (*b*) 2 + 1 REMPI, where absorption of two photons is necessary to reach the intermediate state. (*c*) The combined energy of two photons is not sufficient to reach the ionization energy (IE). (*d*) Two-color, two-photon REMPI, where excitation and ionization steps are carried out with photons of different frequencies. (*e*) One-color, two photon (1 + 1) REMPI, where higher vibronic states of the excited electronic state are used as intermediates. (*f*) Depopulation of the intermediate state by intersystem crossing to a triplet state, which considerably reduces ionization efficiency. (*g*) Depopulation of the intermediate state by dissociation, which also considerably reduces ionization efficiency.

Another potential problem is that although a resonant transition state can be reached, the energies of two photons of the required frequency are not sufficient to complete ionization, and, as such, the ionization threshold cannot be reached (**Figure 1*c***). The application of a second laser with a higher frequency, a two-color, two-photon REMPI scheme, can circumvent this (**Figure 1*d***) (46).

Figure 1*e*–*g* shows more schemes depicting possible problems for the execution of REMPI. It may occur that an intermediate state is reached, but small Franck-Condon factors cause an inefficiency in the second ionization step (47). This can be overcome by addressing a suitable vibrational mode in the excited electronic state (labeled S_{1v} in **Figure 1*e***). As mentioned before, a further difficulty can arise if the transitional states are too short lived. Then the population of the intermediate state is depleted by fast relaxation processes before the second photon can be absorbed. Relaxation processes comprise intersystem crossing to a triplet state (**Figure 1*f***) and dissociation of the intermediate state (**Figure 1*g***). These processes may hinder the resonant ionization even on a nanosecond timescale, which is the most common in REMPI-MS applications. However, this drawback can be circumvented by carrying out the ionization on a shorter timescale. This is made possible by the application of commercially available pico- and femtosecond-pulsed lasers.

As such, the utilization of narrow and widely separated intermediate states to provide a high selectivity often requires the employment of relatively expensive tunable or short pulse laser devices. Another way to mitigate problems with REMPI schemes is the application of fixed-frequency lasers. This addresses in most cases broader, higher energetic transition states, and thus selectivity is reduced to a substance class one. However, if this is sufficient for the planned application, the utilization of REMPI may become less problematic. Typical examples are the wavelengths of 266 nm, provided by the fourth harmonic of an Nd:YAG laser, and excimer lasers such as the KrF laser (248 nm) and the ArF laser (193 nm). These frequencies enable a selective ionization of (poly)aromatic compounds.

As previously mentioned, sampling is a crucial part of process analysis. This is also the case for REMPI-MS applications. **Figure 2** depicts an exemplary scheme of a sampling train for online process gas analysis by means of REMPI utilizing time-of-flight mass spectrometry (TOFMS) as a detection unit for the generated ions. Heating throughout the entire setup, from the sampling location to the mass spectrometer inlet, is most important to prevent condensation of low volatile substances and the occurrence of cold spots, which could lead to memory effects. Because the transfer of gaseous analytes to the ion source of the mass spectrometer is conducted by a capillary (made out of quartz in this example, but other materials such as stainless steel are possible as well), a dust or particle filter is mandatory to prevent clogging.

In this respect, gas inlets to the ion source of the mass spectrometer, producing a molecular beam, are becoming important. One example is the effusive continuous molecular beam, which is formed by a thin metallic needle. Effusive inlets provide the target molecules at room temperature without cooling. Again, this is sufficient if the demand for selectivity is not set too high. Supersonic molecular beams (48–51), generated by even smaller nozzles and operating at higher pressures than atmospheric conditions, are another example. This leads to adiabatic cooling of the molecular beam and cleaner spectra due to the reduced population of electronic and vibronic states. The nozzles are often run in a pulsed manner, but continuously working supersonic beams have also been reported (52).

Because mostly pulsed lasers are used for REMPI, producing ions in a very short time, the best-suited mass analyzers for detecting the generated ions are reflectron time-of-flight mass spectrometers. The main advantage is that every ionizing pulse produces a complete mass spectrum due to the rapidity of TOFMS, which is in the microsecond scale. Therefore, the REMPI-TOFMS combination is well suited for online process analysis applications. A matter of discussion is the available mass resolution. Most applications utilize time-of-flight mass spectrometers with relatively low mass resolutions (2,000–5,000), because they are more rugged and compact as well as less expensive. However, this probably will change in the future as more compact high-resolution time-of-flight mass spectrometers become commercially available at reasonable prices.

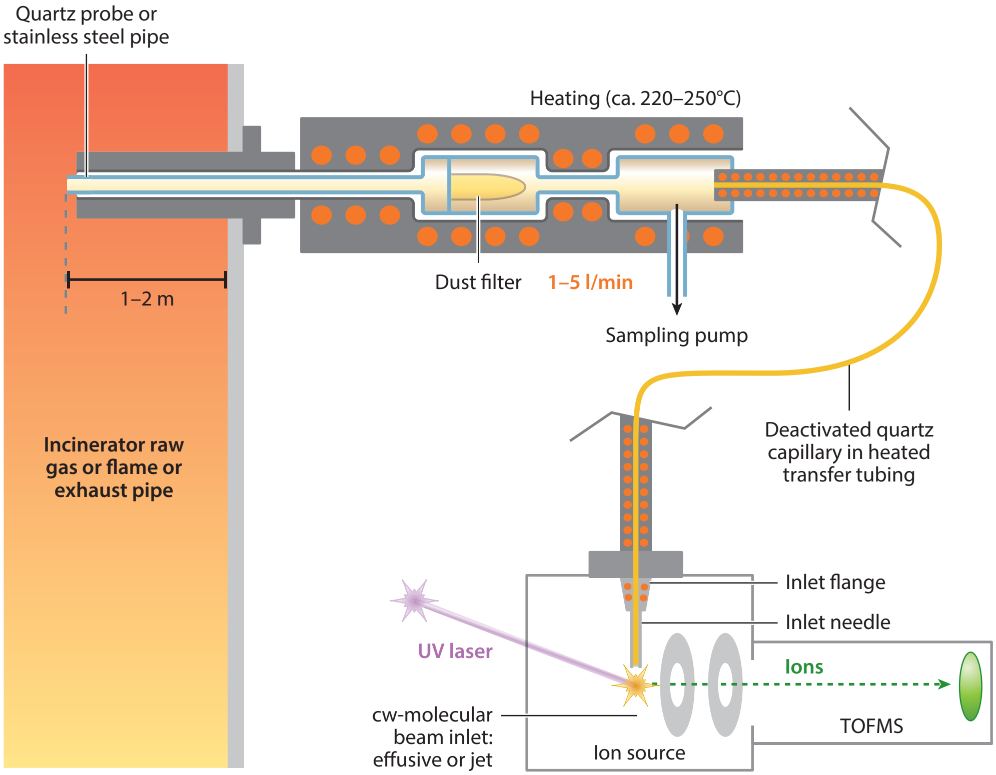

Figure 2

Exemplary sampling setup for monitoring process flows by means of resonance-enhanced multiphoton ionization-time-of-flight mass spectrometry (REMPI-TOFMS).

5. APPLICATION OF REMPI-TOFMS IN PROCESS ANALYSIS

Because the execution of REMPI with fixed-frequency lasers, in particular, is targeted primarily at the detection of (poly)aromatic compounds, applications of REMPI-TOFMS for process analysis in most cases deal with those processes that produce such species extensively. Among such processes, combustion and pyrolysis are predominant.

5.1. Flame Sampling

Model flames are investigated to gain fundamental knowledge about combustion processes and mechanisms and as such, can also serve as model systems for future process analysis in field studies on industrial combustion appliances. Thus, it is no surprise that early applications of REMPI-MS on combustion dealt with model flames. Ahrens et al. (53, 54) succeeded in analyzing very large (15-ring) polycyclic aromatic hydrocarbon (PAH) structures in flames and could extend their approach using REMPI-TOFMS with a tunable dye laser even to the detection of fullerenes. They made use of a mirror system reflecting the laser beam multiple times through the ionization volume. Some studies focused on improving calibration and emphasized sensitivity issues (55, 56), pushing the limit of the detection of naphthalene to 45 ppt in a co-flow diffusion flame with the use of a pulsed supersonic beam inlet (55). Other investigations focused on mechanistic study of PAH growth and soot formation in fuel-rich flames (57–59). Profiles of benzene and other aromatic species in ethanol-blended propene and cyclopentene flames measured by REMPI-TOFMS have been reported (60, 61). REMPI-MS studies of flames are not limited to PAH, however; there are several studies investigating other flame-generated species such as CH_3Cl (62), CH_3PO_2 (63), and dichloroethanol (64).

A promising new approach for flame diagnostics is coherent microwave Rayleigh scattering from multiphoton ionization, termed Radar REMPI (65, 66). Thereby, a tunable laser irradiating the resonance frequency of a target molecule is focused into the selected ionization volume, and REMPI plasma is generated in that volume. This plasma is analyzed by microwave scattering. Spatially resolved quantitative measurements of methyl radicals (66) and relative changes in NO concentration (65) could be carried out with this approach.

5.2. Vehicle Exhaust

Internal combustion engines constitute a major source of PAH and have a huge global impact on environment and health. Nevertheless, relatively few studies employing REMPI-TOFMS for online characterization of PAH emissions from vehicles have been conducted until recently. Boesl and coworkers (67–69) worked with a fixed-frequency Nd:YAG laser (266 nm) to monitor dynamic behavior of PAH emitted by a gasoline passenger car with a catalytic converter. They looked for changes in PAH patterns when the exhaust passes the catalytic converter and investigated the contribution of motor oil. Besides PAH, formaldehyde and acetaldehyde were also monitored, applying a tunable laser with a wavelength of 363 nm (70). Finally, the approach was extended to in-cylinder studies (71). Other studies using 266-nm photons (27) and 248-nm photons (72) for PAH monitoring of gasoline car exhaust have been reported as well.

Diesel exhaust is the other major matrix in this research field to be investigated by REMPI-TOFMS. For this, several studies utilizing a supersonic jet inlet to introduce the analytes to the mass spectrometer (73–77) have been conducted. Suzuki et al. (73) presented a new optical lens system combined with a new detector consisting of a conical lens and a Daly detector, which enabled them to move the nozzle of the jet closer to the ionization volume, resulting in an increase in sensitivity by a factor of 100 (73). Brian Gullett's group at the US Environmental Protection Agency applied their jet-REMPI system on various sources of diesel exhaust, i.e., diesel generators (74), a medium duty diesel engine (75), and aircraft ground equipment (77). **Figure 3**, taken from the latter study, depicts a typical 3D representation of an online monitoring of aromatic species, showing the trends of several compounds with time, and representing the respective signal intensities as well. As a beam source they utilized an Nd:YAG pumped optical parametric oscillator (OPO), which can be continuously tuned in a wavelength region between 240 and 350 nm. This allows adjustment to resonant states of selected compounds such as toluene to enhance their detection limits. Misawa et al. (76) applied the jet-REMPI method using a tunable dye laser tuned to resonant states of benzene, naphthalene, and phenol for investigation of the effects of the oxidation catalyst. The same group also worked with a fixed-frequency laser system (266 nm) to analyze PAH in truck exhaust (78). Adam et al. (79) conducted extensive investigations on various types of internal combustion engines, taking advantage of sophisticated dynamometer installations. In these studies, REMPI-TOFMS was combined with a large variety of other analytical techniques such as Fourier-transform infrared spectroscopy (FT-IR), proton-transfer-reaction mass spectrometry (PTR-MS), and aerosol mass spectrometry (AMS) to get a more comprehensive overview. REMPI-TOFMS was carried out with a 266-nm fourth-harmonic Nd:YAG laser with an effusive inlet. By

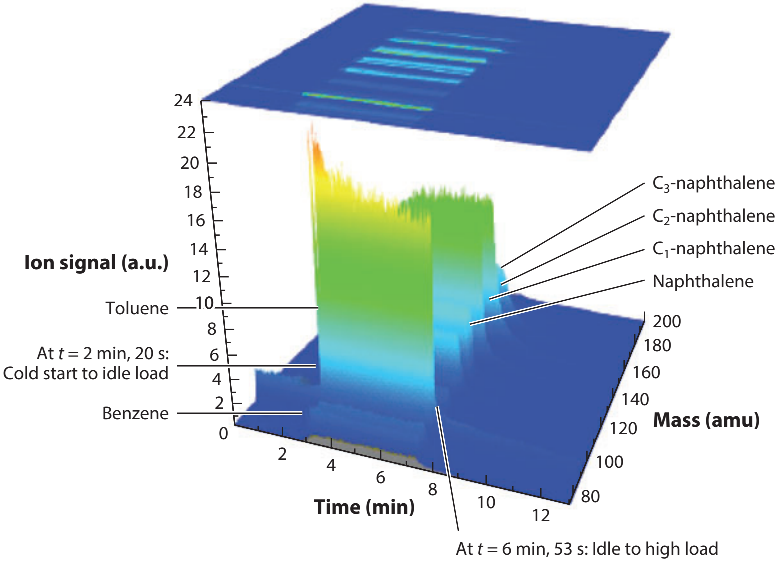

Figure 3

Monitoring of aromatic compounds in real time by means of Jet-REMPI-TOFMS at a wavelength of 267.5 nm, which is optimal for the detection of toluene, in the exhaust of a turbine engine compressor. Abbreviations: REMPI-TOFMS, resonance-enhanced multiphoton ionization-time-of-flight mass spectrometry. Figure modified from Reference 77.

doing this, heavy-duty trucks (79), dual-fuel gasoline cars (80), two-stroke mopeds (81), as well as diesel passenger cars, vans, and a two-stroke string gas trimmer (82) have been investigated. In the latter study, a semiquantization of selected PAH was carried out by means of applying relative response signal intensities or relative ionization cross sections that had been determined in the laboratory.

In vehicle exhaust, PAH are not only emitted with the vapor phase, but also with the particulate phase. Larger, low-volatile PAH, especially, are found predominantly with the particulate matter. To detect PAH from particles, it is necessary to transfer them to the gas phase and subsequently ionize them. Deguchi & Tanaka (83) conceived a unique setup that involved sampling diesel exhaust in a chamber then guiding the particles into a differential mobility analyzer. The sized particles were subsequently heated, and the desorbed PAH were ionized by a 266-nm Nd:YAG laser. An online measurement of PAH from single particles sampled directly from the exhaust pipes of gasoline and diesel passenger cars was realized by Bente et al. (84). To desorb the particles, either a CO_2 laser (84, 85) or a thermal desorption unit (86) was applied, and PAH in the gas phase were ionized by a KrF excimer laser (248 nm), taking place in the same volume following a two-step desorption/ionization scheme. Sakamoto et al. (87) presented an interesting approach, as they sampled diesel exhaust particles on an indium surface. The particles were then irradiated by a Ga beam, and desorbed material was postionized by a tunable laser at a wavelength of 250 nm.

Nitric oxides make up another compound class exhibiting a huge impact on the environment, climate, and health. The standard analytical technique to measure these species is chemiluminescence; however, Bornschlegl et al. conceived of a unique ionization scheme based on REMPI to simultaneously detect NO and NO_2 in the exhaust gas of a diesel engine (88). It involves ionization at a wavelength of 230 nm, producing on the one hand narrow ion signals from NO, and on the other hand widely spaced ion peak pairs of NO fragments generated from NO_2, which can be distinguished.

5.3. Incinerators

Combustion processes on an industrial level are an additional source of air pollution and as such, one of the main sources of PAH emissions. In addition, the emission of polychlorinated dioxins and furans, in particular from municipal waste incinerators, has become an important issue. The concentration levels of dioxins in the exhaust gas of waste incinerators are extremely low; thus, direct detection of those compounds by REMPI-TOFMS is very difficult, especially given that dioxins and furans do not possess the spectroscopic properties favorable for ionization by REMPI. As a consequence, the feasibility of REMPI-TOFMS to detect surrogate compounds for dioxins became a big issue. Early work in this field was carried out by Cool and coworkers (89, 90) and Tanada et al. (91, 92), who selected seven potential dioxin surrogate compounds and investigated their spectroscopic properties to determine the optimal conditions for REMPI-TOFMS detection. Further basic research related to this was conducted by Oser et al. (93–96), who investigated the wavelength-dependent ionization of chlorinated toluenes, relying on the fundamental work of Tembreull et al. (97). For this, a jet-REMPI approach using a tunable dye laser as a beam source was devised. With this, they were able to determine the most suitable wavelengths for the sensitive detection of a large variety of chlorinated aromatic benzenes, phenols, and even some low chlorinated dioxins (98). They also sometimes used a two-color REMPI scheme, the second laser fixed at 266 nm.

Grotheer and coworkers (99–101) continued in this line of work applying jet-REMPI with a tunable OPO laser source. They also conducted extensive spectroscopic work on chlorinated aromatics and applied the obtained knowledge to monitoring the raw gas of a waste incinerator. By fine-tuning the laser system, they could distinguish between the three-ring PAH isomers phenanthrene and anthracene, although the peak wavelengths deviated by only one nanometer. They used deuterated benzene, which could also be distinguished from benzene by irradiating a different frequency, as a calibration standard.

Zimmermann et al. (102) also did extensive work on PAH monitoring in the flue gas of municipal waste incinerators. Employing an effusive inlet and a fixed-frequency laser (KrF excimer laser at 248 nm) (102) a large variety of (poly)aromatic compounds were detected and monitored in real time. The concept was broadened to include a tunable dye laser as well (103), utilizing the specific transition states for enhancing the ionization efficiency of selected compounds such as naphthalene. Other studies pushed the real-time limits of detection down to the parts-per-trillion level (104), investigated the dynamic behavior of PAH concentrations (103, 105–111), and introduced a continuous jet capillary inlet (52). Utilizing the resonant transition of monochlorobenzene, the online detection of this potential dioxin surrogate compound was carried out on the parts-per-trillion level (112). This is illustrated in **Figure 4**, where the effect of resonance-enhanced ionization is demonstrated by comparison with the mass spectrum recorded with a nonresonant wavelength of monochlorobenzene, which shows no signal at all. Finally, spectroscopic information on nitrogen-containing PAH was gathered and applied to the real-time detection of those compounds in incinerator flue gas (113, 114).

More recent work on dioxin surrogate compounds has been conducted at the EPA by Gullett et al. (115) on a hazardous waste fired boiler, verifying the findings on the appropriation of monochlorobenzene as a dioxin surrogate compound. An interesting near real-time approach consisted in the introduction of a fast GC/MS separation (5-minute duration) prior to the REMPI-TOFMS for the selective detection of chlorinated benzenes (116). Another potential

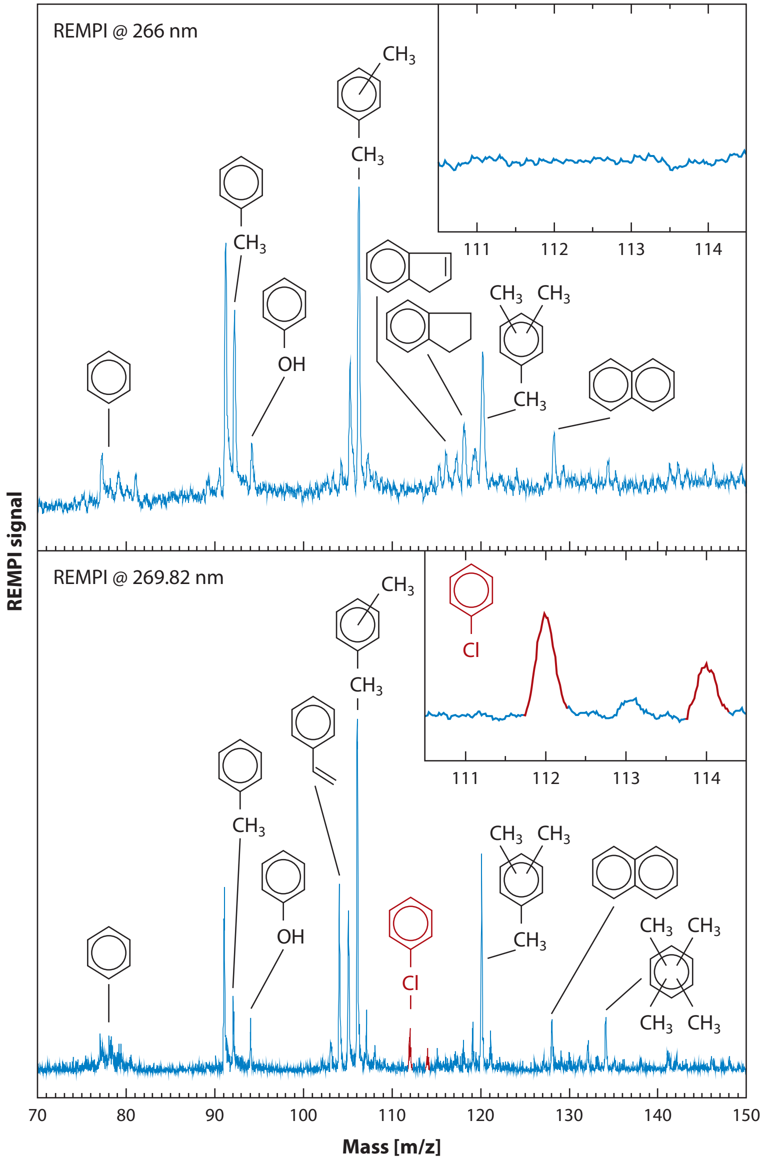

Figure 4

Online monitoring of aromatic compounds in the raw gas of a municipal waste incinerator by means of REMPI-TOFMS. (*Top*) A fixed-frequency laser is applied, showing an overview of the aromatic content. (*Bottom*) A wavelength of 269.82 nm is adjusted, which is the resonance frequency of an intermediate state of monochlorobenzene, thus considerably enhancing the ionization efficiency of this compound. Figure modified from Reference 112.

methodical variation of REMPI-TOFMS for dioxin surrogate compound measurements in the exhaust of chlorine-containing waste combustion is resonance ionization with multimirror photon accumulation (RIMMPA), which utilizes a multimirror system to reflect the laser beam back and forth throughout the ionization region (117, 118).

5.4. Method Development

Most REMPI-TOFMS methods that are applied for purposes of process analysis utilize a combination of tools in their experimental setup. Either an effusive or jet inlet is taken to introduce the gaseous samples directly to the mass spectrometer. Subsequent ionization is then carried out by nanosecond-pulsed fixed-frequency lasers (248 or 266 nm, as these wavelengths are conveniently available in the form of KrF excimers or fourth-harmonic Nd:YAG lasers). To take advantage of the enhancement of ionization by using the resonant transition states, tunable dye lasers and OPOs are employed, mostly Nd:YAG pumped. In this section, we review some alternative concepts and approaches for REMPI-TOFMS that could become interesting and valuable for process analysis in the future.

As previously mentioned, the resonant excited states of some molecules are very short lived, and ionization based on a nanosecond timescale thus is difficult and sometimes impossible. The accomplishment of the REMPI process on a shorter timescale, applying pico- and femtosecond-pulsed lasers, provides one solution. Early work on this was carried out in the 1990s (119–123). With shorter timescales than those of nanosecond-pulsed REMPI, there was an increase in ion signal intensity. This is attributed to a reduction in the rapid depletion of the population of the intermediate state due to intersystem crossing or other mechanisms. In particular, chlorinated aromatic compounds responded favorably to pico- and femtosecond REMPI. However, the high costs of such laser systems have thus far prevented their widespread employment in process analysis.

Recently, Imasaka and coworkers executed several studies of the utilization of pico- and femtosecond REMPI for the detection of persistent organic pollutants such as pesticides (124, 125), PAH (126), and even dioxins (127). Pico- and femtosecond REMPI resulted in a considerable increase in limits of detection. Fourth-harmonic Nd:YAG lasers and a third-harmonic Ti:Sapphire laser (267 nm) have been applied as beam sources. In their studies, they used another development for REMPI, i.e., the coupling to GC. The combination of GC with REMPI-TOFMS is distinct in that due to the softness of REMPI, a 2D separation according to chromatographic retention time and the mass-to-charge ratio can be realized. Irradiation of different wavelengths could further improve identification and selectivity of the analytical process. This hyphenation for the purpose of enhancing the detection efficiency for aromatic compounds such as alkylbenzenes had been reported earlier as well (128–131), and the combination with the supersonic jet inlet technique was also introduced (50, 132–136). However, from the viewpoint of process analysis, the additional step of chromatographic separation has to be executed relatively fast (reported retention times are on the order of ten to twenty minutes), which could be possible by the usage of short polar columns. As a consequence, it still may be a long way before such analytical appliances are established for the purposes of online process analysis. If process analysis is conducted in an off-line manner, however, the GC/REMPI-TOFMS coupling could show potential.

All reviewed applications of REMPI have in common that ionization is carried out in the vacuum of the ion source. Benter's group has reported extensively on the multiphoton ionization under atmospheric pressure conditions (APLI). This resulted in an increase of sensitivity by three orders of magnitude for NO, acetaldehyde, and chlorinated toluenes, to name a few such compounds (137). In the case of NO, a two-color scheme utilizing an excimer pumped dye laser has been developed, including the first excitation step at 215.36 nm and the second ionization step at 308 nm, providing a highly selective ionization of NO and NO_2 (138). APLI can be employed as a detection method for liquid (139) and GC (140, 141), the latter showing great potential as an ultrasensitive detection tool for PAH: Recent developments comprise the usage of a diode pumped Nd:YAG laser (142) and the introduction of dopants such as toluene, which after being photoionized serve as primary ions for further ionization processes of the target analytes (143).

Again, as for the femtosecond REMPI applications, the feasibility for online process analysis will have to be proven in the future, but for offline or atline applications, GC/LC-APLI constitutes a serious alternative.

Other methodical developments in the framework of the REMPI method that have been reported recently comprise circular dichroism mass spectrometry (144), where circular polarized light is utilized for ionization, thus enabling the enantiosensitive detection of chiral molecules, which is exemplified for carbonyls. A novel concept for online enrichment of species on the tip of the inlet capillary column, which involves desorption of the adsorbed analytes by an additional laser beam prior to ionization by REMPI, is demonstrated in Reference 145.

6. CONCLUSIONS

REMPI-TOFMS possesses some unique properties that make it very suitable for online process analysis of especially (poly)aromatic compounds. The very nature of the ionization process provides the necessary selectivity, which is valuable in complex product and process flows. The desired selectivity can be adjusted from a substance class one to the detection of a specific isomer. In addition, it reaches high sensitivities down to the parts-per-trillion level. The combination with time-of-flight mass spectrometry ensures the required rapidity for online applications.

PAH are one of the preferred classes of analytes for process analysis conducted by REMPI-TOFMS. They appear with every combustion incident and are crucial for the environment and climate. Moreover, among them are hazardous substances exhibiting acute health effects. PAH are relatively easy to monitor by means of REMPI-TOFMS, often requiring only compact and comparatively less expensive measurement equipment.

The extension of REMPI-TOFMS to the online detection of other substance classes requires in most cases a more complicated and sophisticated experimental setup but offers the monitoring of target species with high selectivity if needed. Naturally, the selective ionization could also be viewed as a drawback, if a more universal survey of compounds based on mass spectrometry is required in process analysis schemes. However, there are other photoionization techniques such as SPI and proton-transfer reaction mass spectrometry or other CI methods, which could be drawn upon, if REMPI could not provide the necessary result.

In the future, the utilization of high-resolution TOFMS could augment the effectivity of REMPI for process monitoring. Furthermore, hyphenation of REMPI-TOFMS with fast process chromatography could also further enhance the performance of the analysis. New laser sources could provide access to a more convenient detection of compounds, which are otherwise difficult to ionize. Technical improvement in the framework of REMPI-TOFMS is far from finished and leaves still room for new process analysis applications. This also incorporates specific demands arising from the investigation of other combustion appliances such as ship diesel engines, biomass burners, or food processing (e.g., coffee roasting) appliances. Internal combustion engines consuming fuel with increasing biocontent will also become more important, and studies dealing with process analysis of such systems will see publication in the near future.

DISCLOSURE STATEMENT

The Joint Mass Spectrometry Centre under supervision of Professor Ralf Zimmermann works in the field of REMPI-MS and has thereby received several grants (e.g., from the German National Science Foundation).

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Annual Review of
Analytical Chemistry

Volume 7, 2014

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