Development of Two-Step Laser Mass Spectrometry as a Competitive Analytical-Chemical Method

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Summary

Two-step laser mass spectrometry (L2MS) is an innovative technique for the direct analysis of selected compounds in complex mixtures such as environmental samples. In the first step, an infrared laser pulse desorbs intact neutral molecules from the sample surface, or ablates them from a solid matrix. In the second step, a pulse from a tunable ultraviolet laser is used for resonance-enhanced multiphoton ionization (1+1 REMPI) of the desorbed species; this soft ionization scheme prevents fragmentation of the analytes. Mass analysis is then performed in a reflectron time-of-flight mass spectrometer. The mass spectra are dominated by intact parent ions of those mixture components that strongly absorb the selected ultraviolet laser wavelength. Major advantages are the detection limit in the low attomole range and minimal need for sample preparation, therefore giving the possibility to measure large numbers of samples within short periods of time.

In an initial characterization stage, the potential capabilities offered by L2MS for both quantitative and qualitative measurements were assessed. A new fast and convenient sample preparation procedure was developed that allows an accurate and reproducible control over the amount of analytes desorbed by each laser pulse. Quantitative L2MS measurements were demonstrated for polycyclic aromatic hydrocarbons (PAHs) over three orders of magnitude using this sample preparation method. The wavelength (238 - 310 nm) dependence and the laser pulse energy dependence of the 1+1 REMPI ion yield was then studied for 17 PAHs. This data allows one to determine which wavelengths are optimal to measure with high sensitivity and selectivity the analytes of interest using L2MS or related methods.

Chemical analyses of atmospheric aerosol particles were performed during extended field measurement campaigns. First, the aerosols emitted by all major emission sources including Diesel vehicles, gasoline vehicles, residential heating, wood fires, and cigarettes were characterized. For each emission source, tracer mass spectral patterns were identified, notably based on specific PAHs and other polycyclic aromatic compounds (PACs). Only small sample quantities were necessary and the measurements were performed within minutes. L2MS was found to be a valuable
alternative to more laborious chemical analysis techniques that often require extensive sample preparation.

These results were then applied to the study of the dynamic behavior of aerosol-bound PACs in urban air over the course of several whole days, both next to a street with heavy traffic and in a city park. L2MS allowed measurements with 15 minute time resolution. Large variations in particle concentration and chemical composition were observed, reflecting the contributions from Diesel trucks and gasoline-powered cars to urban aerosols. The photochemically induced decay of oxygenated polycyclic aromatic hydrocarbons (OPAHs) was observed in real time. In a similar way, the dynamic behavior of aerosol-bound PACs in air was studied over the course of a whole year at four sites representative of the different types of aerosol exposure in Switzerland. This project was completed in the framework of a collaboration between several research institutes in order to achieve a chemical characterization of the aerosol samples that would be as thorough as possible. L2MS allowed the measurement of about 1000 samples, which would not have been possible within a reasonable amount of time using chromatographic techniques. A strong seasonal dependence of the amount of aerosol-bound PACs was observed.

Finally, to exemplify the versatility of L2MS, studies were undertaken to demonstrate the applicability of L2MS to the chemical analysis of contaminants in environmental water. This thesis establishes L2MS as a competitive analytical-chemical method that can provide innovative contributions to unanswered analytical problems due to its specific advantages.
Zusammenfassung


In einer ersten Charakterisierungsphase wurden die von der L2MS angebotenen Möglichkeiten für quantitative und qualitative Analysen abgeschätzt. Eine neue schnelle und einfache Probenvorbereitungsprozess wurde entwickelt, die eine genaue und reproduzierbare Kontrolle der vom Laser ablatierten Analytenmenge erlaubt. Dank dieser Methode konnten quantitative L2MS Messungen von polyzyklischen aromatischen Kohlenwasserstoffen (polycyclic aromatic hydrocarbons, PAHs) über drei Grössenordnungen demonstriert werden. Die Wellenlängen- (238 - 310 nm) und Laserpulsenergie-Abhängigkeit der 1+1 REMPI Ionenausbeute wurde dann für 17 PAHs studiert. Diese Daten erlauben die Vorhersage der optimalen Wellenlängen für die Messung der ausgewählten Analyten mit hoher Empfindlichkeit und Selektivität in realen Proben mittels L2MS wie auch verwandten Methoden.

Chemische Analysen von atmosphärischen Aerosolpartikeln wurden während extensiven Feldmesskampagnen durchgeführt. Zuerst wurden die von sämtlichen Hauptemissionsquellen (diesel- und benzinbetriebene Motorfahrzeuge, Hausfeuerungen, Holzfeuerungen, Zigaretten) emittierten Aerosole charakterisiert. Für
jede Emissionsquelle wurden massenspektrometrischen Peaks identifiziert, die als Leitpeaks verwendet werden können. Diese beinhalten unter anderen PAHs und andere polyzyklische aromatische Verbindungen (PACs). Nur kleine Probemengen waren notwendig und die Messungen konnten innert Minuten durchgeführt werden. L2MS erwies sich als wertvolle Alternative zu komplizierteren analytischen Methoden, die häufig eine komplexe Probenvorbereitung verlangen.


Um die Vielseitigkeit der L2MS zu zeigen, wurde schliesslich die Anwendbarkeit der L2MS für die chemische Analyse von Vereinigungen in Umweltwässern untersucht. Diese Dissertation etabliert L2MS als eine kompetitive analytisch-chemische Methode, die dank ihrer spezifischen Vorteile innovative Beiträge zu offenen analytischen Problemen leisten kann.
Résumé

La spectrométrie de masse à deux lasers (L2MS) est une technique innovative qui permet d’analyser directement certains composés organiques présents dans des matrices complexes telles que des échantillons provenant de l’environnement. Dans un premier temps, une impulsion émise par un laser infrarouge désorbe les substances à analyser de la surface de l’échantillon, ou les vaporise d’une matrice solide. Un laser ultraviolet pulsé est ensuite utilisé pour les photoioniser par un mécanisme résonnant à deux photons (ionisation multiphotonique amplifiée par résonnance, 1+1 resonance-enhanced multiphoton ionization, 1+1 REMPI). Cette technique particulière d’ionization évite la fragmentation des molécules. La détection des ions est ensuite effectuée au moyen d’un spectromètre de masse à temps de vol pourvu d’un réflectron. Le spectre de masse ainsi obtenu est dominé par les ions parents intacts des constituants de l’échantillon qui absorbent fortement la longueur d’onde du laser ultraviolet. Les principaux avantages de la L2MS sont le seuil de détection de l’ordre de grandeur d’une attomole, ainsi que le minimum de préparation exigé par l’échantillon, ce qui permet d’effectuer un nombre important de mesures en un laps de temps particulièrement court.

Dans une première phase de caractérisation, les possibilités offertes par la L2MS pour les analyses tant quantitatives que qualitatives ont été évaluées. Une nouvelle procedure de préparation d’échantillons, rapide et simple, a été développée. Elle permet un contrôle précis et reproductible de la quantité de substances à analyser désorbee par chaque impulsion laser. Des mesures quantitatives d’hydrocarbones aromatiques polycycliques (polycyclic aromatic hydrocarbons, PAHs) par L2MS ont ainsi pu être démontrées sur trois ordres de magnitude. La dépendance de la longueur d’onde (238 - 310 nm) et de l’intensité de l’impulsion laser du rendement de ions par 1+1 REMPI a ensuite été étudiée pour 17 PAHs. Ces données permettent de déterminer les longueurs d’onde optimales pour mesurer les composés à étudier avec une sensibilité et une sélectivité aussi grandes que possible, tant par L2MS que par d’autres méthodes apparentées.

Des analyses chimiques d’aérosols atmosphériques ont ensuite été effectuées au cours de campagnes de mesures à grande échelle. L’étude a d’abord porté sur leurs
principales sources d’émission: les véhicules Diesel, les voitures à essence, les chauffages domestiques, les feux de bois et les cigarettes. Pour chaque source d’émission, des pics pouvant être utilisés comme traceurs ont pu être identifiés dans les spectres de masse. Ceux-ci sont notamment basés sur des PAHs et d’autres composés aromatiques polycycliques (polycyclic aromatic compounds, PACs). Des quantités minimes d’échantillons ont suffi et les mesures ont été effectuées en quelques minutes. Il a été établi que la L2MS est une alternative valable à d’autres méthodes d’analyse chimique plus laborieuses et qui nécessitent souvent un préparation d’échantillon complexe.

Les données obtenues ont ensuite été appliquées à l’étude pendant plusieurs journées complètes du comportement dynamique des PACs liés aux aérosols, le long d’une route à fort trafic aussi bien que dans un parc urbain. La L2MS a rendu possible des mesures dont la résolution temporelle est de 15 minutes. D’importantes variations tant dans la concentration des particules dans l’air que dans leur composition chimique ont été observées. Elle reflètent en particulier les apports aux aérosols urbains des véhicules Diesel et des voitures à essence. La dégradation induite photochimiquement des hydrocarbones aromatiques polycycliques oxygénés (oxygenated polycyclic aromatic hydrocarbons, OPAHs) a été observée en temps réel. De manière similaire, le comportement dynamique des PACs liés aux aérosols a ensuite été étudié au cours d’une année complète sur quatre sites différents, représentatifs de différents types d’exposition aux aérosols susceptibles d’être trouvés en Suisse. Ce projet a été effectué dans le cadre d’une collaboration entre plusieurs groupes de recherche afin de permettre un caractérisation aussi complète que possible des échantillons d’aérosols. La L2MS a permis de mesurer environ mille échantillons, ce qui n’aurait absolument pas été possible en un temps raisonnable avec des méthodes chromatographiques. Une forte dépendance de la saison a été observée.

Finalement, pour mettre en évidence la polyvalence de la L2MS, des études ont été entreprises pour démontrer l’application de la L2MS à l’analyse de contaminants dans l’eau. Cette thèse prouve que la L2MS est une méthode analytico-chimique compétitive qui, grâce à ses avantages spécifiques, peut offrir des contributions innovatives à des problèmes analytiques non-résolus.
Publications


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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>APh</td>
<td>AlkylPhenanthrene</td>
</tr>
<tr>
<td>BaA</td>
<td>Benz[a]anthracene</td>
</tr>
<tr>
<td>BC</td>
<td>Black Carbon</td>
</tr>
<tr>
<td>CE</td>
<td>Capillary Electrophoresis</td>
</tr>
<tr>
<td>EC</td>
<td>Elemental Carbon (in air particulate matter)</td>
</tr>
<tr>
<td>ECD</td>
<td>Electron Capture Detector</td>
</tr>
<tr>
<td>EI</td>
<td>Electron Impact</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>FT-ICR-MS</td>
<td>Fourier Transform Ion Cyclotron Resonance Mass Spectrometry</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>GPIB</td>
<td>General Purpose Interface Bus</td>
</tr>
<tr>
<td>HAPh</td>
<td>Hydrogenated AlkylPhenanthrene</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>IC</td>
<td>Ion Chromatography</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively-Coupled Plasma Mass Spectrometry</td>
</tr>
<tr>
<td>IT-MS</td>
<td>Ion-Trap Mass Spectrometer</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>L2MS</td>
<td>Two-Step Laser Mass Spectrometry</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid Chromatography</td>
</tr>
<tr>
<td>LD1</td>
<td>Laser Desorption/Ionization</td>
</tr>
<tr>
<td>LDI-MS</td>
<td>Laser Desorption/Ionization Mass Spectrometry</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>MALDI</td>
<td>Matrix-Assisted Laser Desorption/Ionization</td>
</tr>
<tr>
<td>MCP</td>
<td>MicroChannel Plates</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrum, mass spectrometry</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass-to-charge ratio</td>
</tr>
<tr>
<td>NABEL</td>
<td>Swiss national air pollution monitoring network</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>N-PAC</td>
<td>PAC that contains one or several nitrogen atoms</td>
</tr>
<tr>
<td>NRP-41</td>
<td>National Research Program 41</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>OC</td>
<td>Organic Carbon (in air particulate matter)</td>
</tr>
<tr>
<td>O-PAC</td>
<td>PAC that contains one or several oxygen atoms</td>
</tr>
<tr>
<td>OPAH</td>
<td>Oxygenated Polycyclic Aromatic Hydrocarbon</td>
</tr>
<tr>
<td>OPO</td>
<td>Optical Parametric Oscillator</td>
</tr>
<tr>
<td>PAC</td>
<td>Polycyclic Aromatic Compound</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic Aromatic Hydrocarbon</td>
</tr>
<tr>
<td>PM</td>
<td>Air Particulate Matter</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>Air Particulate Matter with an aerodynamic diameter &lt; 10 µm</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>Air Particulate Matter with an aerodynamic diameter &lt; 2.5 µm</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly(vinyl chloride)</td>
</tr>
<tr>
<td>REMPI</td>
<td>Resonance-Enhanced MultiPhoton Ionization</td>
</tr>
<tr>
<td>S5</td>
<td>Sum of the ion signals at 5 masses in aerosol L2MS spectra</td>
</tr>
<tr>
<td>S26</td>
<td>Sum of the ion signals at 26 masses in aerosol L2MS spectra</td>
</tr>
<tr>
<td>S-PAC</td>
<td>PAC that contains one or several sulfur atoms</td>
</tr>
<tr>
<td>σ</td>
<td>Absorption cross section</td>
</tr>
<tr>
<td>TC</td>
<td>Total Carbon (in air particulate matter)</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofurane</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
</tr>
<tr>
<td>TOF</td>
<td>Time-Of-Flight</td>
</tr>
<tr>
<td>US-EPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>YAG</td>
<td>Yttrium-aluminum garnet</td>
</tr>
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</table>
1. General Introduction

The principle of two-step laser mass spectrometry is briefly explained and the work already accomplished by other researchers reviewed. After an introduction on atmospheric aerosol particles in which the analytical-chemical methods commonly employed to analyze them are surveyed and their possibilities and limitations described, the objectives of this thesis are stated. The specific advantages offered by L2MS to contribute to the elucidation of air pollution processes linked to aerosol particles are described. Finally, the steps to accomplish the development of L2MS as a competitive analytical-chemical method are defined.
1.1. Two-Step Laser Mass Spectrometry

Two-step laser mass spectrometry (L2MS) is a technique for the direct analysis of selected compounds in complex mixtures such as environmental samples. In the first step, an infrared laser pulse desorbs intact neutral molecules from the sample surface, or ablates them from a solid matrix. In the second step, a pulse from a tunable ultraviolet laser is used for resonance-enhanced multiphoton ionization of the desorbed species; this soft ionization scheme prevents fragmentation of the analytes. Mass analysis is then performed in a reflectron time-of-flight mass spectrometer. The mass spectra are dominated by intact parent ions of those mixture components that strongly absorb the selected ultraviolet laser wavelength. Major advantages are the detection limit in the low attomole range and minimal need for sample preparation.

L2MS is often considered as a technique to perform fundamental physical-chemical research. For example, several studies in the field of surface science have been reported using L2MS (1-10). Also, the combination of supersonic jet cooling between the desorption and the photoionization steps is an interesting strategy to allow spectroscopic characterization of different types of molecules (11-21). Previously reported analytical applications of L2MS include studies on aerosol particles (22-24), cloud-water aerosol filtrates (25), geological samples (26, 27), soils (27, 28), meteoritic samples (29-32), chemicals in water (16, 33), agricultural samples (34), cancer photosensitizers and other porphyrins (35, 36), amino acids and other biomolecules (37, 38), polymers and their additives (39-41), or dyes (42). Several of these reports clearly show the potential of L2MS to overcome the limitations of conventional analytical techniques. However, very few of the previous experiments or investigations extend beyond demonstrations of feasibility by displaying the results of a few measurements. Studies where L2MS contributed new insights to unanswered or debatable analytical questions remain rare.

1.2. Objective of this Work

The purpose of this thesis is to demonstrate the use of the specific advantages of L2MS such as the high sensitivity, the need for only small sample quantities, and the possibility to measure large numbers of samples within short periods of time, to provide
innovative contributions to unanswered analytical problems. In particular, thorough and reliable analyses of PACs on atmospheric aerosol particles will be reported that allow the identification of their emission sources and the elucidation of poorly understood air pollution processes. Following a more detailed description of L2MS (Chapter 2), this thesis will be divided in three parts.

1. In an initial characterization stage, the potential capabilities offered by L2MS for both quantitative measurements (Chapter 3) and qualitative measurements (Chapter 4) will be described.

2. The results of chemical analyses of atmospheric aerosol particles performed during extended field measurement campaigns will subsequently be presented (Chapters 5 through 7).

3. Finally, to exemplify the versatility of L2MS, studies to assess the applicability of L2MS to the chemical analysis of contaminants in environmental water will be reported (Chapter 8).

1.3. Atmospheric Aerosol Particles

The generic term “atmospheric particulate matter” refers to any substance, except pure water, that exists as a liquid or solid in the atmosphere under normal conditions and is of microscopic or submicroscopic size but larger than molecular dimensions. Particles less than 2.5 μm in diameter are called “fine” and the ones greater are defined as “coarse”. Atmospheric particulate matter is very complex and can result either from direct emission of particles or from condensation of gaseous species. The particles can stem from natural sources and be constituted, for example, by soil and rock debris, sea salt, volcanic debris, natural wood fires, or condensed gaseous emissions. They can also be of anthropogenic origin and be emitted during processes such as fuel combustion, industrial activity, or transportation (43). Aerosol particles play a key role in gas-phase atmospheric processes, for example due to the reactions that may take place at their surface or due to their possible implication in climate changes (44-47). Even more important is their contribution to air pollution and the various health hazards associated to them. The adverse effects of the particles on humans and animals upon breathing and possible retention in the lungs may be caused by both their physical and
chemical properties (47-50). Even though the health effects of the particles are well known, the detailed mechanisms of their action are still poorly understood.

An especially important class of ubiquitous and hazardous particles is carbonaceous aerosol particles, which are emitted into the atmosphere by the incomplete combustion of organic material. They can roughly be described as carbon nuclei with diameters between 10 nm and 10 μm. A very large variety of organic and inorganic compounds are found adsorbed on the carbon surface that are either formed at the same time as the particles, that were already present in the organic material and have survived the combustion process, or that have condensed onto the particles. Only a fraction of these substances has yet been identified. The detailed chemical composition of carbonaceous aerosol particles depends to a great extent on their emission source. More than fifty classes of mobile and stationary sources have been identified (51), and major ones include traffic (47, 52-62), residential heating (63, 64), wood fires (65, 66), industrial processes (67), cigarettes (68), cooking (69, 70), and candles (71).

Among the organic compounds adsorbed to carbonaceous aerosol particles, polycyclic aromatic compounds (PACs) are an especially important class. PACs are often formed at the same time as the particles during incomplete combustion of organic material (45, 72-95). However, PACs can also directly originate from the organic matter itself, for example in kerogens, oil, and plant debris (96-98). Furthermore, atmospheric PACs are not necessarily exclusively particle-bound as the ones with a high volatility can also be found in the gas phase (93, 99). A few of these compounds that are built from fused benzene rings are displayed in Figure 1.1. PACs have been the object of intense research due to their carcinogenic, mutagenic, teratogenic or immunotoxic effects on animals and humans. Gas-phase reactions of PACs with other environmental pollutants can produce compounds such as nitro or nitrosamine PAC derivatives that may be even more toxic than the original PAC (45, 49, 73). PACs may eventually be found in water and in soils as a consequence of scavenging processes in the atmosphere (100-107). The toxic effects of PACs require the availability of reliable, sensitive and selective analytical methods for their identification and their quantitation to estimate the potential health hazards (46). The most widely used method is gas chromatography (GC) (53-55, 62-71, 75-80, 82, 83, 85-91, 94, 97-123), with a flame ionization (GC-FID), an electron capture (GC-ECD), or a mass spectrometric (GC-MS) detector. Several other analytical methods have been reported, such as high-performance liquid chromatography (HPLC) (74, 81, 95, 121, 124-129), thin-layer chromatography (TLC) (87, 121), on-line liquid chromatography coupled with gas chromatography (LC-GC) (52, 130, 131), capillary electrophoresis (CE) (121), laser-
induced time-resolved fluorescence (132), multiphoton ionization-membrane introduction mass spectrometry (133), visible and ultraviolet spectroscopy (134, 135), Fourier transform imaging fluorescence microscopy (136), and mass spectrometry (134, 135, 137).

\[
\text{Phenanthrene C}_{14}\text{H}_{10}, 178 \text{ Da} \\
\text{Anthracene C}_{14}\text{H}_{10}, 178 \text{ Da} \\
\text{Pyrene C}_{16}\text{H}_{10}, 202 \text{ Da} \\
\text{Benz[a]anthracene C}_{18}\text{H}_{12}, 228 \text{ Da} \\
\text{Chrysene C}_{18}\text{H}_{12}, 228 \text{ Da} \\
\text{Benzo[a]pyrene C}_{20}\text{H}_{12}, 252 \text{ Da} \\
\text{Coronene C}_{24}\text{H}_{12}, 300 \text{ Da} \\
\text{Carbazole C}_{12}\text{H}_{9}\text{N}, 167 \text{ Da} \\
\text{Phenanthrenequinone C}_{14}\text{H}_{8}\text{O}_{2}, 208 \text{ Da} \\
\text{Anthrone C}_{14}\text{H}_{10}O, 194 \text{ Da} \\
\text{Dibenzothiophene C}_{12}\text{H}_{8}\text{S}, 184 \text{ Da}
\]

Figure 1.1. Chemical structures of selected PACs.

A better understanding of the behavior of atmospheric particles, the assessment of their health hazards, and the identification of their emission sources require detailed chemical analyses to be performed. After sample collection on filters, various chromatographic methods are used for the quantitation of organic compounds (52-55, 62-65, 67-71, 74-83, 85-91, 94, 95, 97-131) and inorganic ions (46, 123, 138-140) while atomic spectroscopic methods allow the determination of the elemental composition (46, 58, 140-142). These techniques often require tedious and time-consuming sample preparation as well as the collection of relatively large sample quantities over extended periods of time, generally 24 hours, even in polluted urban areas. This renders them less convenient for analyses at sites where aerosol concentrations may be low or the sampling time limited. Furthermore, they are not well-suited for the measurement of large numbers of samples.
A technique specifically developed for particle measurements with high time resolution is single particle laser desorption/ionization mass spectrometry (LDI-MS) (46, 143-160). The particles are pumped directly from the air, collimated, and detected by the scattering of the light emitted by a continuous-wave laser. During this stage, their size can be determined according to their scattering properties or to their flight speed. The single particles are then irradiated by intense ultraviolet laser pulses (LDI). The ions generated by this means are detected using a time-of-flight mass spectrometer, and the simultaneous detection of both positive and negative ions is possible. Single particle LDI-MS allows the identification of the particle emission sources according to their inorganic composition. However, any classification of the carbonaceous particles based on their organic composition, for example for the identification of different emission sources, is still problematic because characteristic organic tracer analytes fragment extensively during LDI-MS analysis. Also, direct comparison with data obtained using conventional methods for monitoring gaseous or particle-bound atmospheric pollutants is not possible due to poorly characterized particle-size dependent sampling efficiency.

By making rapid, speciated, sensitive, and quantitative analyses of substance classes such as PACs with a single method possible, L2MS combines the specific advantages of the techniques mentioned above. However, although the feasibility of L2MS measurements on carbonaceous aerosol particles has already been demonstrated (22-24), no extended studies have been performed until now.

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2. Two-Step Laser Mass Spectrometry

This Chapter focuses on an extended description of two-step laser mass spectrometry (L2MS). The physical-chemical principles of L2MS, the design of the home-built instrument, and the experimental settings used for the work reported in the next Chapters are described in detail.

2.1.1. Principle of two-step laser mass spectrometry

Figure 2.1 displays the principle of two-step laser mass spectrometry (L2MS) (1), using the example of aerosol particles on a filter as a sample (See Chapters 5-7). In the first step, a pulse from an infrared (IR) laser desorbs the analytes from the sample surface. This laser-induced thermal mechanism induces the formation of a rapidly expanding plume containing the analyte molecules. It should be emphasized that neither fragmentation nor ionization of the molecules takes place during this step, in contrast to other laser mass spectrometric techniques such as laser desorption/ionization (LDI) (2) or matrix-assisted laser desorption/ionization (MALDI) (3, 4). In the second step, a pulse from a tunable ultraviolet (UV) laser is used for resonance-enhanced multiphoton ionization (1+1 REMPI, see below) of the gaseous species. This is a soft UV post-ionization scheme: no fragmentation takes place for most analytes, and only one bond is broken for those analytes that contain labile functionalized groups such as a carbamate group.

A, B and C are 3 analytes with different excitation spectra. Time-of-Flight Mass Spectrometer

1. Desorption

2. Selective soft ionization

**Figure 2.1. Principle of L2MS. Aerosol particles collected onto a filter are used as sample. Laser-induced thermal desorption (1) brings the analytes into the gas phase where they are post-ionized using a UV laser (2).**
Figure 2.2 describes the measurement of a few other general types of samples using L2MS. The diameter and the focusing of the IR laser beam determine the energy density, which allows one to control whether desorption or ablation takes place, although often only one of the two is possible. Desorption can be viewed as a process that cleans a surface of the analytes adsorbed onto it while leaving the bulk of the sample intact. This process takes place during the analysis of aerosol particles (Figure 2.1, Chapters 5-7) or of thin layers of analytes deposited onto a glass substrate (Figure 2.2.A, Chapter 3). In the case of ablation, a hole is drilled into a solid matrix. Ablation is required for the analysis of solid samples (Figure 2.2.B, Chapter 8) or of analytes embedded in a thin PVC membrane (Figure 2.2.C, Chapters 3-4).

![Diagram showing different types of L2MS samples]

**Figure 2.2. Different types of L2MS samples.** (A): Thin analyte layer on a silica substrate. (B): Analyte molecules naturally occurring in a complex solid matrix. (C): Analyte molecules embedded in a thin PVC membrane.

After post-ionization of the analytes, the ions are extracted with electrical fields and mass separated in a reflectron time-of-flight mass spectrometer. The mass spectra are dominated by intact parent ions of those mixture components that strongly absorb the selected UV wavelength. Figure 2.3 shows the L2MS spectrum of a mixture of eight PAHs embedded in a PVC membrane (see Chapter 3). No fragment peaks are detected in the low mass region. The zoom around m/z = 178 (phenanthrene) shows some minor elimination of hydrogen as well as the contribution of the $^{13}$C-isotopomers. Figure 2.4 displays an example of a L2MS spectrum recorded directly from urban aerosol particles collected onto a filter (sampling procedure see Chapter 5). The dominant peaks are assigned to PAHs. The origin of the weak fragment peaks in the low mass range remains unclear.
Figure 2.3. L2MS spectrum of a mixture of eight PAH standards embedded in a PVC membrane. A single shot was used to obtain this spectrum.

Figure 2.4. L2MS spectrum recorded directly from urban aerosol particles collected onto a filter. A single shot was used to obtain this spectrum.
2.1.2. 1+1 Resonance-enhanced multiphoton ionization

Figure 2.5. Selected multiphoton ionization mechanisms. (A): 1+1 REMPI, used in L2MS. (B): Absorption of a third photon to induce fragmentation. (C): Non-resonant two-photon ionization.

Figure 2.5 shows the principle of 1+1 resonance-enhanced multiphoton ionization (1+1 REMPI), the ionization mechanism most commonly used in L2MS and in this work as well. In 1+1 REMPI (A), the energy required to induce ionization is provided by the absorption of two UV photons. The gaseous analytes in the ground state absorb a first UV photon and reach their first excited state. After absorption of a second photon, the molecules possess an internal energy higher than their ionization potential. An electron therefore detaches and a positive ion is formed. 1+1 REMPI is a soft ionization mechanism. The small amount of excess energy that remains after ionization is in general not high enough to induce fragmentation. Wavelengths between 220 nm and 310 nm corresponding to photon energies of 5.64 eV and 4.00 eV, respectively, were used; typical ionization potentials for aromatic compounds are in the range of 7 - 9 eV (5). Two other multiphoton processes that would also be possible but do not play an important role in L2MS are displayed in Figure 2.5 as well. The absorption of a third photon (B) would be necessary to induce fragmentation. This process can be triggered by using a higher laser intensity but is typically avoided in L2MS. Non-resonant two-
photon ionization (C) not passing through a well-defined excited state is several orders of magnitude less efficient than 1+1 REMPI. 1+1 REMPI is therefore an optically selective ionization mechanism. It requires the analyte molecules to have a strong enough absorption cross-section (σ) at the selected UV laser wavelength in order to take place. For this reason, aromatic and in particular polycyclic aromatic compounds (PACs) are classes of compounds that can be ionized particularly efficiently. A more detailed description of 1+1 REMPI can be found in the literature (6-8).

2.1.3. Time-of-flight (TOF) mass spectrometers

Figure 2.6 shows the principle of a time-of-flight (TOF) mass spectrometer, the type of mass spectrometer most commonly used in L2MS and in this work as well (9-12). First, ions are produced by the UV laser in the ion source which consists of two electrode plates upon which voltages are applied. The potential energy of the ions is converted into kinetic energy as described by Equation 2.1, with U being the voltage difference between the electrodes, z the charge of the ions, m their mass, and v their speed after the acceleration.

\[
U \cdot z = \frac{1}{2} m \cdot v^2 \tag{Eq. 2.1}
\]

![Figure 2.6. Schematic of a linear time-of-flight mass spectrometer.](image)
The final speed reached by the ions is therefore proportional to their masses and their charge, i.e. light ions move faster than heavier ones. The ions in motion (for example at 50 km/s) then enter a field free drift tube (approximately 1 m long) and fly through at the constant speed they reached after the acceleration. The time they need to pass through the tube, the so-called time-of-flight (TOF), is given by Equation 2.2, with L the length of the drift tube.

\[
\text{TOF} = \frac{L}{v} \quad \text{(Eq. 2.2)}
\]

Finally the ions are detected at the end of the drift tube using a microchannel plate array detector (MCP) connected to a digital oscilloscope. The recorded transient displaying signal intensity vs. TOF can easily be converted to a more conventional mass spectrum by combining Equations 2.1 and 2.2 to yield Equation 2.3.

\[
\frac{m}{z} = \frac{2 \cdot U \cdot \text{TOF}^2}{L^2} \quad \text{(Eq. 2.3)}
\]

In practice, a mass calibration is performed using two compounds with known masses whose TOFs are fitted to Equation 2.4 which is derived from Equation 2.3. The constant a is usually smaller than half a mass unit and can be viewed as a correction for instrumental inaccuracies and delays.

\[
\frac{m}{z} = k \cdot \text{TOF}^2 + a \quad \text{(Eq. 2.4)}
\]

Multiply-charged ions are not formed when using L2MS so that the mass-to-charge ratios m/z commonly used in mass spectrometry can simply be rationalized as the “pure” masses.

### 2.2. The Instrument

Figure 2.7 displays a schematic of the home-built L2MS instrument and of the electronics. The samples are mounted onto the tip of a sample holder that consists of a 45 cm long stainless steel rod, two cm in diameter, that is equipped with a threaded cap. The loaded sample holder is introduced into the main vacuum chamber through a differentially pumped interlock connected to the main vacuum chamber with a gate valve. The complete sample introduction procedure requires less than one minute. The pressure inside the mass spectrometer is below 10⁻⁶ Torr. This vacuum is generated by two magnetic turbomolecular pumps (Turbovac 340 M, Leybold, Cologne, Germany). The whole pumping system, including the forepump (Drytel 31, Alcatel, Annecy, France) is completely oil-free in order to minimize the risk of contamination. In addition, decon-
contamination can be achieved by baking out the instrument at about 80°C using heating tapes (SRT101-200 and SRT201-100, Omegalux, Stamford, CT). This was done after each extensive measurement series or whenever contamination was suspected, for example, after opening of the vacuum chamber.

Desorption/ablation is accomplished using a multimode pulsed CO₂ laser (Alltec 853 MS, Lübeck, Germany, λ = 10.6 μm, 0.6 J/cm², 107.5 ns) at a 45° incident angle. The diameter of the desorption/ablation spot and the intensity of the beam can be controlled by tuning two irises and a plano/convex ZnSe lens (f = 50 mm). The spot size is limited by diffraction and cannot be less than 40 μm. Typical desorption/ablation spot sizes used during this project were in the range of a few hundreds of micrometers.
The ionizing laser radiation is produced by an optical parametric oscillator (OPO) laser (MOPO-730D10, Spectra Physics Lasers Inc., Mountain View, CA, 8 ns) pumped by the third harmonic of a pulsed Nd-YAG laser (GCR-230, Spectra Physics Lasers Inc., Mountain View, CA). This system can produce wavelengths between 220 nm and 340 nm; frequency mixing of the pump beam in a non-linear medium yields photons in the visible range that are then frequency doubled. Alternatively, the third (355 nm) or the fourth (266 nm) harmonics of a ps-YAG laser (PY-61C/20, Continuum, Puchheim, Germany, 30 ps), optionally coupled to a Raman shifter (13) filled with H₂ can be used for ionization. The shorter pulses sometimes allow REMPI to be more efficient in cases where the lifetime in the excited state (τ) of analyte molecules is not long enough to make two-photon processes possible using ns pulses. The substantial jitter (about 25 μs) and the weak beam intensity of the ps-laser however rendered this option highly inconvenient for analytical purposes. The diameter of the ionizing beam was kept constant at about two mm by an iris during all of the work. The beam intensity can be controlled using a CaF₂ polarizer mounted on a motorized rotator. The UV beam is focused by a fused silica cylindrical lens (f = 250 mm) onto a plane a few millimeters above the desorption/ablation spot, in the middle of the ionization source. The energy of the UV beam coming out of the vacuum chamber is measured using a pyroelectric power detector (ED-100, Gentec, Sainte-Foy, Canada) connected to an amplifier (EDX-1, Gentec, Sainte-Foy, Canada).

The custom-designed ion source is of the classical Wiley-McLaren type (11). The sample is positioned in the middle of the repeller plate, at a potential of about 3800 V. The first of the three extraction plates is positioned at 5 mm distance from the sample and is set to about 2400 V. It is connected to the second one through a 10 MΩ resistor, which is itself connected to the grounded third one through another 10 MΩ resistor. The ions then pass between deflection plates for the x- and y-directions as well as through an Einsel lens for ion focusing. The TOF mass spectrometer (modified D-850, R. M. Jordan Co., Grass Valley, CA) is equipped with a reflectron (14) in order to reach a better resolution in the mass spectra by correcting for the different initial velocities of ions at identical masses. A mass resolution of 1200 is routinely achieved as can be seen from the inset in Figure 2.3. The ions are detected by a pair of 40 mm microchannel plates (MCP) (Galileo, Sturbridge, MA) in the chevron configuration. The transients are recorded by a digital oscilloscope (LeCroy 9350A, Geneva, Switzerland) with 5 ns sampling intervals.

The 10 Hz electrical output signal generated by the ionization laser is used as the internal clock for the measurements. After passing through a home-built frequency
divider, the signal is sent to a delay generator (DG-535, Stanford Research Systems, Stanford, CA) that triggers the desorption/ablation laser. The oscilloscope is set in the smart trigger mode: it is triggered by a photodiode that detects the ionization laser pulses, but this trigger only becomes effective for those pulses that come immediately after a desorption/ablation laser pulse. The time delay between the two laser pulses is tuned using the delay generator. Delays between 10 µs and 25 µs were used depending on the type of sample and their plume expansion dynamics.

The measurements, as well as series of measurements, can be completely controlled by a GPIB card (NI-488.2, National Instruments, Austin, TX) in a personal computer. A FORTRAN program written in-house allowed the triggering of the instruments, the storage of the mass spectra and of the data acquisition parameters, the simultaneous measurement of the laser pulse energies via an electronic interface (dt2812, Data Translation Inc., Marlboro, MA) connected to the pyroelectrical power detector, and the rotation of the samples between single laser shots using a remote-controlled motorized rotator. The raw data produced for this work consisted of single shot measurements that sometimes were averaged over series. Further data processing was performed using another FORTRAN program written in-house, and the software Igor Pro (Wavemetrics, Lake Oswego, OR).

2.3. References

3. Characterization of L2MS Using Standards. Optimization of the Sample Preparation and Quantitative Studies

Analytical-chemical techniques are generally required to allow quantitative measurements. This is known to be problematic when using L2MS or various other analytical mass spectrometric and optical spectroscopic methods that require a step during which a non-volatile substance is desorbed by a laser pulse. It is generally not possible to have an accurate control over the amount of analytes desorbed by the laser pulse, especially when mixtures of several substances are used. This Chapter describes a new fast and convenient sample preparation procedure that solves this problem. A solution of the analytes is mixed with a solution of poly(vinyl chloride) to obtain a homogeneous and vacuum-stable thin polymer membrane after the solvent has evaporated. Laser ablation is then performed directly from this membrane, allowing an accurate control of the amount of ablated analytes and excellent reproducibility. Quantitative L2MS measurements are demonstrated for polycyclic aromatic hydrocarbons over three orders of magnitude using this sample preparation method.
3.1. Introduction

Laser desorption has become a widely used method to gain access to gas-phase species for mass spectrometry of large molecules (1-7), optical spectroscopy with or without supersonic jet entrainment (8, 9), and even for pulsed Fourier-transform microwave spectroscopy of non-volatile substances (10, 11). The reliability of the laser desorption step is critical. Strongly varying amounts of material are typically released in the desorption events due to variations in the sample morphology or thickness. This makes quantitative measurements difficult or impossible, and spectroscopic experiments can only be performed with long signal averaging.

A number of solutions have been suggested to solve these problems. Most commonly, thick sample layers deposited from solution or pressed pellets are used in an attempt to obtain a persistent signal for many laser shots (2, 8, 12-15). Thin sample films can also be used to guarantee complete desorption for each laser shot while the sample is moved with respect to the laser focus (16-18). However, re-deposition or diffusion into the freshly desorbed spot are often found. A more elegant way is to soak a porous solid, such as charcoal, with a sample solution (19, 20). Persistent signals can be obtained in this fashion, but the method is limited to semi-volatile compounds that replenish the surface of the porous solid by diffusion. Li and Lubman used laser desorption of compounds dissolved in a high viscosity fluid such as glycerol or silicon diffusion pump fluid for supersonic jet spectroscopy of non-volatile molecules (9, 21-23). A somewhat related approach, albeit not applicable in many cases, is to embed samples in a cryogenic matrix (24, 25).

At present, none of these sample preparation methods is general enough and adequate for laser desorption of compounds with widely varying properties. There are limitations of solubility, volatility, diffusivity, etc., especially when working with mixtures.

Our first attempts to apply L2MS to the analysis of standard PAH mixtures were performed using the usual sample preparation procedure. A standard mixture solution of PAHs was poured onto the surface of a silica substrate and the solvent was evaporated. Laser desorption was then performed from this surface. Soon it became clear that this method does not allow sufficient control of the local composition of the layer with the analytes to allow quantitative analyses: (i) The analytes do not spread homogeneously over the whole surface but have a tendency to form microcrystals at given locations, especially at the edges of the substrate. (ii) The thickness of the analyte
layer is not constant. Spin-coating or electrospraying could perhaps partially solve this problem; these deposition methods are however not well-adapted for the rather thick layers sometimes required for quantitative analyses of substances with very variable UV absorption coefficients over a broad range of concentrations. (iii) Since the total volume ablated by a single pulse can be considered constant, the composition of the mixture has a tremendous influence on the desorption efficiency of the individual compounds. The desorption of trace analytes that are easily desorbed alone is badly impaired if other substances are present in large excess. (iv) The laser desorption takes place under vacuum conditions. Compounds with a high vapor pressure, such as the lower molecular weight PAHs, exhibit a lifetime of only a few minutes on the surface. This greatly influences the amount of analytes that remains available for laser desorption. In addition, contamination of the vacuum system occurs.

As a consequence, a new method for the sample preparation had to be designed. This new procedure consists in mixing a solution of the analytes with a solution of poly(vinyl chloride) (PVC) in tetrahydrofuran to obtain a homogeneous and vacuum-stable thin polymer membrane after the solvent has been evaporated. Laser ablation was performed directly from this membrane. Quantitative two-step laser mass spectrometry measurements have been performed that validate this sample preparation method.

It should be stressed that this sample preparation method is not limited to L2MS but could find applications in most other methods that require laser desorption or ablation, such as the ones previously cited.

3.2. Experimental Section

3.2.1. Sample preparation

All of the PAHs were purchased from either Chem Service Inc. (West Chester, USA) or Aldrich (Switzerland) and had a purity of at least 95%. Stock solutions were prepared in methylene chloride (J. T. Baker, Holland) with nominal concentrations around 2 g/l.

*Method using silica substrates.* The conventional sample preparation described here is the result of several months of optimizations before we came to the conclusion that it is impossible to obtain satisfactory results with such methods. Circular silica
substrates (1/2 inch diameter) were obtained by cutting 3 mm thick slices from a glass rod with a diamond saw. The surfaces were not polished because it was experimentally observed that rough surfaces allow liquids to spread more homogeneously than on polished surfaces. The PAH stock solutions were used to prepare mixture solutions in methylene chloride that contained 5-10 analytes in concentrations around 10 μM. The samples were then prepared by dosing 40 μl of a mixture solution with a microsyringe (Exmire, Japan) onto the surface of a glass substrate. This volume allows the formation of a 1 mm thick film over the complete surface of the substrate due to the surface tension. The solvent evaporated at ambient pressure and temperature, a process that requires only about one minute due to the high volatility of methylene chloride.

Method using thin PVC membranes. The solutions used to produce the thin membranes were prepared by dissolving 3 g of high molecular weight PVC powder (Fluka, Switzerland) in about 40 ml tetrahydrofurane (THF) (Scharlau, Spain) in a 50 ml volumetric flask, adding stock solutions of 5-10 PAHs, and filling the flask to 50 ml with THF; this procedure is optimized to take into account the difficulty to dissolve PVC because a thick gel forms at the bottom of the flask as soon as THF is added to it, and to take into account the high viscosity of the obtained solution. The next step consisted in pouring 2 ml of the solution into a NS 16/9 Petri dish (5 cm diameter). A 50 μm thick membrane was obtained after the THF had evaporated, a process that requires at least one hour to be sure that the membrane is perfectly dry. The addition of methyl red to the solution allowed the visible confirmation that the thickness of the membrane is homogeneous over the whole surface. The solid membrane can then easily be taken out of the Petri dish and circular pieces 12 mm in diameter can be cut at any place to be mounted on the tip of the sample holder. PVC was selected because it absorbs the 10.6 μm IR-radiation of the ablation laser well. Previous attempts with polystyrene instead of PVC failed due to the lack of an absorption band at this wavelength. Another advantage of PVC is that this substance does not yield any peak at all in the mass spectra since it lacks a suitable chromophore for 1+1 REMPI in the wavelength range used here (see below).

3.2.2. L2MS system

The L2MS system has already been described in detail in Chapter 2. Only the characteristics specific to this Chapter are given here. The same CO₂ laser was used for both desorption and ablation. Tuning an iris and a ZnSe-lens (50 mm) mounted on a micrometer screw however allowed one to control the energy density of the beam and
the size of the desorption/ablation spot. Typical settings for the work with silica substrates corresponded to about 1 J/cm² on an elliptical spot of about 300 μm by 400 μm. Typical settings for the work with membranes corresponded to about 6 J/cm² on an elliptical spot of about 135 μm by 180 μm. The higher fluence in the second case generates a hole that completely penetrates the 50 μm thick membrane, as can be seen from Figure 3.1; the membrane was rotated by 4 degrees with a remote controlled motorized rotator between the two single ablation shots. The circular structures around the holes are assumed to be caused by PVC melting; the fact that the edges of the holes are black probably originates from a change in the optical properties of the material and not from pyrolysis of the PVC during the laser pulse.

![Figure 3.1](image)

**Figure 3.1.** Two ablation craters produced by two consecutive IR shots on a PVC membrane. An elliptical spot of about 135 μm by 180 μm is drilled through the 50 μm thick membrane. The structures on the edges are probably caused by PVC melting.

Wavelengths between 238 and 310 nm were used for ionization. The UV-beam passed through the plume of desorbed or ablated analytes 2.5 mm above the sample surface. The UV energy density was kept constant by adjusting a remote controlled motorized polarizer. A pyroelectric power detector was placed after the ionization source to measure the intensity of every UV pulse; the recorded values were necessary for the normalization of the mass spectra.

The delay between the two laser pulses was 25 μs for the work with silica substrates and 10 μs for the work with membranes. These values are the results of optimizations in order to obtain maximal signal intensities. They seem to indicate that the plume expansion is faster for ablation from a membrane. No ions were observed when either laser was blocked.
3.3. Results and discussion

3.3.1. Homogeneity of the analytes' layer

The homogeneity of the analytes layer was checked by measuring single shot mass spectra at various locations on a sample of each type (Figure 3.2). The desorption spots were all on a circle with a diameter of about 9 mm. Their spacing is defined by the angle by which the sample had been rotated between successive laser shots. Naphthalene on glass substrates could not be detected at all due to its high volatility, but it was detected using the polymer matrix preparation as any other PAH. The signal intensities were normalized for each analyte independently to obtain an average signal intensity of 1. A sinusoidal fit was then performed using all the data points together. The fit is suitable to describe glass substrates although it is irrelevant in the case of membranes. The values of the “modulation amplitude” (glass substrate : 0.61; membrane : 0.06) nevertheless allow a good comparison between the two methods. In the membrane, the distribution of the analytes appears to be homogeneous. No systematic angular dependence is observed. The scattering that is observed between the different angles is mainly due to the fact that the membrane has to be placed very close to the focus of the IR beam in order to achieve sufficient ablation. Under these conditions, a very slight fluctuation of the beam intensity or of the sample position has a much stronger influence on the amount of analytes vaporized than in the case of the evaporated sample. The scattering that is observed between different analytes at the same angle may be caused by small fluctuations of the extraction voltages that affect flight times in such a way that the digitalization sometimes exactly catches the maximum of the peaks, and sometimes not. Integrating the peaks instead of simply measuring the peak heights did not solve the problem. This result nevertheless not only proves that the analytes are homogeneously spread, but that the physical properties of the membrane such as its thickness remain identical at different locations. On the other hand, strong local variations are observed on the surface of glass substrates. The analytes all tend to deposit on the same side of the glass substrate, even though extreme care was taken during the sample preparation to keep the substrate perfectly horizontal. It should be pointed out that the example displayed on Figure 3.2 is a typical example, and not just a worst case. The mass spectra can in this case not be interpreted separately but have to be averaged over the complete surface. Spin coating could help solve this problem as long as only very thin layers are required. For the analysis of PAHs thicker layers are however necessary in order to allow quantitative measurements over a broad range of concentrations.
Figure 3.2. Comparison of the homogeneity of the spreading of different analytes. Single shots at selected rotation coordinates of the sample followed by ionization at 255 nm. Sinusoidal fitting of the data. (A) Method using a glass substrate. (B) Method using a membrane. Symbols: ▼: Naphthalene, □: Phenanthrene, ×: Chrysene, ○: Benzo[a]pyrene, +: Dibenz[a,h]anthracene

3.3.2. Successive shots onto the same spot

An efficient strategy for an accurate control over the amount of desorbed/ablated analytes is to have the first IR laser shot perform total desorption/ablation on the target spot, while leaving the rest of the sample unmodified. Series of shots on the same spot were performed using both types of samples (Figure 3.3). The membrane sample exhibited a behavior that was close to this goal. Already at the second shot no signal is observed for benzo[a]pyrene and dibenz[a,h]anthracene anymore. Peaks with weaker intensities however remain present for a few shots in the cases of phenanthrene and especially naphthalene. Compounds with a higher vapor pressure are probably also vaporized from the edge of the hole for a few shots, due to temporary heating by the laser pulse. It is nevertheless certain that the material does not originate from the exact location of the spot as shown in Figure 3.1 (total ablation) and by the fact that compounds with a lower vapor pressure are not observed at all. The silica substrate sample exhibited an unexpected behavior, as the signal remained strong even after several shots. The phenomenon described for the volatile analytes in a membrane
cannot explain this observation, since coronene was especially chosen due to its low vapor pressure. Redeposition and/or diffusion processes are probably the reason for the persistence of the signal in this case. An additional experiment was performed to further investigate this process. A special substrate was prepared by dosing a small amount of coronene only onto a 2 mm in diameter spot. After a few laser shots at this spot, significant amounts of coronene could be detected at a location 9 mm away from the original spot. This result clearly shows of the importance of the redeposition/diffusion process.

![Figure 3.3](image.png)

**Figure 3.3.** Dependence of the signal on the number of successive laser shots on the same spot.

(A) Coronene on a glass substrate. Ionization at 288 nm. Significant redeposition and/or diffusion takes place. △: Coronene.

(B) Different analytes in a membrane. Ionization at 255 nm. Almost no signal is observed already at the second shot.

▽: Naphthalene, □: Phenanthrene, ×: Chrysene,
○: Benzo-[a]pyrene, +: Dibenzo[a,h]anthracene.

### 3.3.3. Vacuum stability

The lifetime of the analytes in the vacuum chamber (p = 60 μPa) was studied for samples of both types (Figure 3.4). The lifetime of anthracene (p = 0.4 mPa at 20 °C) (26) on a glass substrate is about 6.3 minutes. As a consequence, the time between the
introduction of the sample into the vacuum chamber and the measurement has to be kept short and constant if quantitative measurements are to be performed using a glass substrate. It would therefore not be possible to perform a long series of measurements with the same sample. On the opposite, the signal of the more volatile phenanthrene (p = 10.2 mPa at 20 °C) (26) ablated from a membrane was observed to remain constant during more than four hours. Quantitative measurements are in this case not affected by the time the sample spent in the vacuum chamber, and contamination of the system does not occur.

Figure 3.4. Study of the lifetime of volatile analytes in the vacuum chamber. (A) Method using a glass substrate: Anthracene signal. 50 shots summed average on rotated sample. Each point is a new sample. Ionization at 240 nm. Fit: signal = exp(-0.11 • t). (B) Method using a membrane: Phenanthrene signal. Single shots. Each point is a new spot on the same sample. Ionization at 250 nm. Fit: S = exp(+0.00028 • t).
3.3.4. Quantitative measurements

The use of thin membranes allowed for the first time quantitative L2MS measurements from mixtures to be performed. Figure 3.5 displays the calibration curve for chrysene; the data points can successfully be fitted with a linear model. Each point of the graph corresponds to a single laser shot; no averaging was performed and no point was dumped. The scattering of the points is quite low and permits a reliable interpretation of the data. This scattering is now mainly caused by remaining instabilities of the system, such as fluctuations of the intensity of the desorption pulses or small shifts of the position of the UV beam, and not by inhomogeneities of the sample. Note that recording the same number of data points using glass substrates would have been extremely time consuming. The limit of quantitation is around 500 amol and is typical for most PAHs. This limit of quantitation is still about 500 times higher than the one that can be estimated in the case of glass substrates because more background noise over the whole mass range originates from the PVC than from the glass. The origin of this noise is still unknown, but it is clear that it originates neither from the PVC nor from the metallic sample holder. As a comparison, it was absolutely impossible to obtain linear calibration curves from sample mixtures deposited on glass substrates, because the amount of each analyte at the desorption spot has an influence on the efficiency of the desorption of the other analytes.

Figure 3.5. Quantitative analysis of chrysene. Chrysene is ablated from membranes containing 7 other PAHs. Ionization at 260 nm. The line is a linear fit: signal = k \cdot \text{mol ablated}
3.4. References


(26) Thermodynamics Research Center Texas A&M University, U. S. A., Thermodynamic Tables, Hydrocarbons: College Station, 1976.
4. Characterization of L2MS Using Standards. 1+1 REMPI Spectroscopy

1+1 REMPI is used not only in L2MS but also in various analytical techniques because it is an efficient and optically selective soft ionization method. While 1+1 REMPI of jet-cooled molecules has been extensively studied, little has been reported so far about this mechanism as it is used in analytical techniques, in the cases where the molecules are not jet-cooled and where widely varying ionization wavelengths are used. Such studies however are of special importance to optimize L2MS for analytical applications. In particular, they are necessary to determine which wavelengths allow the determination of the analytes of interest with optimal sensitivity, as well as to assess the potential for the distinction between isomers. This Chapter reports on the study of the wavelength (238 - 310 nm) dependence and the laser pulse energy dependence of the ion yield for 17 PAHs. We then discuss how this data allows one to predict the efficiency of 1+1 REMPI for a given compound.
4.1. Introduction

1+1 REMPI has often been used to ionize analyte molecules prior to their mass spectrometric detection. In particular, 1+1 REMPI of jet-cooled molecules has been extensively studied because it is an elegant technique to sharpen absorption spectra of organic molecules while reaching a high selectivity (1-5). However, little has been reported so far about this mechanism as it is used in analytical techniques such as L2MS, that is in the case where the molecules are not jet-cooled and where widely varying ionization wavelengths are used. To fill this gap, we used standards to measure optical 1+1 REMPI spectra for 17 PAHs, at ionization wavelengths covering the complete range between 238 nm and 310 nm. This broad wavelength range has recently become available using optical parametric oscillator (OPO) lasers. The spectra we present below can be very useful to assess the ionization efficiency if using fixed wavelength lasers or dye lasers in L2MS (6-15) or related techniques such as 1+1 REMPI coupled with TOF-MS for the on-line analysis of room temperature gases (16-20) or 1+1 REMPI coupled with membrane introduction mass spectrometry for water analysis. The ultimate goal was to select suitable ionization wavelengths for selective isomer ionization. It turned out that this goal could only be partly achieved; we will discuss here the reasons for this finding and the possibilities that our results nevertheless offer. In particular, a much better interpretation of L2MS spectra obtained directly from more complex mixtures such as environmental samples is now possible.

4.2. Experimental section

All of the chemicals were purchased from either Chem Service Inc. (West Chester, Pa) or Aldrich (Switzerland) and had a purity of at least 95%. Stock solutions were prepared in methylene chloride (J. T. Baker, Holland) with concentrations around 20 mg/10 ml. The procedure described in Chapter 3 was used to prepare thin poly(vinyl chloride) (PVC, high molecular weight, Fluka, Switzerland) membranes containing the analytes that could be used to perform laser ablation. The L2MS instrument was run under the same conditions described in Chapter 3.
4.3. Results and discussion

4.3.1. UV-Energy dependence of the signals

The energy of the UV laser pulses is known to greatly influence the intensity of the signals in REMPI experiments so that an optimum energy setting had to be found. In addition, pulse-to-pulse energy fluctuations of the OPO laser made it necessary to record the energy of each ionization pulse to normalize the mass spectra.

The energy dependence discussed below follows the treatment by Johnson and Otis (27). If an unfocused UV beam is used, and in the absence of saturation, a quadratic dependence of the signal intensity \( S \) on the UV energy \( E \) is expected for a two-photon process with identical absorption cross sections for the ground state \( \sigma_1 \) and for the excited state \( \sigma_2 \): \( S \propto E^2 \). If, however, one of the two cross sections is much larger than the other one, the signal simply becomes linearly proportional to the energy: \( S \propto E \). The general case is \( S \propto E^{\sigma_1} \). To ensure good mass resolution, we had to use a slightly focused laser beam in our experiment. In this case, saturation of the ionization in the focus region may occur at elevated energies. If this happens, an increase of the laser intensity creates no more ions in the Rayleigh length. Rather, the ionization region begins to move out of the laser focus region. It can be shown that \( S \propto E^{\sigma_1} \), independent of how many photons are involved in the ionization. Spectroscopic studies require one to work below the saturation threshold, as was done for all of the spectroscopic data presented below.

The UV energy dependence of the L2MS signals was measured at an ionization wavelength of 255 nm for seven PAHs of various sizes (Figure 4.1). Two cases were observed. (a) The two smallest analytes, naphthalene and acenaphthene, were observed to exhibit a behavior close to \( S \propto E^2 \); this probably means that \( \sigma_1 = \sigma_2 \). (b) For all other PAHs (phenanthrene, fluoranthene, chrysene, benzo[a]pyrene, dibenz[a,h]anthracene), a linear behavior was found. At the laser energies used, no saturation was observed. Therefore, we interpret this finding as indicative for either \( \sigma_1 \gg \sigma_2 \) or \( \sigma_1 \ll \sigma_2 \). Another finding was that the signal intensities decreased when pulse energies greater than about 32 \( \mu \)J were applied; fragment ions not present at lower fluences simultaneously appeared in the mass spectra. This means that a third photon was absorbed, either by neutral molecules that have already absorbed two photons or by newly formed ions, and that this additional energy induces fragmentation. It is only possible to speculate why two different patterns of behavior are observed. The number of conjugated rings and differences in the electronic states accessed may play a role.
Therefore all of our spectroscopic measurements were performed using pulse energies of 25-30 μJ. The recorded mass spectra were normalized by dividing them by the energy of the UV pulses. This is completely justified for PAHs showing a linear energy dependence of the signal, i.e. for most of them. It is considered a good enough approximation for naphthalene and acenaphthene as long as the energies are kept in the well-defined window between 25 and 30 μJ, a range that allows sensitive detection of PAHs without leading to fragmentation. A strict data analysis would require the measurement of the power dependence at each wavelength. Although this may be of spectroscopic interest, it is definitely not an important step towards our goal of chemically analyzing complex mixtures.

4.3.2. 1+1 REMPI spectra

1+1 REMPI spectra were measured for all 17 PAHs using two mixture solutions, one containing eight analytes and the other ten analytes (Figure 4.2). Isomers were not present in the same solution. Coronene was present in both solutions. The data acquisition procedure was the following one. (i) Measure 8 single shot mass spectra at each wavelength. (ii) Normalize the single mass spectra by the energies of the
Figure 4.2. 1+1 REMPI spectra for 17 PAHs. Each point is the average of 8 measurements. The normalized units on the ordinates (signal/energy ablated amount) are mV/μJ·pmol). For example, 500 mV, 25 μJ and 0.2 pmol yield 100 normalized units. Coronene was measured twice.
corresponding UV pulse as described above. (iii) For each wavelength, average the peak heights of the eight mass spectra. (iv) Normalize the 1+1 REMPI spectra obtained for each compound by the number of moles calculated to be present in an ablation crater. This final step allowed the direct comparison of the spectra obtained for different analytes. The units used on the ordinate of the 1+1 REMPI spectra are mV/pmol·μJ.

**Precision.** Errors bars were not drawn on the graphs of Figure 4.2 in order not to overload them. Typical 95% confidence intervals are in the range of ± 15 %, less in the case of strong signals and more in the case of weak signals. The scattering of the points is mainly due to uncompensated pulse-to-pulse fluctuations of the IR laser. Another reason is a slight shift of the UV beam position when the wavelength is changed. The membrane is considered homogeneous enough not to cause scattering, as shown in the previous Chapter. These experimental uncertainties should be kept in mind when interpreting the spectra. Any vibronic structure of the bands can probably not be studied.

**Linewidth.** The 1+1 REMPI spectra exhibit widths of a few tens of nanometers. Therefore, the wavelength of the maxima is often not clearly defined. Rather, a range of a few nanometers where efficient ionization takes place can be given. The width is a consequence of the fact that the ablated analyte molecules are not cold. Hager et al. reported bands with 0.03 nm halfwidths by cooling the gaseous molecules in a supersonic jet (7). However, this technique caused significant losses due to dilution. Their detection limit was 0.5 pg; this is much higher than the one reached by L2MS (22, 23).

**Selective ionization of isomers.** A claim that is often made by users of resonance ionization methods is that the great selectivity inherent to the process allows to optically pick-out single compounds in a complex mixture. While this may be true for compounds with sharp optical lines, e.g. atoms or jet-cooled molecules, the validity of this claim is questionable for REMPI of room temperature gas-phase molecules. One question we want to address here is to what extent REMPI can be used for selective ionization of isomers. Two cases can be distinguished. (i) Take, for example, the isomer pairs phenanthrene and anthracene (m/z=178), and fluoranthene and pyrene (m/z=202). One of the two isomers is ionized much more efficiently than the other one, independent of the wavelength; only the ratio of the signals changes. Unambiguous identification and quantitation of such isomers is not really possible. Zare’s group have noted this difficulty before in the case of phenanthrene/anthracene. They simply assigned the peaks at mass 178 in their L2MS spectra to the isomer with the highest ionization efficiency, phenanthrene. (6, 22, 24). (ii) Consider the isomer pairs
benz[a]anthracene and chrysene (m/z=228), and benzo[b]fluoranthene and benzo[a]pyrene (m/z=252). Wavelengths that allow efficient absorption can be found for both isomers. However, the bands in the 1+1 REMPI spectra overlap considerably, preventing a clear distinction at a single wavelength. A strategy to alleviate this problem may take advantage of the different band structures by performing experiments at multiple fixed wavelengths. The data would then have to be processed using chemometric methods, similar to the data evaluation common in near infrared spectroscopy (25).

Comparison of 1+1 REMPI spectra to absorption spectra. If, on the one hand, the first photon absorption event is the rate limiting step of the ionization process (i.e. $\sigma_1 \ll \sigma_2$), then similarities are expected between the absorption or fluorescence excitation spectra and the 1+1 REMPI spectra. If, on the other hand, the second photon absorption event is the rate determining step (i.e. $\sigma_1 \gg \sigma_2$), then the spectroscopy of the molecules in the excited state is expected to dominate the spectrum. In the following, we will discuss the comparison between the experimental 1+1 REMPI spectra and the absorption spectra in solution taken from the literature (26-28). These references do not mention absolute extinction coefficients for fluorescence excitation spectra so that the closely related absorption spectra are used here. Table 4.1 summarizes the main characteristics of both types of spectra: the wavelengths of the maxima ($\lambda_{\text{max}}$) are given together with a value to characterize their intensities (extinction coefficient $\varepsilon(\lambda)$ for the absorption spectra and normalized signal intensity $S(\lambda)$ for the 1+1 REMPI spectra). The ionization potentials (IP) are indicated after transformation to the maximum wavelength with an energy high enough for two-photon ionization (29). This parameter should be kept in mind since ionization via 1+1 REMPI cannot be expected if the energy of two photons lies below the IP. Internal excitation resulting from the ablation process can however contribute to the energy necessary for ionization. The lifetime ($\tau_s$) of the lowest excited singlet state ($S_1$) is also given since efficient ionization requires this lifetime to be long enough to allow absorption of a second photon before relaxation. Data for $\tau_s$ can be determined in two different media: in a supersonic jet (1, 30, 31) or in solution (32). The supersonic jet is the environment that is closest to our measurement conditions but the $\tau_s$-values are generally published as part of detailed spectroscopic studies of only one or a few compounds. Very few such values are reported in the literature. The lifetimes in solution can differ greatly from jet data. Nevertheless, solution data for $\tau_s$ are given in the table for comparison. It has to be pointed out that the main relaxation mechanism from $S_1$ for PAHs in solution is not fluorescence but intersystem crossing, yielding molecules in the triplet state $T_1$. This state exhibits a long lifetime and can often not be ionized because its energy is too low
<table>
<thead>
<tr>
<th>Analyte</th>
<th>IP/2 (nm) [a]</th>
<th>(\tau_s) in jet (ns)</th>
<th>(\tau_s) in sol (ns) [e]</th>
<th>(\lambda_{\text{max}}(\text{abs})) (nm) [f]</th>
<th>(\lambda_{\text{max}}(\text{L2MS})) (nm) [g]</th>
<th>(\varepsilon(\lambda_{\text{max}})) [f]</th>
<th>(S(\lambda_{\text{max}})) [g]</th>
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<tr>
<td>Naphthalene</td>
<td>304.6</td>
<td>n.f.</td>
<td>105</td>
<td>276</td>
<td>260</td>
<td>0.67</td>
<td>40</td>
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<td>Acenaphthylene</td>
<td>301.7</td>
<td>n.f.</td>
<td>n.f.</td>
<td>&lt; 243 nm</td>
<td>243</td>
<td>&lt; 1</td>
<td>13</td>
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<tr>
<td>Acenaphthene</td>
<td>322.9</td>
<td>n.f.</td>
<td>46</td>
<td>298.3</td>
<td>288</td>
<td>0.9</td>
<td>34</td>
</tr>
<tr>
<td>Fluorene</td>
<td>314.7</td>
<td>n.f.</td>
<td>10</td>
<td>301</td>
<td>298</td>
<td>1.04</td>
<td>65</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>315.5</td>
<td>76 [b]</td>
<td>61</td>
<td>252</td>
<td>245</td>
<td>6.41</td>
<td>507</td>
</tr>
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<td>Anthracene</td>
<td>332.8</td>
<td>8 [b]</td>
<td>6</td>
<td>252</td>
<td>&lt; 250</td>
<td>20.8</td>
<td>150-250</td>
</tr>
<tr>
<td>Fluoranthenne</td>
<td>311.9</td>
<td>38 [c]</td>
<td>53</td>
<td>237</td>
<td>&lt; 260</td>
<td>4.49</td>
<td>&lt; 37</td>
</tr>
<tr>
<td>Pyrene</td>
<td>334.6</td>
<td>1400 [b]</td>
<td>650</td>
<td>241.5</td>
<td>&lt; 270</td>
<td>8.84</td>
<td>100-300</td>
</tr>
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<td>1-Methylpyrene</td>
<td>n.f.</td>
<td>n.f.</td>
<td>n.f.</td>
<td>n.f.</td>
<td>&lt; 275</td>
<td>n.f.</td>
<td>100-250</td>
</tr>
<tr>
<td>Benz[a]anthracene</td>
<td>333.7</td>
<td>n.f.</td>
<td>n.f.</td>
<td>289</td>
<td>&lt; 285 (max 265)</td>
<td>8.87</td>
<td>100-300</td>
</tr>
<tr>
<td>Chrysene</td>
<td>326.7</td>
<td>n.f.</td>
<td>45</td>
<td>269</td>
<td>&lt; 270 (max 254)</td>
<td>15.2</td>
<td>342</td>
</tr>
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<td>Benzo[b]fluoranthene</td>
<td>n.f.</td>
<td>n.f.</td>
<td>44</td>
<td>302 and below</td>
<td>&lt; 290 (max 250)</td>
<td>4.06</td>
<td>30-90</td>
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<tr>
<td>Benzo[a]pyrene</td>
<td>348.3</td>
<td>270 [d]</td>
<td>49</td>
<td>297 and below</td>
<td>&lt; 290 (max 260±5)</td>
<td>6.44</td>
<td>50-130</td>
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<td>3-Methylcholanthrene</td>
<td>n.f.</td>
<td>n.f.</td>
<td>n.f.</td>
<td>297.5</td>
<td>&lt; 295 (max 285)</td>
<td>9.33</td>
<td>50-110</td>
</tr>
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<td>336.0</td>
<td>n.f.</td>
<td>37</td>
<td>285</td>
<td>not resolved</td>
<td>6.61</td>
<td>-</td>
</tr>
<tr>
<td>Benzo[g,h,i]perylenne</td>
<td>346.8</td>
<td>n.f.</td>
<td>203</td>
<td>287</td>
<td>&lt; 290 (max 265±5)</td>
<td>9.07</td>
<td>50-120</td>
</tr>
<tr>
<td>Coronene</td>
<td>340.2</td>
<td>n.f.</td>
<td>320</td>
<td>301.9</td>
<td>not observed</td>
<td>26.29</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.1: Comparison of the features of the absorption spectra in solution and of the experimental 1+1 REMPI spectra. Units for the extinction coefficients \(\varepsilon(\lambda)\): l mol\(^{-1}\) cm\(^{1}\) 10\(^{4}\). Units for the 1+1 REMPI signals: see text. n.f.: not found. IP/2 is the value for half the ionization potential, expressed in wavelength units. \(\tau_s\) is the excited singlet state lifetime. References: [a]: ref. (27); [b]: ref. (1); [c]: ref. (28); [d]: ref. (29); [e]: ref. (30); [f]: refs. (24) (25) (26); [g]: this work.
to allow ionization with a single additional photon. Also, Franck-Condon factors for ionization out of the T₁ state are unfavorable.

The following observations from Table 4.1 are interesting for discussion: (i) In both absorption and 1+1 REMPI spectra, the bands move towards lower energies as the size of the chromophore units increases. This behavior is easily explained with a simple “particle in a box” picture. (ii) The position of the maximum is often shifted by a few nanometers towards the blue in the 1+1 REMPI spectra with respect to the absorption spectra. This difference is explained by the fact that the analytes are in the gas phase and not in solution. (iii) The agreement between absorption and 1+1 REMPI spectra is very good for naphthalene, acenaphthylene, acenaphthene and fluorene: the peaks are at the same position and a good correlation is observed between the extinction coefficients ε(λ) and the corresponding normalized signal intensities S(λ). This would mean that the first photon absorption dominates the 2-photon ionization spectrum for small two ring PAHs. This statement, however, needs to be qualified in light of the study of the measured UV-energy dependence of the signal intensities. A nearly quadratic dependence was observed, indicating that both photon absorptions are involved. (iv) The agreement between absorption and 1+1 REMPI spectra is not as good for the heaviest analytes, although similarities are obvious. Striking differences are: (a) The very strong band at 301 nm in the absorption spectrum of coronene is not observed at all in the 1+1 REMPI spectrum although the ionization potential is low enough. This is an extreme case of a more general observation that the large analytes, despite extinction coefficients at least as high as the ones of the small ones, generally yield less intense signals. The somewhat broader peaks in the mass spectra cannot fully explain that observation. A better explanation may be that the absorption of the first photon brings the large analytes to a highly vibrationally excited level where the Franck-Condon factors become less advantageous for the absorption of a second photon. (b) The isomers phenanthrene and anthracene both exhibit a maximum of their absorption spectra at the same wavelength (252 nm), with an intensity 3 times higher for anthracene than for phenanthrene. However, the ionization efficiency of phenanthrene is much greater than that of anthracene. (c) The isomers fluoranthene and pyrene exhibit rather similar absorption spectra, with a slightly weaker absorption for fluoranthene than for pyrene; on the other hand, the ionization efficiency of fluoranthene is about one order of magnitude lower than that of pyrene. This observation and the previous one can be explained by considering the lifetime of the excited singlet state S₁ that is about ten times longer for phenanthrene vs. anthracene and for pyrene vs. fluoranthene. (d) The differences in the 1+1 REMPI spectra of the isomers benz[a]anthracene and chrysene are obvious, nevertheless much smaller than in
the absorption spectra. (v) For all PAHs studied, the ionization potentials are low enough to allow two-photon ionization in the studied range. Such considerations are not a valid argument to explain for example why it is not possible to ionize fluoranthene around 288 nm despite a strong absorption band. (vi) It has been proposed that one-laser excitation near 280 nm induces significant non-resonant ionization of several large aromatic molecules, most notably of pyrene (7). We have not observed a strong signal for pyrene in this range and are therefore confident that the ions were effectively generated by 1+1 REMPI.

4.3.3 1+1 REMPI of PAH-related compounds

Our initial goal was to study environmentally important classes of compounds such as nitro-PAHs or S-PACs. Preliminary measurements were conducted using the nitro-PAHs 2-nitrofluorene, 9-nitroanthracene, 1-nitropyrene, and 6-nitrochrysene, and the S-PAC dibenzothiophene. Measurements at various ionization wavelengths between 230 nm and 300 nm never resulted in the detection of any signal for any of the four nitro-PAHs. In addition, the ionization efficiency for dibenzothiophene was found to be more than one order of magnitude lower than for PAHs with an average ionization efficiency. These results clearly question interpretations found in the literature for complex mass spectra recorded from environmental samples such as aerosol particles (33, 34). The short lifetime of nitro-PAHs and S-PACs in their excited state (35) is probably responsible for the difficulty to ionize them. Comparative measurements were conducted using 30 ps laser pulses from the ps-YAG laser instead of 8 ns pulses from the MOPO. This resulted in a slightly improved ionization efficiency for dibenzothiophene, but even under these conditions no signal could be detected for the nitro-PAHs.

4.4 Conclusion

We have used two-step laser mass spectrometry to study the 1+1 REMPI process for 17 polycyclic aromatic hydrocarbons. First, the dependence of the ion yield on the energy of the ionization laser pulses was determined. Then, 1+1 REMPI spectra were recorded between 238 nm and 310 nm. The spectral intensity was normalized to the
laser energy and to the amount of ablated analyte, allowing comparison with absorption spectra taken from the literature. Our observations can be summarized by saying that an intense absorption band is a necessary condition for efficient ionization, but that it is only one of them. The properties of the excited singlet state \( S_1 \) seem to have the greatest influence on the ion yield in the case of compounds with three or more rings. A long \( S_1 \) lifetime is essential for efficient photoionization via 1+1 REMPI. The difference between the photon energy and the energy of the 0-0 absorption transition probably influences the absorption of the second photon by determining the Franck-Condon factor for ionization. The excitation spectrum of \( S_1 \) cannot be simply considered as a continuum. Finally, we can now better understand the previously stated observation that one of the two photon absorption events is rate determining in the ionization of PAFIs with three or more rings and can propose that it is the second one.

4.5. References

5. Characterization of Aerosol Emission Sources

Major aerosol emission sources include Diesel vehicles, gasoline vehicles, residential heating, wood fires, and cigarettes. The chemical characterization of the particles is essential to the identification of their origin. This Chapter describes how this task can be accomplished using L2MS. Only small sample quantities were necessary and the measurements were performed within minutes. L2MS was found to be a valuable alternative to more laborious chemical analysis techniques that often require extensive sample preparation. Tracer mass spectral patterns were identified, notably based on specific polycyclic aromatic hydrocarbons (PAHs) and other polycyclic aromatic compounds (PACs). Their specificity allows the identification of different particle emission sources at sites of exposure.
5.1. Introduction

The importance of aerosol particles in environmental processes (1, 2) and the potential health hazards associated with them (3) have made the identification of their emission sources an essential aspect of air monitoring. The techniques used most often to achieve this task, chromatography and atomic spectroscopy, have been described extensively in Chapter 1. These methods require a tedious and time-consuming sample preparation as well as the collection of relatively large sample quantities. This Chapter establishes L2MS as a valuable alternative for more rapid identification of aerosol emission sources using smaller sample quantities.

Several anthropogenic emission sources, among them Diesel vehicles, gasoline vehicles, residential heating, wood fires, and cigarettes, have been shown to contribute significantly to the total aerosol load (4-8). Our study using L2MS aimed to classify exhaust particles from these sources according to their organic chemical composition. The emphasis of our work was to rapidly identify various emission sources in a qualitative way using specific mass spectral patterns and tracer compounds such as polycyclic aromatic compounds (PACs). Our strategy based on emission profiles will be further validated for the reliable identification of different types of particle emission sources at sites of exposure in the next Chapter.

5.2. Experimental Section

5.2.1. Sampling apparatus

Pieces of standard quartz fiber filter (Pallflex, Putnam, CT) of about 1 cm² area were mounted on custom designed filter holders (Figure 5.1) used both for sampling (10-20 L/min) and for L2MS measurements (see below). The possibility to record L2MS spectra without any further manipulation greatly simplified sample handling and minimized the risk of contamination. The sampling time was adjusted between several seconds and several minutes in order to obtain good quality mass spectra for emission sources with strongly varying particulate emission intensities.

Samples were stored for no longer than 20 hours in individual containers (13 mm diameter x 32 mm, high-density polyethylene), under argon, at 2°C, and in the dark.
Control experiments were performed by collecting two samples simultaneously. One of them was measured immediately after while the other one was stored for 48 hours before analysis. There were no discernible differences in their mass spectra.

Figure 5.1. Custom designed filter holder used for both sampling and L2MS measurements. During sampling, the assembly is mounted at the end of a tube connected to a flowmeter and to a vacuum pump. (A) Expanded view before assembly of the holder, filter, and retaining ring. The air is pumped through the three slits of the holder at a rate of 10-20 L/min. (B) Mounted assembly, with particles retained on the filter at the location of the slits. The custom designed filter holders can be rotated so that a new spot is exposed at each laser shot (see text).

5.2.2. Sampling of emission sources

The strategy for the evaluation of the emission sources was to study them under real working conditions, and to sample their contributions at the very location where particles are given off into the atmosphere. Therefore no test benches were used. Vehicles were sampled by mounting the filter holders at a few centimeters distance from the exhaust pipes. The sampled exhaust gases had already significantly cooled down by the time they were sampled. Therefore, the sampled particles can be assumed to represent the ones found in the atmosphere. A transformer was used to power the pump
using the battery of the vehicle, thus allowing sampling of vehicles in motion. Various driving cycles were selected that are representative of the different conditions under which vehicles are typically used, as described in Table 5.1. Two gasoline-powered cars with manual gears, one automatic gasoline-powered car, and one medium-duty Diesel truck were sampled.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Description</th>
<th>Distance (km)</th>
<th>Speed (km/h)</th>
<th>Sampling Duration (Min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>idle 1</td>
<td>800 rounds/min</td>
<td>0</td>
<td>0</td>
<td>1 - 10</td>
</tr>
<tr>
<td>idle 2</td>
<td>2000 rounds/min</td>
<td>0</td>
<td>0</td>
<td>1 - 10</td>
</tr>
<tr>
<td>urban 1</td>
<td>slightly uphill</td>
<td>2.2</td>
<td>0 - 50</td>
<td>6 - 8</td>
</tr>
<tr>
<td></td>
<td>altitude difference 50 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>about 5 traffic lights</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>urban 2</td>
<td>slightly downhill</td>
<td>1.9</td>
<td>0 - 50</td>
<td>5 - 8</td>
</tr>
<tr>
<td></td>
<td>altitude difference 50 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>about 5 traffic lights</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>uphill</td>
<td>mountain road with curves</td>
<td>1.4</td>
<td>20 - 80</td>
<td>2 - 3</td>
</tr>
<tr>
<td></td>
<td>altitude difference 150 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>downhill</td>
<td>mountain road with curves</td>
<td>1.4</td>
<td>20 - 80</td>
<td>2 - 3</td>
</tr>
<tr>
<td></td>
<td>altitude difference 150 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>highway</td>
<td>flat</td>
<td>4.0</td>
<td>120</td>
<td>4</td>
</tr>
<tr>
<td>freeway</td>
<td>flat</td>
<td>1.5</td>
<td>80</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Table 5.1. Driving cycles for the characterization of vehicle emission profiles.**

Twelve residential heating systems were randomly selected within a 1 km² area of the city center of Zurich. Samples were collected either directly from the chimney on the roof or from openings in the chimney just under the roof. The furnaces are typically located in the basement so that the sampled aerosol particles had already cooled down at least partially prior to sampling.

Other emission sources such as open wood fires or cigarettes were sampled by directly placing the filter holder in the smoke.
5.2.3. L2MS system

The home-built L2MS system described in Chapter 2 was used. The post-ionization laser was tuned to 250 nm; this wavelength was found to be well-suited for the ionization of aromatic compounds of various sizes, as demonstrated in Chapter 4. A pyroelectric power detector (ED-100 with EDX-1 amplifier, Gentec, Sainte-Foy, Canada) was placed behind the ion source to measure the energy of each laser pulse; the recorded values were used to normalize the mass spectra, as described previously. A delay of 14 μs between both lasers was found to yield maximal signal intensities.

Rotating the aerosol samples by 5 degrees between each shot of the desorption laser allowed a new spot to be exposed at each laser shot (see Figure 5.1). Preliminary studies proved that a single laser shot was sufficient to desorb nearly all detectable analytes at the target spot. The data from shots where the desorption laser was aimed at the crosspieces of the filter holders, as well as the data where the ionization laser intensity was not within a suitable range, were discarded as explained in Chapter 4. Approximately 50 shots out of the initial 72 were averaged to yield the final spectra. Typical standard deviations of the averaged peak intensities were around 10-20%.

5.3. Results and Discussion

5.3.1. Diesel trucks

It should be first mentioned that in Switzerland virtually all cars are powered by gasoline engines. Most of them are now equipped with catalytic converters. Trucks are therefore by far the main contributors to Diesel exhaust. For the emission of the medium-duty Diesel truck, varying driving cycles induced little variation in the mass spectra with respect to the most dominant peaks, namely the ones assigned to alkylphenanthrenes (m/z = 192, 206, 220, 234). Their distribution remained almost constant. No peaks were observed in the lower mass range. The mass spectrum in Figure 5.2A is a typical example, collected during an urban cycle. Note here that anthracene and alkylanthracenes are discriminated against their phenanthrene-based isomers due to a greatly reduced L2MS ionization efficiency of the latter (see Chapter 4). The presence of four-ring PAH skeletons (m/z = 202: pyrene, fluoranthene, ...; m/z = 228: chrysene, benz[a]anthracene, ...) can be observed among the other peaks present.
in the mass spectra. The sequence of peaks at m/z = 194, 208, and 222 could in principle be caused either by partially hydrogenated alkylphenanthrenes or by oxygenated polycyclic aromatic hydrocarbons (OPAHs) such as polycyclic aromatic ketones (PAKs) or polycyclic aromatic quinones (PAQs). The mass differences caused by strongly varying numbers of hydrogen atoms are considerable, for example 208.12465 Da for hydrogenated C2-alkylphenanthrenes vs. 208.051881 for OPAHs at the same nominal mass. The high resolution of the mass spectra allowed the unambiguous assignment of the peaks to OPAHs (m/z = 194: anthrone, phenanthrone, 2-methylfluorene-9-one, ...; m/z = 208: anthraquinone, phenanthrenequinone, ...; m/z = 222: methylanthraquinones, methylphenanthrenequinones, ...), as demonstrated in detail in Appendix B. This finding is in good agreement with previous reports on the detection of large amounts of OPAHs in urban aerosol particles (9), especially from Diesel engines (4). It does not provide additional evidence for the presence of hydrogenated alkylphenanthrenes in Diesel exhaust particles (10) as suggested by other authors (11). It should also be mentioned here that the high sensitivity of L2MS for OPAHs has been demonstrated previously (12). The inset in Figure 5.2A shows how the relative intensity of selected peaks compared to the intensity of the dominant one at m/z = 206 (C2-alkylphenanthrenes) depends on the driving cycle. A higher load on the engine (highway driving at maximal speed or going uphill on a mountain road) enhances the formation or survival of PAH skeletons relative to alkylphenanthrenes. This finding is exemplified by the ratio of the peaks at m/z = 202 (pyrene and isomers) and at m/z = 206. A lower load on the engine (standing vehicle, mountain road downhill) not only diminishes the formation of PAH skeletons, but simultaneously induces the formation of larger amounts of OPAHs. This parameter is displayed using the example of the ratio of the peaks at m/z = 208 and at m/z = 206. Hence, in the case of Diesel engines, the combustion process quite significantly influences the chemical composition of the exhaust. Our observations seem to indicate that optimal burning conditions allow increased oxidation of the PAHs. Simultaneously, the probability of incomplete combustion of organic compounds, such as the naturally present alkylphenanthrenes, that would yield higher amounts of unsubstituted PAHs appears to be lowered. For comparison, Figure 5.2B displays the L2MS spectrum of the National Institute of Standards (NIST) Standard Reference Material (SRM) 1650 (Diesel particulate matter) suspended in clean air that was pumped through one of our filters. Despite a different engine and a different sampling technique, there is a strong similarity with the Diesel particulate matter collected from our truck. Again, the dominant peaks are the ones assigned to phenanthrene and alkylphenanthrenes, although the overall degree of alkylation of phenanthrene is slightly lower.
Figure 5.2. (A) Typical L2MS spectrum from particles emitted by a Diesel truck. Inset: an increased load on the truck engine enhances the formation of PAH skeletons, while a decreased load increases the formation of OPAHs. Both effects correlate. ▲: Idle 1 and 2 cycles. □: Urban 1 cycle (slightly uphill). ■: Urban 2 cycle (slightly downhill). ○: Mountain 1 cycle (uphill). ●: Mountain 2 cycle (downhill). ◇: Highway cycle. The point for NIST SRM 1650 (different engine) is plotted only for comparison. (B) L2MS spectrum of NIST SRM 1650.
5.3.2. Gasoline-powered cars

It was observed during sampling that the total particulate emission is much weaker for cars compared with Diesel exhaust, which is in agreement with other studies such as (4), and with our own field studies (13). In the mass spectra, the dependence of the emission profile of the same vehicle on the driving cycle (Table 5.1) was stronger for cars than for Diesel trucks. Nevertheless, driving the same cycle with varying styles (aggressively vs. quietly, slowing down using the brakes vs. using the engine, ...) did not yield major differences, and similar mass spectra were obtained from different cars. Car emission profiles were usually dominated by a pattern in the mass range between m/z = 178 and 234 that includes the peaks of phenanthrene (178), alkylphenanthrenes (192, 206, 220, 234), and four-ring PAHs (202, 228). This pattern was virtually the only one present in the exhaust of idling vehicles, as shown by Figure 5.3A. Although these peaks are also characteristic for Diesel engine exhaust, they appear here with completely different relative intensities. In particular, the degree of alkylation of phenanthrene was much higher in the case of Diesel exhaust. Note also that, in contrast to what was observed for Diesel trucks, only low amounts of OPAHs were observed from gasoline-powered cars, which is in agreement with findings by other authors (4).

Under certain driving conditions, a second pattern was also observed from gasoline engine exhaust in the higher mass range. Figures 5.3B and 5.3C represent two cases with different intensities of this second pattern relative to the first one depicted in Figure 5.3A. The causes for the formation of the peaks of the second pattern remain largely unknown. Driving downhill was found to enhance their formation, and they were detected in almost all samples. The sequence of peaks with mass differences of 14 (addition of one methylene group) at the masses 217, 231, 245, 259 is remarkable in Figures 5.3B and 5.3C since strong peaks at odd masses, characteristic for nitrogen-containing aromatic compounds, are rather uncommon in L2MS spectra of environmental samples. Especially important is the fact that intense peaks at these masses were quite systematically observed from gasoline-powered cars, but never from any other emission source, therefore making them ideal tracer compounds. These peaks can possibly be assigned to alkylbenzocarbazoles naturally present in crude oil, shale oil (14, 15), and kerogens (16). These compounds may survive the combustion process under certain driving cycles. Other possible assignments could be amino or cyano PAH derivatives (17).
Figure 5.3. L2MS spectra from particles emitted by gasoline-powered cars. (A) Idle 1 cycle. (B) Urban 1 cycle (slightly uphill). (C) Urban 2 cycle (slightly downhill). Both traffic cycles (B) and (C) included a few stops at traffic lights during which the engine was idling.
5.3.3. Residential heating

Residential heating in Switzerland is usually carried out either by burning natural gas or extra-light oil, while almost no coal is used anymore. Gas heating systems are known to have very low particulate emissions (18). This was confirmed by several measurements that yielded spectra close to field blanks (data not shown). However, it was occasionally observed that exhaust from a gas furnace can resuspend soot when its chimney is shared with one that is used for an oil furnace at other times. The particulate emission of a properly functioning oil heating system remains weak, which makes them unlikely to be a major urban aerosol emission source. However, some of the arbitrarily chosen oil furnaces were found to be poorly functioning and to have much stronger particulate emission intensities. They therefore did not meet the Swiss regulations based on the Bacharach number, a simple method to assess emission intensities based on the darkening of a filter. Figure 5.4A shows the emission profile of a properly functioning (in terms of Bacharach number) oil heating system. The mass spectrum is dominated by PAH skeletons (m/z = 178, 202, 228, 252, 276, ...), by alkylphenanthrenes (192, 206, 220, 234, 248), and by alkylanthaquinones/alkylphenanthrenequinones OPAHs (222, 236, 250, ...). No major differences were observed between properly functioning oil furnaces whose chimney had or had not been swept recently. This indicated that the emission is dominated by the actually burnt material and not by what is accumulated on chimney walls or produced through wall interactions. Figure 5.4B displays the emission profile of an oil burner sampled immediately after it had been switched on. The intense particulate emission, which was much stronger than in the previous case, was dominated by peaks assigned to phenanthrene and alkylphenanthrenes. The close similarity to Diesel engine particle emission can be understood by the similarity of the fuels used. Poorly functioning oil heating systems (data not shown) exhibited mass spectra that were closer to the case of Figure 5.4B than to the one of Figure 5.4A. The degree of alkylation of phenanthrene was however much lower in those cases, an extreme case being the one of a furnace that produced particulate matter in which virtually only phenanthrene was detected. Nothing at all was detected in a sample collected from the chimney of the main waste incineration plant of the city of Zurich. Obviously all particulate matter is efficiently trapped in the incinerator’s exhaust cleaning system.
5.3.4. Wood fires

Figure 5.5 displays emission profiles for wood burning under different conditions. A striking feature is their complexity, with a larger number of intense peaks than in the case of the previously described mass spectra. The presence of peaks at higher mass should also be pointed out, for example in the case of beech wood burning in a residential furnace (Figure 5.5B) where dominant peaks were found even above 350 Da.
Figure 5.5. L2MS spectra of particles emitted by wood fires. (A) Open wood fire, fresh pine branches. (B) Residential wood furnace, dry beech logs.

Note that the heavier compounds are generally discriminated against in L2MS spectra due to reduced ionization efficiency (see Chapter 4). The especially high peak at m/z = 234 (C₄-alkylphenanthrenes) in Figure 5.5A is very likely due to retene (1-methyl-7-isopropylphenanthrene), an isoprene derivative commonly used as a tracer for burning coniferous wood (6). The high amount of this C₄-alkylphenanthrene is particularly remarkable because the peaks for the other Cₙ-alkylphenanthrenes are rather low as compared to the emission profiles described previously. As opposed to the emission
profiles described earlier, several peaks are observed in the mass range below 175 Da which is characteristic for substituted benzenes. These peaks can be rationalized as lignin pyrolysis products, lignans, and resin acids, substance classes that have been described as specific tracers of plants in emissions from biomass combustion (6, 19). The comparison with these references allows one to tentatively assign the peak at m/z = 168 to vanillic acid (C_9H_8O_4), the one at m/z = 180 to guaiacylacetone (C_{10}H_{12}O_3), the one at m/z = 194 to 3,4-dimethoxyphenylacetone (C_{11}H_{13}O_3), the one at m/z = 196 to 1-(3,5-dimethoxy-4-hydroxyphenyl)ethanone and homoveratric acid (C_{10}H_{12}O_4), the one at m/z = 198 to syringic acid (C_{9}H_{10}O_5), and the one at m/z = 210 to 1-syringylethanone or 1-(3,4,5-trimethoxyphenyl)ethanone (C_{10}H_{14}O_4).

5.3.5. Cigarettes

Figures 5.6A and 5.6B display mass spectra for cigarette smoke sampled at two different steps of the smoking process. A comparison between two brands of cigarettes did not yield major changes in the mass spectra. Differences between exhaled cigarette smoke (Figure 5.6A) and a freely burning cigarette (Figure 5.6B) are obvious and may be explained by different combustion conditions as well as by retention of certain particles in the filters or in the respiratory system of the smoker. The intensity of the peaks at mass m/z + 1 relative to their neighboring even mass m/z is remarkable as well. It is higher than for any other emission source and can not simply be explained by contributions of the 13C-isotopomers. We believe that large amounts of N-containing heterocycles are present, conversion products of nicotine (5). Several peaks can be found in the lower mass range that might be assigned to alkaloids such as myosmine (m/z = 146) or harman (m/z = 182), compounds that were identified in reference (5). These peaks can be considered as highly specific tracers when using L2MS for the identification of aerosol emission sources. Although cigarettes are not a dominant outdoor aerosol source, the measurements reported here indicate that L2MS can also serve as an analytical tool for indoor air quality surveillance and occupational health studies. The ability of L2MS to not only identify substance families such as “PAH skeletons”, “alkylphenanthrenes”, or “OPAHs” but also specific tracer compounds is further exemplified in Figure 5.6C, the mass spectrum of exhaled cannabis smoke: the intense peak at m/z = 310 is most likely due to the substance cannabinol, a compound known to be present in substantial amounts in cannabis.
Figure 5.6. L2MS spectra of cigarette smoke particles. (A) Exhaled cigarette. (B) Burning cigarette. (C) Exhaled cannabis cigarette. The strong peak at m/z = 310 is assigned to cannabinoil (structure shown in inset).
<table>
<thead>
<tr>
<th>Emission source</th>
<th>Dominant peaks</th>
<th>Ratio Phen./ ( \Sigma(C_n-APhs) )</th>
<th>Specific identification patterns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel engine</td>
<td>- ( C_n-APhs ) (( n \leq 5 ))&lt;br&gt;- Phen.</td>
<td>0.05 - 0.2</td>
<td>- High proportion of ( C_n-APhs ) ( (n \geq 2) )</td>
</tr>
<tr>
<td>Gasoline engine</td>
<td>- Phen.  &lt;br&gt;- ( C_n-APhs ) (( n \leq 5 ))</td>
<td>0.4 - 0.8</td>
<td>- Peaks at m/z = 231, 245, 259</td>
</tr>
<tr>
<td>Gas heating system</td>
<td>- None</td>
<td>n.c.</td>
<td>-</td>
</tr>
<tr>
<td>Properly functioning oil heating system</td>
<td>- Weak particulate emission</td>
<td>0.4</td>
<td>- High levels of alkylanthraquinones/alkylphenanthrene-quinones OPAHs</td>
</tr>
<tr>
<td>Poorly functioning oil heating system</td>
<td>- Phen.  &lt;br&gt;- ( C_n-APhs ) (( n \leq 2 ))</td>
<td>0.8 - (&gt; 1)</td>
<td>- High proportion of ( C_n-APhs ) ( (n \geq 2) )</td>
</tr>
<tr>
<td>Open wood fire</td>
<td>- Wide range</td>
<td>n.c.</td>
<td>- Retene ( (m/z = 234) )&lt;br&gt;- Peaks in the range m/z = 120 - 175</td>
</tr>
<tr>
<td>Residential wood furnace</td>
<td>- m/z = 180, 194, n.c.  &lt;br&gt;- 196, 210, 228</td>
<td>- Peaks at high masses ( (m/z = 326, 356, 368...) )&lt;br&gt;- Peaks in the range m/z = 120 - 175</td>
<td></td>
</tr>
<tr>
<td>Cigarette</td>
<td>- Wide range</td>
<td>n.c.</td>
<td>- Small aromatic compounds ( (m/z = 132, 146, 160, 182) )&lt;br&gt;- Peaks in the range m/z = 120 - 175</td>
</tr>
<tr>
<td>Cannabis</td>
<td>- Wide range</td>
<td>n.c.</td>
<td>- Cannabinol peak ( m/z = 310 )&lt;br&gt;- Peaks in the range m/z = 120 - 175</td>
</tr>
</tbody>
</table>

**Table 5.2. Summary of the main features of the sampled emission sources.**

(Phen. = Phenanthrene, APhs = Alkylphenanthrenes). The Ratio Phen./ \( \Sigma(C_n-APhs) \) was only calculated in the mass spectra where these peaks are dominant (n.c.: not calculated).
5.4. Conclusion

The mass spectra displayed in Figures 5.2 through 5.6 whose features are summarized in Table 5.2 prove that L2MS does allow the identification of aerosol emission sources based on the organic chemical composition of the particles. Specific tracer peaks that are dominant only in the mass spectra generated by samples stemming from a single emission source can often be identified. For example, this is the case for gasoline-powered cars: the compounds of the $m/z = 231$ family are not found at such a high intensity in samples from any other emission source. Another example is cigarette smoke particles, where specific alkaloids can be detected. Furthermore, even for cases where no single tracer compound is found, specific mass spectral patterns typical for a single emission source are observed. This is the case for Diesel trucks that emit aerosol particles in which the degree of alkylation of phenanthrene is especially high. These findings open the way for the identification of the dominant particle emission sources in mixed aerosol samples collected at sites of exposure. L2MS, requiring only small sample quantities and short measurement times, makes such studies possible with a high time resolution. This is the object of the next Chapter.

Supporting information: The complete set of 75 L2MS spectra recorded from emission sources can be found in Appendix A.

5.5. References

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(16) Zhan, Q.; Zenobi, R.; Buseck, P. R.; Teerman, S. Energy & Fuels 1997, 11, 144-149.


6. Behavior of Aerosol-Bound PACs over the Course of Single Days

The dynamic behavior of aerosol-bound polycyclic aromatic hydrocarbons (PAHs) and other polycyclic aromatic compounds (PACs) in urban air was studied over the course of several whole days, both next to a street with heavy traffic and in a city park. Two-step laser mass spectrometry allowed measurements with 15 minute time resolution. Large variations in particle concentration and chemical composition were observed, reflecting the contributions from Diesel trucks and gasoline-powered cars to urban aerosols. These sources were clearly identified using the specific mass spectral patterns identified in Chapter 5. The photochemically induced decay of oxygenated polycyclic aromatic hydrocarbons (OPAHs) was observed in real time. Rapid speciation of aerosol-bound organic carbon is now possible to complement data on routinely monitored atmospheric pollutants.


6.1. Introduction

Carbonaceous aerosol particles given off during the combustion of organic material are known to play a key role in environmental processes (1, 2) and to be hazardous for human health (3). Their physical properties and their chemical composition however can strongly vary depending on their emission source. These can include Diesel vehicles, gasoline vehicles, residential heating, wood fires, or cigarettes (4-8). The relative contributions of different emission sources to the total aerosol load at urban sites of exposure change on a short time-scale and are dependent for example on traffic rush hours, residential heating cycles, and meteorological parameters such as wind intensity, precipitation, and solar irradiation. A true understanding of the processes that aerosols take part in therefore requires characterization measurements to be performed on a time scale similar to these dynamic changes. The chromatographic and atomic spectroscopic techniques commonly used to determine the chemical composition of particles have been described in Chapter 1. They require tedious sample preparation as well as the collection of relatively large sample quantities on filters over extended periods of time, generally 24 hours, even in polluted urban areas. They are therefore not well-suited for the real-time identification of emission sources. Studies with a time resolution on the scale of one or two hours remain exceptions (9-11).

Single particle laser desorption/ionization mass spectrometry (LDI-MS) (12-14), also described in Chapter 1, does allow measurements with a high time resolution. However, this method is not adapted to the speciation of carbonaceous aerosol particles, in particular because characteristic organic tracer analytes (4-7) fragment extensively during LDI-MS analysis. Furthermore, direct comparison with data obtained using conventional methods for monitoring gaseous or particle-bound atmospheric pollutants is not possible.

L2MS appeared to offer an exciting potential to identify the relevant urban aerosol emission sources in real time. L2MS uses samples collected on filters and therefore allows quantitative analyses of particle-bound organic compounds, as demonstrated in Chapter 3. In addition, data can be obtained within minutes through direct measurements, with a sensitivity in the low attomole range for some analyte compounds. L2MS therefore permits the analysis of a large number of samples, collected during short periods of time.

In the previous Chapter, we have shown how L2MS allows the identification of various aerosol emission sources based on tracer mass spectral patterns, notably specific
polycyclic aromatic compounds (PACs). This Chapter now reports on field studies at urban sites of exposure during which these tracers were monitored with a 15 minute time resolution over the course of several whole days. First, principal component analysis (PCA) was performed on the data, which confirmed the reliability of the identified tracers. The different developments of the relative amounts of the tracer compounds then allowed the evaluation of the importance of the contributions of different emission sources as a function of time.

6.2. Experimental Section

6.2.1. Sampling technique

The custom designed filter holders described previously in Chapter 5 were used for both sampling and L2MS measurements without further manipulation. The samples were stored under argon, at 2 °C, in the dark, and were measured within less than 20 hours.

6.2.2. Study of the variation during the day

Measurement campaigns were conducted in the summer (June and July 1998, two weekdays and two Sundays) as well as in the winter (January and February 1999, two weekdays and two Sundays) in Zurich, Switzerland. The buildings are not heated in summer so that this emission source is only relevant during the winter. Sampling was performed with 15 minute time resolution at daytime (from about 4:30 to 21:30), and 30 minute time resolution at night time. The first sampling site was located in the city center next to a street with heavy urban and transit traffic (about 30,000 vehicles a day) and is therefore typical for street emissions. Comparative urban background measurements were simultaneously performed in a city park enclosed by buildings. The distance between the two sites is about 900 meters. Both sites are part of the Swiss national air pollution monitoring network (Nationales Beobachtungsnetz für Luftfremdstoffe, NABEL) so that records of all main standard gaseous pollutants, of black carbon (BC), and of weather data were available for comparison. Furthermore, trucks and cars passing at the street site were counted.
6.2.3. L2MS system

The L2MS measurements were performed on the home-built system described in Chapter 2, run under identical conditions as for the characterization of the emission sources reported in Chapter 5. The peak intensities were averaged over about 50 shots on different spots for each sample. Their standard deviations were around 10-20%.

6.2.4. Principal component analysis

Principal component analysis (PCA) is a technique to reduce the dimensionality of a data set. PCA aims to determine few principal components (PC) that can explain as much of the total variance in the measured data as possible. The PCs are linear combinations of the observed variables, mass spectral peak intensities in the case of this study. After matrix calculations, a loading is determined that quantifies the correlation between each pair of observed variable and new PC. A detailed description of the mathematical principles of PCA is beyond the scope of this Chapter and can be found in the literature (15-17). PCA was performed using the data processing software SPLUS (MathSoft, Inc.). After keeping only those PCs with an eigenvalue greater than 70% of the mean of all eigenvalues, orthogonal (varimax) rotation of the loading matrix was performed in order to simplify the interpretation of the results.

6.3. Results and Discussion

6.3.1. Principal component analysis

Figure 6.1 shows as an example one of the 1070 averaged L2MS spectra recorded during the measurement campaigns. The peaks previously identified as emission source specific tracers, together with the ones that were found with high signal intensities in the emission profiles reported in Chapter 5, were selected for PCA. The peaks at several of the PAH skeleton masses and a few whose intensities were remarkably high in the spectrum displayed in Figure 6.1 or in other mass spectra were included in this data set as well, resulting in a selection of 26 peaks.
Figure 6.1. Example of a L2MS spectrum. Street site, Wednesday, July 1998, sampling between 5:45 and 5:59. Average of 49 shots on different spots of the filter sample. The peaks used for PCA are marked.


■ : PAHs (202, 216, 226, 228, 252, 266, 276, 278, 302, 326).


Performing PCA on all 1070 mass spectra recorded during the summer and the winter field campaigns, at both sampling sites, led to the identification of four PCs. The results are displayed in Figure 6.2. A large data set was selected to allow a clearer interpretation. This was possible because the same classes of particles are found at both sampling sites with only their relative proportions varying, and because there were no major differences between the results of the summer and winter field campaigns. Similar PCs were observed using reduced data sets, for example by analyzing the winter and the summer data separately or by considering only one sampling site at a time.
Figure 6.2. Results of the PCA on all of the 1070 mass spectra recorded during the summer and winter field campaigns, at the two sampling sites.

■: PAHs (202, 216, 226, 228, 232, 266, 276, 278, 302, 326).
*: m/z = 231 family (231, 245, 259). ▲: Oxygenated PAHs (194, 208, 222, 236). ◇: Other peaks (218, 242, 254, 268). See text for the assignment of the PCs.
**PC1.** PC1 is dominated by phenanthrene and especially by the alkylphenanthrenes. PC1 is in very good agreement with the Diesel truck emission displayed in Figure 5.2. It therefore most likely reflects the contribution of this emission source.

**PC2.** PC2 correlates mostly with PAH skeletons. However, none of the studied emission sources, including vehicles, residential heating, wood fires, and cigarettes, was observed to be dominated by PAH skeletons exclusively. Rather than being directly linked to a well-defined emission source, this PC could possibly be assigned to road dust. Road dust is a very complex variable because practically any anthropogenic or biogenic source can add to the dust accumulation on the road surfaces. Contributors include among others particulate vehicle exhaust, lubricating oil residues, tire wear particles, weathered street surface particles, and brake lining particles (18). High PAH levels in road dust were reported by Rogge et al. (18). Furthermore, Harrison et al. (19) have shown that the largest fraction of most PAHs actually stems from road dust, and not directly from vehicle exhaust.

**PC3.** Only the peaks of the m/z = 231 family (231, 245, 259) exhibit a strong correlation with PC3. These are the ones that were identified in Chapter 5 as highly specific tracers for gasoline-powered cars so that this PC can be assigned to them (Figure 5.3). The distinction between trucks and cars is quite clear cut in Switzerland because virtually all cars are powered by gasoline engines equipped with catalytic converters. Trucks are therefore by far the main contributors to Diesel exhaust.

**PC4.** The last of the four PCs, PC4, is the least substance class specific. It is nevertheless dominated by oxygenated polycyclic aromatic hydrocarbons (OPAHs) such as polycyclic aromatic ketones (PAKs) or polycyclic aromatic quinones (PAQs). PC4 could possibly be assigned to open wood fires or properly functioning oil heating systems where these compounds were found at high levels. However, this interpretation does not seem satisfactory since a high correlation with alkylphenanthrenes should also be observed, which is not the case. Rather, PC4 seems to be representative of meteorological parameters, especially the solar irradiance, to which the levels of the OPAHs seem to be especially sensitive. This will be discussed in more detail below.

**Summary.** Two studies based on completely independent strategies, the direct measurement of emission samples described in Chapter 5 on one hand and PCA analysis of samples collected at sites of exposure on the other hand, have shown excellent agreement and resulted in the identification of the same tracer mass spectral patterns. This confirms the suitability of L2MS for the on-site and time-resolved identification of the contributing aerosol emission sources.
6.3.2. Comparison of L2MS vs. Black carbon

Figure 6.3. Temporal developments recorded at the street site on Wednesday, July 15, 1998. (A) Sum of 26 L2MS signals, monitored by L2MS (15 min. intervals). (B) Black carbon, monitored by an aethalometer (10 min. intervals).
Figure 6.3A shows the variation of a parameter we define here as S26, the sum of the 26 ion signals selected for PCA (Figure 6.1), for July 15 (Wednesday) at the street site. The dynamic behavior is striking, with a sharp increase starting around 5:00. The lowest values were observed at night when the traffic intensity was low. For comparison, Figure 6.3B displays the black carbon (BC) concentration monitored simultaneously by an aethalometer (AE-10, Magee Scientific Co., Berkeley, CA). Both temporal developments look quite similar. Even spikes can be observed in both curves at the same times, for example around 7:30, 9:45, or 15:00. Hence, S26 is found to correlate with the total amount of carbonaceous particles present. This result demonstrates the ability of L2MS to provide accurate data that can be directly and quantitatively compared to data obtained using standard monitoring techniques. A rather fast spreading of the combustion aerosols within the area under investigation can be implied based on the observation that no lag was observed between the rush hours and the increase of the pollutant signals at the park site (data not shown).

The peak around 20:45 in Figure 6.3, which is present in the BC curve and especially intense in the S26 curve, deserves further discussion. This data point is not an experimental artifact. The high intensity is only due to certain mass spectral peaks. All of them correspond to dominant peaks in the previously reported emission profile of Diesel engine exhaust (Figure 5.2). Therefore, the high levels observed for these analytes at 20:45 were probably caused by one or several vehicles with poorly running Diesel engines that passed by the sampling site at that particular time. This type of observation clearly proves that L2MS can provide much more detailed information than BC. Indeed, the parameter S26, although being useful to provide information on the concentration of carbonaceous particles, loses the emission source specificity of its separate components. It is much more interesting to consider the temporal development of single masses, as will be shown now.

6.3.3. Temporal development of trucks and car tracers

Similar behaviors of these tracers were observed in winter and in summer, although the total particle concentration was higher in winter. This confirms what we observed during the characterization of the emission sources (Chapter 5), namely that the low particulate emission generated by residential heating makes this source unlikely to be an important one in Zurich.
Figure 6.4. Variation of the proportion of a truck tracer (ion signal at m/z = 206) over the course of entire days. (A) Street site, Wednesday, February 10, 1999. (B) Park site, Wednesday, February 10, 1999. (C) Street site, Sunday, January 24, 1999. (D) Park site, Sunday, January 24, 1999.

Figures 6.4 and 6.5 display the temporal evolution of the proportion of tracer peaks for trucks (Figure 6.4) and cars (Figure 6.5) at both sites, on a weekday (Wednesday, February 10, 1999) and on a Sunday (January 24, 1999). The ion signal at m/z = 206, which corresponds to C₂-alkylphenanthrenes, was selected to represent trucks because it was the dominant one in the Diesel exhaust emission profile (Figure 5.2), and also the one with the highest correlation with the principal component related to trucks (Figure 6.2). The ion signal at m/z = 231, which may correspond to methylbenzocarbazoles, was selected to represent cars because it was the most intense.
one in the car emission profiles, and therefore the one most likely to be detected at remote sites where the concentration of car aerosol may be low. The displayed proportions were calculated by dividing the ion signals at m/z = 206 and 231 by the summed ion signal from S26. The S26 factor correlates with the concentration of carbonaceous particles in air (see above). This normalization was necessary to provide a clearer comparison between the behavior of different analytes at different sites on different days.
To better understand the behavior of the tracer peaks, Figure 6.6 displays the traffic numbers recorded for trucks and cars at the street site on a weekday (Wednesday, February 10, 1999) and on a Sunday (February 14, 1999). The traffic patterns observed for trucks are due to the strict air quality and traffic regulations in Switzerland. Truck traffic is banned on Sundays as well as on working days between 22:00 and 06:00. Virtually no variation in traffic patterns was observed between different weekdays and between different Sundays (data not shown) so that the data plotted in Figure 6.6C and 6.6D can reasonably be used to discuss the L2MS data recorded on Sunday, January 24 for which no traffic numbers were available.


Let us first compare the street emissions on the weekday to the ones on the Sunday. The concentration of the truck tracer remained at low levels during the whole Sunday (Figure 6.4C) as well as during the night on Wednesday (Figure 6.4A), for those
periods when truck traffic is forbidden. In contrast, a significant increase was observed during the day on Wednesday. Similar patterns were also observed for the other alkylphenanthrenes observed in the Diesel emission profile (m/z = 192, 220, ...) and for the other sampling days in winter and in summer. The behavior of the car tracer was complementary: while an almost constant level was observed on Wednesday (Figure 6.5A), a strong increase was observed on Sunday between 10:00 and 20:00, that is when car traffic was most intense (Figure 6.5C). It should be noted that increases in the proportion of the respective tracers occurring to a similar extent, that is roughly to a doubling of the proportion, were in one case caused by about 200 trucks per hour and in the other case by about 1600 cars per hour. This confirms that particulate emissions are much stronger from trucks than from cars. It also explains why the daytime increase in the proportion of the car tracer (Figure 6.5A) is partly suppressed by the concomitant increase of S26 caused by the truck tracer peaks.

The discussion can now be extended to the data for the urban background at the park site recorded in parallel to the street emission measurements. Figure 6.4B shows that the daytime proportion of dimethylphenanthrenes is also enhanced at the park site, although to a lesser extent than at the street site. This evidences the transport and dilution by mixing of the particles between both sampling sites. The fact that Diesel exhaust particles are not as dominant at the park site as at the street site may be due to the fact that an important fraction of the aerosol particles that reach the park site originate from other emission sources, in particular from streets in the vicinity which mainly carry local car traffic, and not only from a few transit streets with a large number of trucks. Hence, data collected close to a strong emission source can not be considered to be representative of urban background sites, not even nearby ones. Official air pollution monitoring sites should therefore not only be selected near emission sources but also at locations where the population is more typically exposed to air pollution. A similar conclusion can be reached from Figure 6.5D: the high level of the car tracer observed during daytime at the street site is hardly observed at all at the park site.

6.3.4. Direct observation of atmospheric photochemical processes

Figure 6.7A displays the temporal variation of the proportion of the OPAHs at m/z = 208 on Sunday, January 24, 1999 at the park site. All other suggested OPAHs (m/z = 194: anthrone, phenanthrone; m/z = 208: anthraquinone, phenanthrenequinone; m/z = 222: C₁-alkyl-208; m/z = 236: C₂-alkyl-208) exhibited the same behavior. Table 6.1 summarizes the behaviors observed for all 26 components of S26 during the event. The
Figure 6.7. Temporal developments at the park site, Sunday, January 24, 1999. (A) Proportion of a typical oxygenated PAH (ion signal at m/z = 208). (B) Proportion of the ion signal at m/z = 178 (phenanthrene). (C) \(\times\): Balanced irradiance. \(\odot\): \(O_3\). (D) \(\bullet\): NO. \(\square\): \(NO_2\). The data were recorded simultaneously and at the same location as for the Figures 4D (truck tracer) and 5D (car tracer).
dramatic decrease of the proportion of the OPAHs between 10:30 and 20:00 took place in parallel with a major increase of pyrene and especially phenanthrene as shown by Figure 6.7B. The behavior of the OPAHs on that day was especially remarkable because it was the only case during our measurement campaigns where major changes in the levels of certain analytes occurred to the same extent at both the park site (Figure 6.7A) and the street site (data not shown). This is a clear indication that the observed variations were not simply caused by changes in the relative intensity of the particulate emission of urban vehicular sources. In this case the changes would have been more pronounced at the street site than at the park site. Note that for this specific reason, the increase of the proportion of phenanthrene was less pronounced at the street site (data not shown) than at the park site (Figure 6.7B).

<table>
<thead>
<tr>
<th>Behavior</th>
<th>Analytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major decrease</td>
<td>m/z = 194, 208, 222, 236 OPAHs</td>
</tr>
<tr>
<td></td>
<td>C₄-alkylphenanthrenes</td>
</tr>
<tr>
<td>Medium decrease</td>
<td>m/z = 242, 268 compounds</td>
</tr>
<tr>
<td>Minor decrease</td>
<td>m/z = 218, 254 compounds</td>
</tr>
<tr>
<td></td>
<td>C₂- and C₁-alkylphenanthrenes</td>
</tr>
<tr>
<td></td>
<td>m/z = 266, 278 PAHs</td>
</tr>
<tr>
<td>Constant</td>
<td>m/z = 231, 245, 259 car tracers</td>
</tr>
<tr>
<td></td>
<td>m/z = 226, 228, 252, 276, 302, 326 PAHs</td>
</tr>
<tr>
<td>Minor increase</td>
<td>m/z = 216 PAHs</td>
</tr>
<tr>
<td></td>
<td>C₁-alkylphenanthrenes</td>
</tr>
<tr>
<td>Major increase</td>
<td>m/z = 178 (phenanthrene)</td>
</tr>
<tr>
<td></td>
<td>m/z = 202 (pyrene)</td>
</tr>
</tbody>
</table>

Table 6.1. Variation of the proportion of the components of S26 on January 24, 1999 between 10:30 and 20:00 at the park site.

A possible explanation for the behaviors observed in Figures 6.7A and 6.7B could be that the total aerosol load as quantified by S26 at that particular time was dominated and significantly increased by the contribution from an unusually intense remote or ubiquitous emission source such as an explosion. This hypothesis can however be ruled out because a strong increase was only observed for phenanthrene and pyrene among all the components of S26. No emission source was identified neither by us (see Chapter 5) nor, to the best of our knowledge, by other authors, that gives off particles loaded with high amounts of these two compounds exclusively. Furthermore, such a strong
contribution from an emission source would have induced an increase of the BC concentration and of the overall intensity of S26, which were not observed (data not shown).

It is therefore more than likely that degradation of the OPAHs was due to atmospheric chemical reactions induced by intense solar irradiance. The especially high balanced irradiance in the afternoon of January 24, 1999 (Figure 6.7C) initiated photochemical ozone formation from NO\textsubscript{2} and O\textsubscript{3} between 10:00 and 16:30. This reaction and the simultaneous ozone degradation through its reaction with NO to regenerate NO\textsubscript{2}, form a cycle (20, 21). This mechanism, together with the partial disappearance of the inversion layer during the day and the corresponding enhanced dilution, explains the variation of the concentrations of O\textsubscript{3} (Figure 6.7C), NO (Figure 6.7D) and NO\textsubscript{2} (Figure 6.7D) during the afternoon. The NO concentration started to rise again after the disappearance of the sun at 16:30, and reached its initial level around 20:00. The close similarity between the evolution of the NO concentration and that of the OPAH proportion, with virtually simultaneous start and finish of the event, seems to indicate that these compounds may undergo similar degradation reactions, such as oxidation by O\textsubscript{3} or by OH-radicals. The detailed reaction pathways leading to degradation of the OPAHs however remain unknown. A better understanding of these processes would also contribute elements to explain the increases in proportion of phenanthrene and pyrene which seem to be intimately linked with them.

6.4. Conclusion

Our results clearly demonstrate that by monitoring the sum parameter S26, L2MS provides quantitative information similar to the BC concentration (Figure 6.3). In addition, the possibility to follow the variation of tracers at specific masses makes the identification of emission sources possible. The use of tracers for this purpose has already been described in detail by several researchers (4, 9, 11). This report, however, introduces a new analytical tool that can accomplish the same task with much higher time resolution. The agreement between the new L2MS data shown here and the results simultaneously obtained for other major pollutants and traffic intensity confirms the suitability of L2MS for real-world studies. Further developments of the method for routine operation could include the design of a small, portable field instrument, the use of alternative ionization laser wavelengths adapted to organic compounds other than PAHs, and an interface that would allow automated on-site measurements immediately
after aerosol sampling.

The results presented here are not only useful for studying aerosol emission sources. The fact that the relative contributions of the ion signals at the different masses do not remain constant implies that the molecular composition of the organic carbon fraction of urban aerosol particles is highly variable in time. The possibility to use L2MS to measure these dynamic changes in the molecular composition of aerosol particle surfaces with high time resolution opens new avenues for studying emission and transport dynamics, heterogeneous chemistry, and health hazards linked to aerosol particles.

Supporting information: The complete experimental results on which this Chapter is based can be found in Appendix C. They include air pollutant concentrations, L2MS results, weather data, and traffic numbers, for both sampling sites and for each one of the four summertime and four wintertime measurement days.

6.5. References

(2) Finlayson-Pitts, B. J.; Pitts, J. N. Science 1997, 276, 1045.


7. Behavior of Aerosol-Bound PACs over the Course of a Year

The dynamic behavior of aerosol-bound polycyclic aromatic hydrocarbons (PAHs) and other polycyclic aromatic compounds (PACs) in air was studied over the course of a whole year at four sites representative of the different types of aerosol exposure in Switzerland. This study was part of a collaboration between several research institutes in order to achieve the most complete chemical characterization of the aerosol samples as possible. Two-step laser mass spectrometry allowed the measurement of about 1000 samples, which would not have been possible within a reasonable amount of time using chromatographic techniques. A strong seasonal dependence of the amount of aerosol-bound PACs was observed. L2MS-independent artifacts caused by an inappropriate sampling procedure prevented a quantitation of all emission source specific tracers identified in Chapter 5. Adequate sampling strategies that should allow this task to be accomplished in future studies are discussed.
7.1. Introduction

Studies of the behavior of aerosol-bound polycyclic aromatic hydrocarbons (PAHs) and other polycyclic aromatic compounds (PACs) over the course of days have been reported in Chapter 6. The observed changes in chemical composition were found to correlate with discrete events such as the passing of a truck next to the sampling site, or with events taking place during periods of time not exceeding a few hours, such as rush hour traffic. The observation that increased solar irradiance during one afternoon had dramatic effects on the amount of oxygenated PAHs (OPAHs) in the particles was clear evidence for the close link between meteorology and aerosol composition. Measurements on a much longer time-scale, that is during a whole year, are therefore necessary to achieve a more complete understanding of the processes that aerosol particles take part in. For example, comparing data collected during wintertime with data collected during summertime when the solar irradiance and the ozone concentration are higher could contribute new elements to explain the relationship between OPAHs and the solar irradiance.

The “Particle Emissions of Road Traffic” project of the Swiss National Research Program 41 “Transport and environment: Interaction” (NRP-41) started in August 1998 and will be terminated in July 2000. It aims at identifying the major sources of air particulate matter (PM$_{10}$: particles with an aerodynamic diameter smaller than 10 μm; PM$_{2.5}$: particles with an aerodynamic diameter smaller than 2.5 μm) and at quantifying their contributions at different locations in Switzerland. For this purpose, four sites were selected that are differently affected by local pollution sources. PM$_{10}$ and PM$_{2.5}$ samples were collected at each of these sites over the course of a whole year. A collaboration between several research institutes was started in order to achieve a chemical characterization of the PM$_{10}$ and PM$_{2.5}$ samples that would be as complete as possible. Analyses include: (i) Determination of elemental and organic carbon concentrations (EC and OC) with the coulometric method (1). (ii) Determination of the concentrations of water-soluble inorganic ions (SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$, Cl$^-$) by ion-chromatography (2-4). (iii) Analysis of trace elements by inductively coupled plasma mass spectrometry (ICP-MS) (4-6). Source identification and quantitative determination of source impacts will be carried out with the use of a receptor model, a technique which consists of analyzing the generated data set by means of factor analysis (7-10). Although quantitative determination of organic tracers characteristic for various emission sources (11-19) would have been very useful, none were planned initially because performing the approximately 1000 analyses necessary using the classical chromatographic techniques described in Chapter 1 was impossible.
for reasons of both time and costs. The variation of aerosol-bound organic compounds over the course of one year using chromatographic techniques was investigated by other authors. For example, Harrison et al. analyzed 55 samples collected over single days at one sampling site (20), and Rogge et al. analyzed 48 samples collected over one-month periods at four sampling sites (21).

Measuring 1000 samples by L2MS is possible within less than 100 work hours. The possibility to perform highly sensitive and quantitative analyses on aerosol particles has been demonstrated in Chapter 6. Therefore, joining the NRP-41 project was an ideal opportunity to establish L2MS as a competitive analytical technique by filling the gap in the conventional techniques for aerosol analysis, and to simultaneously study the variation of the organic composition of aerosol particles on the time scale of a year. This Chapter reports on the results of the L2MS measurements of the NRP-41 samples. The applicability of L2MS to this type of analyses is demonstrated, and the L2MS-independent sampling problems that caused the data to be of restricted use in this case are discussed.

7.2. Experimental Section

7.2.1. Sampling sites

Four different sites were selected that are representative of the various types of aerosol exposure in Switzerland. All of them are part of the Swiss national air pollution monitoring network (NABEL). The site in Bern is located next to a road with heavy traffic. It is similar to the street site described in Chapter 6 but less influenced by trucks as the road is not part of a transit axis. The site in Basel is suburban and located about 2 km from the city center. The site in Chaumont is located in a rural area. It is located about 7 km away from the next city and is elevated (1140 m a.s.l.) so that it is sometimes above the inversion layer in winter. Finally, the site in Zurich is the park site described in Chapter 6, typical for urban background.

7.2.2. Study of the variation during the year

Sampling was performed between February 1998 and January 1999. Although a
sample was collected every day, only about every fourth one was effectively measured for the NRP-41 project. Note that January 1, 1998 was defined as day #1 in all Figures.

The samples were collected using high volume samplers and standard quartz fiber filters 15 cm in diameter (Schleicher & Schuell, Keene, NH) mounted on typical holders. Note that the filters were heated for two hours at 600 °C and then preconditioned for 48 hours at 22 °C and at 50% relative humidity prior to sampling. During the sampling campaigns, the filters were changed automatically at midnight every day, and they remained at approximately 20 °C in the air-conditioned sampling devices until they were picked up, generally about twice a month. The filters were then conditioned at 22 °C and at 50% relative humidity to ensure a reliable determination of the mass of the sampled particles. The pieces cut out of the filters for L2MS analysis were stored in the dark until they were measured. The ones after about day #300 were additionally stored at -18 °C. Control experiments were performed to assess the importance of the storage temperature. They revealed no discernible changes between filter pieces stored at -18 °C and filter pieces cut from the same sample but kept at room temperature. This indicated that sample alteration, if any, took place in the high volume samplers and during conditioning rather than during storage (see below). The filter pieces for L2MS measurements were circular, 14 mm in diameter, and were directly mounted onto the sample holder.

7.2.3. L2MS system

The L2MS measurements were performed on the home-built system described in Chapter 2, run under identical conditions as for the measurements reported in Chapters 5 and 6. The peak intensities were averaged over about 30 shots on different spots for each sample. Their standard deviations were around 10-20%.

Unlike what was done for the other studies reported earlier in this thesis, the measurement conditions could not be kept constant for all measurements displayed in this Chapter. The filter samples collected at different locations during different seasons were loaded with aerosol quantities varying over two orders of magnitude. In most cases, the IR absorption of the samples was not dominated by the constant absorbance of the filter material as was the case for the weakly loaded samples used for the studies reported in Chapters 5 and 6. Instead, it was dominated by the stronger absorbance of the particles themselves. This required the IR lens (focal length 50 mm) to be moved slightly out of its original position to prevent plasma formation due to too high an
energy density when measuring the samples with the strongest absorption, a process that would destroy the analytes. Therefore, the position of the IR lens was tuned for each sample just below the threshold for plasma formation to ensure measurement conditions that would be as constant as possible while maximizing the desorption efficiency from the target spot. More than 90% of the measurements were performed with the lens position varying by no more than ±1 mm, and the variability was smaller within series of samples collected from the same site. The changes in diameter of the desorption spot could theoretically be calculated using equations found in the literature assuming an ideal Gaussian laser beam. However, the CO$_2$ laser we used was not ideal so that the equations are not applicable. For this reason, and because the correction terms would be expected to be small anyway, no correction was done to compensate for the shifts of the IR lens.

7.3. Results and discussion

7.3.1. Recovery from the high volume filters

Due to the procedure used to sample the aerosols and to condition the filters, the sampled particles were stored during several weeks or even months at room temperature and exposed to moist air. Although this is not a major problem in the case of the analysis of non-volatile and non-reactive inorganic species, it appeared to be a potential cause for major artifacts in the L2MS measurements. To avoid this problem, other authors performing similar studies using gas chromatography stored their samples in glass jars in complete darkness at -70°C (20), similarly to how we stored the samples used for the studies reported in Chapters 5 and 6.

To assess the recovery of the 26 analytes that constitute S26, and to allow a detailed identification of the contributing carbonaceous aerosol emission sources (see Chapter 6), the mass spectra recorded from the NRP-41 high volume filters were compared with the corresponding mass spectra summed over all of the measurements with 15 minute time resolution reported in Chapter 6. The latter were tentatively assumed not to be affected by losses. For each analyte, a recovery was defined by Equation 7.1.

\[
\text{Recovery} = \frac{\text{Signal}_{\text{NRP-41}}}{\sum \text{Signals}_{\text{daily measurements}}} \quad \text{(Eq. 7.1)}
\]
Comparisons were possible for July 15, 1998 and January 24, February 4, February 10, and February 14, 1999. A very good agreement was found between all five days. As an example, Figure 7.1 displays the recoveries determined for Sunday, February 14, 1999. For an easier interpretation of the data, the values were scaled so that the peak with the highest recovery would exhibit 100% recovery.

Figure 7.1. Recovery of the 26 components of S26 according to Equation 7.1. Zurich, February 14, 1999.

- : PAHs (202, 216, 226, 228, 252, 266, 276, 278, 302, 326).

PAHs. The PAHs at m/z = 252 and 266 are among the compounds with the highest recovery. The lighter PAHs, and in particular phenanthrene and pyrene, however exhibit more than a 60% of loss. This finding is easily explained by the high vapor pressure of these compounds, and their sublimation during the extended storage at room temperature. The reason for the losses of the heavier PAHs, in particular the ones at m/z = 302 and 326 which are characterized by low vapor pressures that should not allow them to disappear by sublimation, is unclear.

C_n-Alkylphenanthrenes (Truck tracers). The high vapor pressure of these compounds also caused extensive losses. Therefore, the variation of the proportion of the truck tracers over the course of a year can not be studied.


\[ m/z = 231 \text{ family (Car tracers).} \] No definite structural interpretation for these peaks could be found so that the causes for their disappearance remain unknown. The losses that exceed 50% also prevent the variation of the car tracers over the course of a year to be studied.

\textit{Oxygenated PAHs.} All four suggested OPAHs were among the compounds that exhibited the highest recoveries. One may propose that the high recovery observed for these compounds is actually an artifact generated by the oxidation of other compounds to OPAHs during sample storage that could be caused, for example, by moist air. This hypothesis however seems unlikely as the recovery does not exceed the one of the \( m/z = 252 \) and 266 PAHs.

Therefore, the sum parameter \( S_{26} \) could not be used for the study over the course of a year as it was used for the study over the course of single days. \( S_{26} \) had to be replaced by \( S_{5} \), a variable that is only composed by analytes that did not exhibit losses, defined here as the sum of the 5 ion signals at \( m/z = 194, 208, 252, 266, \) and 268. Only the temporal development of these 5 analytes could be reliably studied, which means that none of the emission source specific tracers identified in Chapter 5 were available.

7.3.2. Variation of PM\(_{10}\) during the year

Figure 7.2 displays the variation of the sum parameter \( S_{5} \) and of the proportion of three of its components for the PM\(_{10}\) fraction collected at the Zurich site. The behaviors of the OPAHs at \( m/z = 194 \) and of the PAHs at \( m/z = 266 \) were qualitatively identical to the behaviors of the OPAHs at \( m/z = 208 \) and of the PAHs at \( m/z = 252 \) respectively and were not displayed on Figure 7.2 in order not to overload it. The results found for the PM\(_{10}\) fraction collected at the Zurich site were very similar to the ones for the PM\(_{10}\) fractions collected at the Basel and the Chaumont sites displayed in Appendix D so that the following discussion applies to these two sites as well. The only obvious difference is that the intensity of \( S_{5} \) was about 10 times higher for the suburban and urban background sites of Basel and Zurich than for the rural site of Chaumont. This close similarity is rather surprising when considering that the Chaumont site is exposed to aerosol emission sources very different from the ones at the two other sites. It could be caused by the non-specificity of the components of \( S_{5} \) displayed on Figure 7.2.

A strong seasonal variation was observed for the \( S_{5} \) intensity measured for the PM\(_{10}\) fraction collected at the Zurich site (Figure 7.2, top), with about ten times lower values observed in summer than in winter. This finding is in good agreement with
Figure 7.2. Variation of S5 (top) and of the proportion of three of its components in PM$_{10}$ (bottom), Zurich. Day #1: January 1, 1998. Day #366: January 1, 1999. Sampling was performed between February 1998 and January 1999.
Figure 7.3. Variation of S5 (top) and of the proportion of three of its components in PM$_{10}$ (bottom), Bern. Day #1: January 1, 1998. Day #366: January 1, 1999. Sampling was performed between February 1998 and January 1999.
similar studies conducted using gas chromatography. For example, Schläpfer et al. studied in 1994 the sixteen priority PAHs of the US-EPA at four sites in Switzerland and observed similar major decreases during summertime, the extent of which was much more pronounced for the PAHs above mass 228 Da than for the more volatile ones below mass 228 (22). Also, Rogge et al. (21) observed in data from 1982 major decreases during summertime for benz[ghi]perylene, 7H-benzo[d,e]anthracene-7-one, 6H-benzo[c,d]pyrene-6-one, and retene at four sites in California (27). A possible cause for the decrease during summertime could be that the total particulate emissions during that season are weaker due to the absence of heating. This interpretation however seems unlikely as the furnaces were observed to have weak particulate emissions (Chapter 5) and not to significantly affect the aerosol composition even in an urban environment (Chapter 6). Meteorological factors seem to be a more likely explanation as an enhanced dilution, faster photochemical degradation reactions, and shortened residence time of the particles in the atmosphere are expected during summertime.

The proportions of the components of S5 measured for the PM$_{10}$ fraction collected at the Zurich site (Figure 7.2 bottom) remained roughly constant throughout the year, although a weak decrease of the proportion of the m/z = 208 OPAHs seems to have taken place during summertime. This finding could possibly indicate a constant composition of the carbonaceous fraction of PM$_{10}$ and therefore could mean that the chemical composition of the aerosol particles is not influenced by seasonal climate changes. This interpretation however is subject to caution. It appears reasonable in the case of the primary aerosols at the Zurich site which is primarily exposed to the same traffic and industrial aerosol emission sources throughout the year. It appears less likely in the case of the secondary aerosols collected at the remote site of Chaumont where some alterations of the chemical composition due to the long transport distance and residence time in the atmosphere would be expected. Indeed, another cause for the constant behavior of the proportion of the components of S5 could again simply be that these compounds are not specific for any emission source and independent from the atmospheric processes undergone by their carrier particles.

Figure 7.3 displays the variation of the sum parameter S5 and of the proportion of three of its components for the PM$_{10}$ fraction collected at the Bern site. The intensity of S5 (Figure 7.3 top) appears to be less influenced by seasonal changes than in the cases of Basel, Chaumont, and Zurich (Figure 7.2 top) but this is due to a measurement artifact. The filters collected at that site located next to a street with intense traffic were loaded with such high amounts of particles that a single laser shot was no longer sufficient to completely desorb the analytes from the target spot. Therefore, saturation
occurred, which prevented quantitative measurements to be performed at that site. This is a clear indication that the sampling technique was not appropriate.

This artifact however probably does not affect the reliability of the measured proportions of the components of S5 (Figure 7.3 bottom). The patterns observed at the Bern site were markedly different than the ones observed at the three other sites. In particular, the proportion of the OPAHs as represented by the ones at m/z = 208 exhibited a much stronger seasonal dependence, the summertime values being only one half of the wintertime values. This finding can be compared with the observation described in section 6.3.4 that intense solar irradiance during one winter afternoon induced a dramatic decrease of the proportion of OPAHs in the aerosol particles. In the present case, similar photochemical processes leading to the degradation of the OPAHs seem to have taken place at summertime when the solar irradiance was high. Note that the proportion of OPAHs at Bern during summertime is similar to the one at the three other sites throughout the year, and that the seasonal behavior is caused by higher wintertime values. No explanation could be found for the differences at the Bern site compared to the other sites.

7.3.3. Winter 1999 campaign, Zurich

An intense measurement campaign was performed for the Zurich site between January 17, 1999 and February 15, 1999 during which all the PM$_{10}$ samples were analyzed to study the relationship mentioned above between the L2MS results and the meteorology in more detail. Figure 7.4A describes the weather during that period. After the sunny and warm days #381 to #385, an inversion layer formed that disappeared on day #389. Precipitations, mostly snow, occurred between days #392 and #396 that were interrupted by more sunny periods. The precipitations resumed between days #401 and #405 after the partly covered days #397 to #400, while the final period between days #406 and #411 was partly sunny with temperatures not exceeding 0 °C.

Figure 7.5 displays the results of a few analyses performed on the aerosol particles. The black carbon (BC) concentration (Figure 7.5A) peaked during the inversion layer days #385 and #389 and during the covered days #397 to #400, most likely due to reduced air mixing and dilution. The sum L2MS parameter S5 (Figure 7.5B) was observed to roughly correlate with the BC concentration after day #391. This observation is similar to the conclusion drawn in section 6.3.2 that established the sum parameter S26 as a valuable alternative to the BC concentration monitored by an
Figure 7.4. Weather during the winter 1999 campaign in Zurich. (A) Description of the weather. S-R: Mixed snow and rain. D.R.: Drizzling rain. Lines connect measurements during same days. (B) Temperature and atmospheric pressure. (C) Sunshine duration and precipitation.
Figure 7.5. Selected aerosol data collected during the winter 1999 campaign in Zurich. (A) Black carbon concentration, calculated by averaging the 30 minute values recorded by an aethalometer. (B) S5 for the PM$_{10}$ fraction. (C) Proportion of three components of S5.
aethalometer. No clear trend was observed in the variation of the proportions of the components of S5 (Figure 7.5B). One might however observe that the concentration of the OPAHs, as shown by the curve for the OPAHs at m/z = 208, appears to be lower on those days when precipitations occurred.

Major discrepancies between S5 and the BC concentration were observed during the foggy days #386 to #388. One explanation for this could be the especially strong IR absorbance of these three samples that made it necessary to shift the IR lens two millimeters away from the usual position as explained earlier. The mechanisms that caused the peak intensity to decrease however are unclear. Tuning the IR lens to the position just below the threshold for plasma formation, as was done for all other samples, should have provided an identical energy density at the sample surface. The only difference from the other samples should then have been that the target spot was larger, but this is not a good explanation for a weaker signal intensity. It might have been better to simply keep the measurement conditions constant and not to perform any tuning of the coordinate of the IR lens if it had been possible. This example proves again the importance of the sampling method to obtain satisfactory L2MS results. An appropriate technique, the one using the sample holders pictured in Figure 5.1 to collect very thin layers of particles, made the studies reported in Chapters 5 and 6 possible. The current example shows that collecting thick particle layers on filters is not a suitable technique. Note finally that the explanation of the discrepancies between the BC concentration and S5 as caused by the shift of the IR lens is only one hypothesis. The fact that the three samples discussed here exhibited an especially high absorbance proves that their chemical composition had unique characteristics as well, the nature of which however could not be determined.

7.3.4. PM$_{2.5}$ - PM$_{10}$ distribution

Figure 7.6 displays the evolution of the ratio of the intensity of the S5 sum parameter in the PM$_{2.5}$ fraction divided by the one in the PM$_{10}$ fraction during the course of the year at the four sampling sites. It seems that the amount of S5 analytes present in the PM$_{2.5}$ fraction is on the same order of magnitude as the amount present in the PM$_{10}$ fraction, which would be in agreement with previous studies (23-26). The strong scattering of the data however prevents any definitive interpretation to be made, and renders comparisons of the particle-size distributions of the different analytes impossible. The data collected for the days after about day #250, often indicating higher amounts of analytes in the PM$_{2.5}$ fraction than in the PM$_{10}$ fraction, evidence the
occurrence of measurement artifacts. Their nature remains undetermined.

Figure 7.6. PM$_{2.5}$ - PM$_{10}$ distribution of the components of S5 during the course of the year at the four sampling sites.

7.4. Conclusion

L2MS allowed speciated organic chemical analysis to be performed on about 1000 aerosol samples in the framework of a project where none was originally planned because of financial and time constraints. This represents about 20 times more analyses than reported in similar studies using gas chromatography (20-22). A strong seasonal dependence of the amount of aerosol-bound polycyclic aromatic compounds was observed at four sampling sites representative of the different types of aerosol exposure in Switzerland. This finding is in agreement with other studies (21, 22).

The importance of the sampling technique for optimal L2MS analyses was demonstrated. Sampling during 24 hour periods using high volume samplers as was done during this study was found not to be suitable because the particle layers on the
surface of the filters are often too thick. This prevented reproducible desorption by the IR laser due to the too strongly varying IR absorption properties of samples, and in extreme cases made complete desorption from the target spot impossible using a single laser shot, therefore preventing reliable quantitative analyses to be performed. This problem could however easily be avoided by using an optimized sampling technique, such as the one described in section 5.2.1 and used for the studies reported in Chapters 5 and 6.

Also, it was shown that adequate storage of the aerosol samples after their collection is critical. They have to be kept in the dark, under inert atmosphere, and at a low temperature, as was done during the studies reported in Chapters 5 and 6. Leaving the filter samples during two weeks in the automatic sampling devices prior to conditioning them under water vapor, although appropriate for most analyses originally planned for the project, is a cause for major losses of the volatile and possibly labile organic compounds measured by L2MS. This prevented the analysis of any of the emission source specific tracers identified in Chapter 5. Note that this problem is not specific to L2MS but would have equally affected organic analyses performed using chromatographic techniques.

While the applicability of L2MS to the study of the analysis of aerosol-bound PACs over the course of a year has been proven, L2MS-independent sampling artifacts prevented all of the initial goals to be reached. The know-how gained during this preliminary study however allows future measurement campaigns to be planned that should provide the detailed and quantitative information desired.

Supporting information: The complete experimental results on which this Chapter is based can be found in Appendix D. They include among others the temporal developments of S5 and of the proportion of selected analytes as well as the corresponding PM, TC, EC, and OC concentrations for the four sampling sites and for both the PM$_{10}$ and the PM$_{2.5}$ fractions.
7.5. References


8. Analysis of Water Contaminants

To further expand the fields of applications of L2MS, this Chapter assesses the applicability of L2MS to the analysis of environmental water samples. In a first stage, the ionization efficiencies of a selection of naphthyl and carbamate pesticides and of phenol were determined. All compounds exhibited a linear UV energy dependence of their ion signals within the range investigated (20 to 200 μJ). Ion yields were highest at 225 nm, and ten- to 100-times higher for phenol and naphthyl pesticides than for carbamate pesticides. This data is useful to estimate the detection limits of these analytes in a variety of matrices once they are known for a reference compound. In a second stage, a measurement procedure was optimized for the direct analysis of phenol and PAHs in natural water samples. Method detection limits were in the low μg/l concentration range, and recoveries of phenol from spiked rain water samples were above 90%. The specific advantages of L2MS allowed the dynamic washout process of atmospheric organic pollutants to be monitored during a rain event with a resolution of 0.01 mm of precipitation.
8.1. Introduction

The vast number of anthropogenic compounds released into the environment, the persistence and ubiquitous distribution of a significant fraction of them, and their potential adverse effects to both environmental and human health represent major challenges in environmental analytical chemistry. For these reasons, several current developments in instrumentation are aiming towards on-line, in-situ, and high-throughput analysis. In this context, L2MS appeared to offer unique advantages over conventional trace-analytical methods. No sample preparation and only small sample volumes are required, measurements with high sensitivity can be performed within minutes, and matrix effects are largely excluded. Given the high versatility of L2MS in terms of measurable matrices, it is surprising that aqueous samples have not been given more attention (1-3) and that studies on the large number of pesticides have remained marginal (4, 5). Moreover, routine measurements of real aqueous environmental samples have not been presented yet.

This Chapter expands the applications of L2MS mentioned above within both dimensions of analyte selection and investigated matrices. In a first stage, the ionization efficiencies of several environmentally relevant pesticides of the naphthyl and carbamate compound classes (Figure 8.1 and Table 8.1) were systematically determined using the PVC membrane sample preparation technique described in Chapter 3. The determination of these parameters is a prerequisite for the efficient analysis of these compounds in natural samples. In a second stage, L2MS was applied to the direct analysis of atmospheric pollutants in natural waters. For these measurements, the water samples were frozen onto the sample holder and laser ablation performed from ice. The dynamic washout process of phenol and PAHs during a rain event was monitored.

8.2. Experimental section

8.2.1. Materials

Methanol (MeOH; p.a. > 99.5 %) and dichloromethane (MeCl₂; p.a. > 99.8 %) were from Baker (Deventer, The Netherlands). Tetrahydrofuran (THF, > 99 %) was from Scharlau (Barcelona, Spain). Deionized water was further purified with a nanopure water purification device (Millipore, Bedford, MA). Polyvinyl chloride (PVC) powder
Table 8.1. Investigated naphthyl and carbamate pesticides. For each compound the molecular mass, the main mass spectral peaks, as well as the wavelength of maximum UV absorbance are given. a: (ref. 6). b: (ref. 7). n.f.: not found.
was obtained from Fluka (Buchs, Switzerland). Benzo[a]pyrene (> 98 %) was obtained from Aldrich (Steinheim, Germany) and naphthalene (> 99 %) from Fluka (Buchs, Switzerland). All other PAHs (fluorene, phenanthrene, 9-methylanthracene, pyrene, 9,10-dimethylanthracene, 1-methylpyrene, and benz[a]anthracene (BaA)) were purchased from Chem Service (West Chester, PA). D10-phenanthrene (98 %) was from Cambridge Isotope Laboratories (Andover, MA). Phenol and all pesticides (atrazine, bendiocarb, carbofuran, carbosulfan, carbaryl, ethiofencarb, folpet, imazquin, isoproturon, metolcarb, metamitron, met-sulfuron-methyl, naphthyl acetic acid (NaAcAc), naphthyl acetamide (NaAcAm), propan, propoxur, and warfarin) were purchased from Riedl-de Haën (Seelze, Germany).

### 8.2.2. Standard solutions

To prepare PVC membranes, 2 g/l of each pesticide and of phenol were dissolved in MeOH. For the direct water analyses, stock solutions of the individual PAHs, of phenol, and of the internal standard d10-phenanthrene were prepared at 200 mg/l in MeCl2. All solutions used for water analysis were further diluted with MeOH to obtain a concentration of 20 mg/l per compound.

### 8.2.3. Preparation of membranes for ionization studies of pesticides

The PVC membranes were prepared as described in Chapter 3. After complete dissolution of the PVC, 50 µl of the internal standard BaA, and 50 µl (naphthyl pesticides), 2 ml (carbamate pesticides), or 5 ml (all other compounds) of the respective analytes’ stock solutions were added.

### 8.2.4. Water calibration solutions

From the 20 mg/l stock solutions, mixtures containing all PAHs and phenol in MeOH were prepared and added to nanopure water to yield the desired concentrations (15 different levels covering a range from 0.15 to 100 nM) and a constant MeOH content of 1 %. The MeOH content was kept constant as it was observed to influence the freezing process and ice consistency. The internal standard d10-phenanthrene was added to all samples at a level of 1 µg/l.
8.2.5. Rain water samples

Sequential rain water sampling was performed in Dübendorf (Canton Zürich, Switzerland) with a 5.06 m² funnel coated with a Teflon foil as described earlier (8). The sampler was covered with a plastic sheet, and washed with ethanol and nanopure water prior to sampling. During the first 0.15 mm of precipitation, fifteen 50 ml samples were collected, corresponding to a resolution of 0.01 mm. The sample volume was increased to one liter for the next 2 mm of rain. After the twenty-fifth sample, only every fifth liter was kept and the four liters in between discarded.

All natural water samples were filtered (mixed cellulose nitrate and -acetate, 1.2 μm pore size, Millipore, Bedford, MA) and spiked with 1 pg/l of d10-phenanthrene. All samples were stored at 5 °C in the dark. To determine the recoveries of phenol in natural waters, 10 ml of two rain water samples were fortified with 9.6, and 19.3 μg/l, respectively.

8.2.6. L2MS system

The home-built L2MS system described in Chapter 2 was used. Wavelengths between 225 and 280 nm were used for ionization efficiency studies. For water analysis, the laser was tuned to 250 nm. The pyroelectric power detector was placed behind the ion source to measure the energy of each laser pulse; the recorded values were used to normalize the mass spectra, as described previously. The delay between the ablation and post-ionization lasers was set to 10 μs for membrane measurements, and to 8 μs for frozen water samples. These values were the results of optimizations to achieve maximum signal intensities. The shorter delay found for water samples might be indicative of a faster plume expansion from the water than from the PVC plume. For water analysis, a liquid nitrogen trap was built in the ionization chamber to avoid recondensation of evaporated water onto the sample surface.

8.2.7. L2MS measurements of PVC membranes

Circular pieces 12 mm in diameter were cut from the PVC membranes, mounted onto the L2MS sample holder, and introduced into the instrument. Seventy-two single
laser shot measurements separated by 5° from each other were performed on each piece of membrane. To determine the relative ionization efficiencies, the mass spectra for which the UV energy was not in the range between 22 and 32 μJ (Chapter 4), as well as the ones during which plasma formation caused by the ablation laser was observed, were rejected. From the remaining mass spectra, the signal intensities of the mass spectral peaks of the analytes (see Table 8.1) were normalized to the one of BaA at m/z = 228.

8.2.8. L2MS measurement of water samples

To maximize the reproducibility, the water samples were prepared and measured according to an optimized standard procedure based on preliminary experiments. 200 μl of water sample were carefully poured into a brass cup (inner diameter: 11.55 mm, depth: 1.8 mm, outer diameter: 12.8 mm, total height: 3.2 mm) which had been precooled in liquid nitrogen for 20 seconds. Within a minute, the water was completely frozen. The sample was then placed again into liquid nitrogen for one minute. The sample was then mounted onto the sample holder and introduced into the instrument. After introduction of the sample, the vacuum chamber was allowed to equilibrate for two minutes. The sample rotator (1 Hz) was then switched on and the measurement started. The first 120 shots (2 minutes) were discarded, as they could have been influenced by surface effects. Thereafter, measurements were performed up to a total of 600 shots. Mass spectra for which the UV-energy was not in the range between 27 and 42 μJ, as well as the ones during which plasma formation caused by the ablation laser was observed, were rejected. From the remaining mass spectra, the signal intensities of the individual mass spectral peaks of the molecular ions were normalized to the one of d10-phenanthrene at m/z = 188. Note that an alternative way to freeze the water samples would consist of using a cryogenic sample holder with a hollow center which can be filled with dry ice or liquid nitrogen instead of the simple one described in Chapter 2. This technique is not as convenient as the one utilized but would be necessary in order to work at lower temperatures. Appendix E contains the schematics of this cryogenic sample holder.
8.3. Results and discussion

8.3.1. Ionization efficiencies of pesticides in PVC membranes

Figure 8.2 shows as an example the L2MS spectrum recorded for NaAcAc. The investigated naphthyl and carbamate pesticides revealed either complete (carbaryl, propoxur, propham, metolcarb, carbofuran, and bendiocarb), or partial (NaAcAc, NaAcAm) fragmentation of the analyte molecule, generally yielding one major fragment ion. Analyte fragmentation was caused in particular by the labile carbamate groups (Figure 8.1).

![Fragment 141](image)

**Figure 8.2.** L2MS spectrum of NaAcAc measured using a PVC membrane. Post-ionization at 225 nm. The data was averaged over 37 laser shots.

The signal intensities of the molecular and higher fragment ions were found to be linearly dependent on the UV energy over the investigated range of 20 to 200 μJ for all pesticides investigated, and at all wavelengths. In contrast to the findings with pesticides, no increase in the ion yield of BaA was observed above 30 μJ due to the fragmentation of this analyte, as discussed in Chapter 4. These findings indicate that the fragmentation threshold for pesticides is much higher than for the large PAHs. Furthermore, they show that the UV absorbance of the molecules (see below) is only one of the parameters that determine the sensitivity reached by L2MS. Hence, to obtain maximum sensitivity, both the UV wavelength and the energy should be optimized according to the analytes to be detected. The lower UV absorbance of
pesticides relative to PAHs can thus be compensated by the possibility to work at higher laser fluences.

Despite the much higher ion yields at elevated ionization energies for both carbamate and naphthyl pesticides, the UV energy used for the subsequent ionization study was restricted to 22 to 32 μJ per laser pulse to ensure a linear response of the internal standard BaA. Figure 8.3 depicts the measured ionization efficiencies of a selection of naphthyl and carbamate pesticides relative to BaA. This parameter is defined here as the ratio of the ion signal at the mass of the largest fragment of the analyte molecule divided by the ion signal at mass 228 (BaA). The normalization to BaA was useful because it allowed a direct comparison of the ion yields of different compounds at different wavelengths. BaA was chosen because its REMPI spectrum exhibited a relatively constant signal intensity over the wavelength range under investigation (Figure 4.2), and because linear calibration curves for the quantitation of this compound embedded in PVC membranes have been shown earlier (Figure 3.5). For all compounds, the relative ion yield corresponded well with their respective UV spectra (see Table 8.1 for wavelengths of maximum UV absorbance) and exhibited maximum signal intensities at 225 nm. Note that for most compounds, ions could be detected over the whole UV range from 225 to 280 nm. This indicates that the ablated analytes were not subject to jet-cooling effects. Generally, the naphthyl pesticides showed a roughly ten to 100-fold higher ion yield than the carbamate pesticides, with maximum ionization efficiencies of up to 30 % relative to BaA. The observed laser ionization efficiency of 2.6 ± 1.0 % at 266 nm for phenol is in the same range as for the naphthyl pesticides (Figure 8.3A). Other investigated carbamate pesticides, such as ethiofencarb or carbosulfan were not ionizable (< 0.1 % ion yield), most probably due to the heavy atom effect of sulfur (9, 10). Other pesticides, such as isoproturon, imazaquin, and warfarin could also be ionized but were not systematically evaluated. Atrazine, folpet, metamitron, and metisulfuron-methyl were not ionizable under the selected conditions.

Additional experiments were conducted using ps instead of ns post-ionization laser pulses. This did not significantly increase the ion yields in the case of the naphthyl pesticides (Figure 8.3A, 266 nm, ps-laser). However, the ion yields of the carbamate pesticides were five to ten times higher with ps-laser pulse ionization (Figure 8.3B, 266 nm, ps-laser). Carbendazim even revealed a relative ionization efficiency of 6 ± 5 % (n = 31), comparable to that of carbaryl. This result clearly indicates that the short lifetime of the carbamates in their first excited state is the limiting factor for their ionizability in the case of ns-laser systems (9-11).
Figure 8.3. Ionization efficiencies of (A) Naphthyl pesticides and (B) Carbamate pesticides relative to BaA. Values are averages from $n = 5$ to 35 individual mass spectra, and error bars represent standard deviations. $n$: not detected. $x$: not analyzed.
The ionization efficiencies reported for the analytes investigated here are useful to predict their detection limits in a variety of matrices once they are known for one reference compound, such as a PAH or phenol. For example, based on their comparable ionization efficiencies (Figure 8.3A), detection limits of naphthyl pesticides in natural waters can be expected to lie in the same range as for phenol (see below), assuming a similar behavior of these compounds in these types of samples.

8.3.2. Direct analysis of water samples

The potential of L2MS for the direct analysis of organic contaminants in natural waters is exemplified with phenol and a selection of PAHs. Linear relationships between UV-energies and ion signals were observed up to 250 µJ for these analytes when measured in ice (data not shown). The higher fragmentation threshold observed for PAHs ablated from ice than from PVC membranes could be indicative of lower internal energies of the molecules ablated from frozen water (12). However, to ensure comparable conditions as with PVC membranes, the UV energy was kept at moderate levels between 27 and 42 µJ.

For most compounds, the investigated range of the calibration in nanopure water encompassed one to two orders of magnitude (Figure 8.4). At high concentrations the linear range of methylphenanthrene, 9,10-dimethylanthracene, BaA and benzo[a]pyrene was restricted by their aqueous solubility (13). Method detection limits (using a signal to noise ratio of three) were in the low µg/l concentration level for most compounds. Note that for fluorene, phenanthrene, methylphenanthrene, and pyrene, the method detection limits were elevated due to background signals of unknown origin that were observed in all mass spectra, including the ones for nanopure water. For phenol, a 15-times lower method detection limit was reported earlier using a comparable experimental setup (1). However, the 250 nm wavelength chosen for post-ionization here as a compromise to allow the determination of a range of different analytes was not specifically well-suited for phenol. Selecting the 275 nm wavelength that corresponds to the \( \pi-\pi^* \) transition of phenol, and applying elevated UV laser energies of a few hundred µJ (see above), would result in the similar phenol sensitivity as obtained by Alimpiev et al. (1). The analytes’ precision obtained from the 95 % confidence interval of their linear regression curves was between 20 to 40 %. Duplicate, and triplicate determinations of phenol in rain water samples (0.01, 1.15, 5.15, and 0.95 mm, respectively, see below) resulted in an averaged 20 % standard deviation of the obtained concentrations. Spiked rain water samples exhibited recoveries of phenol of 98.9 %
(9.6 µg/l added) and 90.6 % (19.3 µg/l added). This indicates that the sample matrix did not cause any adverse effect on quantification and confirms that the observed ion signal at m/z = 94 was not caused by fragments of other pollutants present.

One of the main advantages of L2MS when applied to water analysis is its short and easy sample preparation. The only manipulations required are filtration, spiking with the internal standard to account for the shot-to-shot variability of the ablated water volume, and freezing. The sample volume needed was small, only about 200 µl, and the total analysis time just a few minutes per sample. These characteristics render L2MS especially well-suited in cases when sample volumes are limited, for example in the case of sediment pore water samples or fog water, when high sample frequencies are required, for example to allow higher resolution of dynamic process studies, or when large numbers of samples have to be processed. This is illustrated with an investigation on the occurrence and behavior of organic compounds in rain water.
8.3.3. Washout dynamics of atmospheric contaminants

Figure 8.5 depicts the wet deposition of organic air pollutants during a rain event that took place June 10, 1999. The measurements were performed with a resolution as low as 0.01 mm of rain. Figure 8.5A displays the case of phenol. As expected from its large atmospheric water to air partitioning coefficient (3.8·10^{-4} to 2.1·10^{-5}) (14), phenol was readily washed out from the atmosphere, with maximum concentrations at the very beginning of the precipitation. Whereas the levels observed after the first mm of rain (5 to 10 μg/l) correspond well with values given in the literature for rain water (15-17), the initial concentrations of up to 50 μg/l are, to our knowledge, some of the highest ones ever reported for these waters, reaching levels that were only measured in fog (17, 18). The consequence of such ‘first flush’ washout behavior of a number of organic air pollutants for urban water management is discussed in detail elsewhere (8).

Fluorene (Figure 8.5B) was mainly detected within the first two mm of precipitation at concentrations up to 0.4 μg/l, and was mostly below the method detection limit of 0.2 μg/l afterwards. Again, the numbers are rather high as compared with data from the literature (19). Opposite to the immediate washout of phenol, fluorene exhibits a marked delay in its atmospheric deposition, reaching its maximum concentration after 0.1 mm of precipitation. It is known that smaller PAHs are in general mainly distributed in the gas phase (20-22), where the scavenging efficiency is largely determined by the compound’s Henry constant. Due to the much higher Henry constant of fluorene (logK_H = -1.14 l·atm·mol^{-1}) (13), this compound is not as immediately and efficiently scavenged from the atmosphere as phenol (logK_H = -3.39 l·atm·mol^{-1}) (13).

8.4. Conclusions

The potential for the application of L2MS to environmental samples is presented, including limitations and perspectives. Ionization studies indicate that aromatic compounds such as naphtyl and carbamate pesticides, phenol, and PAHs are suitable for analysis with L2MS in the environmental water compartment. Although trace analysis might not be possible for all analytes, L2MS can serve as a rapid screening tool and early warning system for a wide range of analytes in cases of elevated concentrations.
Figure 8.5. Wet deposition dynamics of (A) phenol and (B) fluorene during a rain event from June 10, 1999. The insets are enlargements of the first 0.2 mm of precipitation. *x*: not detected. Error bars represent ±30% of the measured number, corresponding to the determined average precision.
The versatility of L2MS is further illustrated with the development of a method for the routine analysis of natural water samples. The specific advantages of L2MS, in particular the low sample volume required, enabled the observation of dynamic atmospheric processes that would most probably have been overlooked with conventional analytical techniques. Conclusively, new avenues are now opened for the future application of L2MS in the field of aquatical analytical chemistry.

8.5. References

(6) Sadler UV spectra library.
(7) Gynkotek pesticide UV spectra library (Gynkotek, Germering, Germany).


9. Conclusions and Future Perspectives

9.1. Conclusions

9.1.1. Quantitative analyses

The most critical experimental parameter when performing quantitative analyses using L2MS is to have an accurate control over the amount of analytes desorbed/ablated. In the case of analytes in solution, a new fast and convenient sample preparation technique was developed that consists of mixing the analyte solution with PVC in THF to form a thin polymer membrane from which laser ablation is performed (Chapter 3). Quantitative measurements were demonstrated over at least three orders of magnitude using this sample preparation method. Another way to achieve quantitative measurements of analytes in aqueous solutions consists of rapidly freezing the solution in order to perform laser ablation from ice (Chapter 8). Preliminary experiments showed that this technique also allows quantitative measurements over three orders of magnitude. Nevertheless, performing quantitative analyses from solid samples still remains difficult. An elegant way was found to make quantitative measurements of a wide variety of analytes bound to atmospheric aerosol particles possible (Chapters 5 and 6). The layer of particles collected on a filter has to be thin enough to enable complete desorption of the analytes from the target spot using a single laser shot. When the layer of particles becomes too thick, this is no longer possible and quantitative measurements are hindered (Chapter 7).

9.1.2. Qualitative analyses

L2MS can be used as a screening method to rapidly determine which analytes are present in the sample. For this type of measurement, it is essential that 1+1 REMPI, the ionization mechanism based on the absorption of two UV photons that was used for this project, efficiently ionizes a wide range of analytes. The characterization experiments conducted on PAHs (Chapter 4) and on pesticides (Chapter 8) allowed them to be
roughly classified. The analytes can be assigned to three groups. Most PAHs belong to the first one which can be ionized efficiently at any wavelength up to 266 nm. The ionization efficiency of the analytes of the second group, constituted by the other PAHs and by the pesticides of the naphthyl and carbamate classes, was observed to strongly increase at wavelengths in the lower UV range around 220 nm. Finally, the analytes of the third group, composed by most other pesticides and by the vast majority of all analytes that one might look for, simply could not be ionized using 1+1 REMPI for various spectroscopic reasons.

9.1.3. Chemical analysis of aerosol particles

The chemical analysis of aerosol-bound particles is the most important achievement reported in the context of developing L2MS as a competitive analytical-chemical method. The specific advantages of L2MS such as the high sensitivity, the need for only small sample quantities, allowed the measurement of large numbers of samples within short periods of time to perform extended field measurement campaigns. A total of more than 2000 aerosol samples were measured within a reasonable amount of time, and new elements could be provided that contributed to the elucidation of poorly understood air pollution processes.

First, the aerosols emitted by all major emission sources, including Diesel vehicles, gasoline vehicles, residential heating, wood fires, and cigarettes were characterized (Chapter 5). For each emission source, tracer mass spectral patterns were identified, notably based on specific PAHs and other PACs. Only small sample quantities were necessary and the measurements were performed within minutes. L2MS was found to be a valuable alternative to more laborious chemical analysis techniques that often require extensive sample preparation.

These results were then applied to the study of the dynamic behavior of aerosol-bound PACs in urban air over the course of several whole days, both next to a street with heavy traffic and in a city park (Chapter 6). L2MS allowed measurements with 15 minute time resolution. Large variations in particle concentration and chemical composition were observed, reflecting the contributions from Diesel trucks and gasoline-powered cars to urban aerosols. The photochemically induced decay of oxygenated polycyclic aromatic hydrocarbons (OPAHs) was observed in real time. In a similar way, the dynamic behavior of aerosol-bound PACs in air was studied over the course of a whole year at four sites representative of the different types of aerosol
exposure in Switzerland (Chapter 7). This project was completed in the framework of a collaboration between several research institutes in order to achieve a chemical characterization of the aerosol samples that would be as thorough as possible. A strong seasonal dependence of the amount of aerosol-bound PACs was also observed.

9.1.4. Analysis of water contaminants

To exemplify the versatility of L2MS, studies were conducted to assess the applicability of L2MS to the chemical analysis of PAHs and various pesticides in environmental water (Chapter 8). Limits of detection below 1 µg/l were determined and measurements could be performed with only 200 µl of water sample. The dynamic washout process of atmospheric pollutants was then monitored during a rain event with a resolution of 0.01 mm of precipitation during a preliminary field study.

9.2. Future perspectives

9.2.1. Analysis of aerosol particles

The feasibility of aerosol chemical analysis using L2MS and the environmental significance of the results obtained have now been clearly established (Chapters 5-7). Therefore, future research should focus on instrumental developments.

Portable field instrument. All of the measurements reported in this thesis were performed in a laboratory remote from the sampling locations. This procedure, although standard for most analytical methods applied to the study of aerosol particles, presents various disadvantages. The simple fact of transporting the samples from one site to another is expensive and time-consuming, and prevents routine monitoring. The storage of the samples and the delay until they are measured can alter their chemical composition. While these chemical changes could be minimized in some cases by using an appropriate procedure (Chapters 5 and 6), it was observed to be a major problem in other cases (Chapter 7). Also, the delay between sampling and data collection prevents the immediate detection and response to high pollution events. This would be especially problematic when monitoring indoor aerosol during occupational health studies. Finally, this procedure does not render L2MS flexible enough for the vast
number of sites which require pollution screening. All of these reasons motivate the
development of a small, robust, and cheap L2MS instrument. This is made possible by
recent developments in instrumentation, as shown by various reports on miniaturization
applied to analytical techniques related to L2MS (1-3). Smaller, cheaper, and more
robust lasers are now available. MCP detectors that work at higher pressure reduce the
demand for powerful pumps. Faster digital oscilloscopes make mass separation in
shorter TOF mass spectrometers possible.

**Automatization of the measurements.** Large numbers of samples should be
measured in order to provide a better understanding of the atmospheric processes
aerosol-bound PACs are involved in. For example, a thorough study of their behavior
over the course of single days (Chapter 6) would require measurements to be performed
on at least ten days during each season of the year. This large number of measurements
however is not possible with the current experimental setup as each day studied required
the continuous work of two persons for 36 hours straight. Also, the study of the
behavior of aerosol-bound PACs over the course of a year required the measurements to
be performed continuously during 120 hours with two persons working in 12 hour
shifts. Therefore further automatization is required. A simple development in this
direction would consist in designing robotics for the sample introduction. A more
sophisticated development would be to develop the portable instrument to enable true
on-line measurements. Sampling would be performed on filter rolls that would be
scrolled into the instrument immediately after sampling. This design is widely used in
aethalometers, and the feasibility of the coupling of the sampling stage with a laser
ablation stage has been demonstrated (4).

**Analysis of further substance classes.** A consequence of the classification of the
analytes in three families according to their ionizability is that in terms of costs and
maintenance time, the OPO laser used for this project is not well-suited if L2MS is to be
used as a competitive analytical chemical method. The aerosol-bound PACs studied
during this thesis and post-ionized at 250 nm, all members of the first group, could as
well be ionized simply using the fourth harmonic of a Nd-YAG laser (266 nm) or the
radiation from an KrF excimer laser (248 nm). Smaller aerosol-bound aromatic
compounds that belong to the second group, in particular the tracers for biomass
burning (5-7), would be detected with a much better sensitivity if ionized using the fifth
harmonic of a Nd-YAG laser (212 nm) or probably even the radiation of an ArF excimer
laser (193 nm). Finally, using vacuum UV wavelengths for non-resonant single-photon
post-ionization, for example the 9th harmonic of a Nd-YAG laser (117 nm), would
enable the detection of all of the analytes of the third group (8, 9). This would allow the
study of a considerably broadened range of emission source specific tracers, chemical processes, and degradation pathways at the surface of the aerosol particles. In this context, alkanes, alkanoic and alkenoic acids, alkanols, steranes, and terpenes, among others, would be especially interesting analytes (6, 10-14).

**User-friendly instrument.** The instrument used during this thesis can only be used by qualified workers. A broader use of L2MS for standard monitoring purposes would require a more user-friendly design for greater ease of manipulation. This development could be combined with other ones mentioned above.

**Particle-size resolved measurements.** Various studies showed that the distribution of the analytes on particles of different sizes can widely vary (15-18). The samples for the characterization of the aerosol emission sources (Chapter 5) and for the studies over the course of single days (Chapter 6) were collected by simply pumping ambient air directly through the filter. This simple method was sufficient for the first studies reported in this thesis, but an important future development would be to perform size-resolved measurements by using an impactor to separate the air particulate matter fractions of different aerodynamic diameters.

**Ion-trap mass spectrometer.** Distinction between compounds at the same nominal mass based on their different UV absorption spectra was shown not to be possible due to the broad width of the absorption bands of desorbed/ablated molecules. A better way to add a second dimension to the separation would consist of replacing the TOF mass spectrometer by an ion-trap mass spectrometer (IT-MS) (19) or even by a Fourier transform ion cyclotron resonance mass spectrometer (20) that would enable MS/MS experiments. This type of instrument would not contribute to the distinction between isomeric PACs since they exhibit too similar fragmentation patterns. They would however be very helpful to identify unknown compounds or to confirm tentative structure assignments to mass spectral peaks (Chapter 5).

### 9.2.2. Analysis of water contaminants.

In the longer term, instrumental developments such as the development of a portable field instrument and its automatization, as proposed above, would be beneficial for the analysis of water contaminants as well. However, additional characterization and optimization studies should be given first priority in order to lower the limits of detection reported in Chapter 8. Strategies to achieve this goal include the elimination of the background signals, the use of a post-ionization laser with a higher energy in the
low UV range, the development of a technique to allow larger ice volumes and hence analyte quantities to be desorbed by the IR laser, and a better understanding of the dynamics of the water plume expansion after desorption in order to improve the tuning and maybe the geometry of the ion source.

9.2.3. New applications

This thesis reported exclusively on environmental applications of L2MS but the range of possible applications is much broader. For example, the possibility to detect cannabinol and other alkaloids in aerosol particles collected from cigarette smoke (Chapter 5) illustrates potential application of L2MS in forensics (21, 22). Another interesting application of L2MS would be the screening of contaminants such as dioxins (23) or mycotoxins (24) in large number of food and agricultural samples.

9.3. References


Appendix A: Complete set of L2MS spectra from emission sources (c.f. Chapter 5)

Only twelve among the 78 L2MS spectra recorded from aerosol particles collected at various emission sources are displayed in Chapter 5. For reasons of clarity, a selection had to be made among the samples that displayed similar mass spectra. This Appendix displays all 78 L2MS spectra.
A.1. Car No 1

Opel Astra, gasoline-powered, with catalytic converter, manual gears.

The driving cycles are described in Table 5.1. Sampling was performed on March 8 and 9, 1999.

Figure A.1.1. Emission profile of the car No1, idle 1 driving cycle, cold start. rz15

Figure A.1.2. Emission profile of the car No1, idle 1 driving cycle, rather cold system. rz17

Figure A.1.3. Emission profile of the car No1, idle 1 driving cycle, warm system. rz 25
Figure A.1.4. Emission profile of the car No1, idle 1 driving cycle, warm system. rz 27

Figure A.1.5. Emission profile of the car No1, idle 2 driving cycle, rather cold system. rz 16

Figure A.1.6. Emission profile of the car No1, idle 2 driving cycle, warm system. rz 26

Figure A.1.7. Emission profile of the car No1, urban 1 driving cycle, 6’ 15”, 4 traffic lights. rz 19
Figure A.1.8. Emission profile of the car No1, urban 1 driving cycle, 8’
00”, 6 traffic lights. rz22

Figure A.1.9. Emission profile of the car No1, urban 1 driving cycle, 6’
00”, 2 traffic lights. rz24

Figure A.1.10. Emission profile of the car No1, urban 2 driving cycle, 5’
00”, 4 traffic lights, cold start. rz18

Figure A.1.11. Emission profile of the car No1, urban 2 driving cycle, 5’
40”, 5 traffic lights. rz20
**Figure A.1.12.** Emission profile of the car No1, urban 2 driving cycle, 7’40”, 7 traffic lights. rz23

**Figure A.1.13.** Emission profile of the car No1, uphill driving cycle, 2nd and 3rd gear. rz02

**Figure A.1.14.** Emission profile of the car No1, uphill driving cycle, aggressive driving. rz04

**Figure A.1.15.** Emission profile of the car No1, uphill driving cycle, quiet driving. rz06
Figure A.1.16. Emission profile of the car No1, downhill driving cycle, engine brake. rz01

Figure A.1.17. Emission profile of the car No1, downhill driving cycle, aggressive driving. rz03

Figure A.1.18. Emission profile of the car No1, downhill driving cycle, quiet driving. rz05

Figure A.1.19. Emission profile of the car No1, highway driving cycle. rz07
Figure A.1.20. Emission profile of the car No1, highway driving cycle. rz09

Figure A.1.21. Emission profile of the car No1, highway driving cycle. rz08

Figure A.1.22. Emission profile of the car No1, highway driving cycle. rz10

Figure A.1.23. Emission profile of the car No1, freeway driving cycle. rz30
Figure A.1.24. Emission profile of the car No1, freeway driving cycle. rz31

Figure A.1.25. Emission profile of the car No1, freeway driving cycle. rz32
A.2. Car No 2

Opel Omega, gasoline-powered, with catalytic converter, automatic gears.

The driving cycles are described in Table 5.1. Sampling was performed on March 10 and 12, 1999.

Figure A.2.1. Emission profile of the car No2, idle 1 driving cycle, cold start. op01

Figure A.2.2. Emission profile of the car No2, idle 1 driving cycle. op03

Figure A.2.3. Emission profile of the car No2, idle 2 driving cycle. op02
Figure A.2.4. *Emission profile of the car No2, urban 1 driving cycle, 7’ 30”, 5 traffic lights. op11*

Figure A.2.5. *Emission profile of the car No2, urban 2 driving cycle, 10’ 00”, 10 traffic lights. op10*

Figure A.2.6. *Emission profile of the car No2, urban 2 driving cycle, 6’ 15”, 6 traffic lights. op12*

Figure A.2.7. *Emission profile of the car No2, uphill driving cycle. op17*
Figure A.2.8. Emission profile of the car No2, uphill driving cycle. op19

Figure A.2.9. Emission profile of the car No2, downhill driving cycle. op18

Figure A.2.10. Emission profile of the car No2, downhill driving cycle. op20

Figure A.2.11. Emission profile of the car No2, highway driving cycle. op14
Figure A.2.12. Emission profile of the car No2, highway driving cycle.

Figure A.2.13. Emission profile of the car No2, highway driving cycle.
A.3. Diesel truck

Citroën C35 Diesel truck, manual gears.

The driving cycles are described in Table 5.1. Sampling was performed on March 11, 1999.

Figure A.3.1. Emission profile of the Diesel truck, idle 1 driving cycle, cold start. di02

Figure A.3.2. Emission profile of the Diesel truck, idle 1 driving cycle, cold start. di03

Figure A.3.3. Emission profile of the Diesel truck, idle 1 driving cycle. di16
Figure A.3.4. Emission profile of the Diesel truck, urban 1 driving cycle, 6' 25", 4 traffic lights. di07

Figure A.3.5. Emission profile of the Diesel truck, urban 1 driving cycle, 9' 20", rush hour. di15

Figure A.3.6. Emission profile of the Diesel truck, urban 2 driving cycle, 5' 45", 4 traffic lights. di08

Figure A.3.7. Emission profile of the Diesel truck, uphill driving cycle. di09
Figure A.3.8. Emission profile of the Diesel truck, uphill driving cycle.

di11

Figure A.3.9. Emission profile of the Diesel truck, downhill driving cycle.

di10

Figure A.3.10. Emission profile of the Diesel truck, downhill driving cycle.

di12

Figure A.3.11. Emission profile of the Diesel truck, highway driving cycle.

di14
Figure A.3.12. Emission profile of the Diesel truck, highway driving cycle.

di13
A.4. Residential oil heating systems

Sampling was performed between January 11 and 13, 1999. The sometimes poor resolution of the mass spectra was caused by surface effects due to light filter wetting during sampling. All the buildings are located within a 1 km² area of the city center of Zurich which also encloses the two stations where on-site time-resolved identification of emission sources was to be performed (Chapter 6).

Figure A.4.1. Emission profile of an oil heating: Ackerstrasse 1, Zurich, old building, strong particulate emission. ac12

Figure A.4.2. Emission profile of an oil heating: Badenerstrasse 108, Zurich, old building. ba12

Figure A.4.3. Emission profile of an oil heating: Kernstrasse 45, Zurich, school, strong particulate emission. ke14
Figure A.4.4. Emission profile of an oil heating: Strassburgstrasse 9, Zurich, big building, immediately after switch on. st12

Figure A.4.5. Emission profile of an oil heating: Zentralstrasse 6, Zurich, chimney swept recently. ze13

Figure A.4.6. Emission profile of an oil heating: Zollstrasse, Zurich, old building. zo12
A.5. Residential gas heating systems

Sampling was performed between January 11 and 13, 1999. The low signal-to-noise ratios of the mass spectra, comparable to the one of the field blank (Figure A.9.1), is caused by the extremely weak or even nonexistent particulate emission of the gas furnaces. All the buildings are located within a 1 km² area of the city center of Zurich which also encloses the two stations where on-site time-resolved identification of emission sources was to be performed (Chapter 6).

![Figure A.5.1. Emission profile of a gas heating: Elisabethenstrasse 5, Zurich, large hangar. el11](image1)

![Figure A.5.2. Emission profile of a gas heating: Strassburgstrasse 9, Zurich, big building. st11](image2)

![Figure A.5.3. Emission profile of a gas heating: Kehlfrasstrasse 15, only gas used for years. ke52](image3)
Figure A.5.4. Emission profile of a gas heating: Kanzleistrasse 56, Zurich, chimney shared with an oil furnace. ka11
A.6. Residential wood heating systems

Sampling was performed on January 13, 1999. The yellow-colored particulate emission was particularly intense. The building is located within the same 1 km² area of the city center of Zurich as all the other sampled furnaces (see above).

Figure A.6.1. Emission profile of a residential wood heating:
Brauerstrasse 9, Zurich, before adding wood. br11

Figure A.6.2. Emission profile of a residential wood heating:
Brauerstrasse 9, Zurich, after adding a piece of beech wood. br13

Figure A.6.3. Emission profile of a residential wood heating, same as in Figure A.1.6.2 with another scale. br13
A.7. Open wood fires

Sampling was performed on March 9, 1999. The yellow-colored particulate emission was particularly intense. The 2-3 m² fire was located on an about 30 degree slope. Mainly pine wood but also some beech wood was burnt.

Figure A.7.1. Emission profile of an open wood fire, on the side of the fire. hfo1

Figure A.7.2. Emission profile of an open wood fire, on the side of the fire. hfo2

Figure A.7.3. Emission profile of an open wood fire, at the bottom of the fire, very thick smoke. hfo3
Figure A.7.4. Emission profile of an open wood fire, at the top of the fire, very thick smoke. hf04

Figure A.7.5. Emission profile of an open wood fire, at the top of the fire, very thick smoke. hf05

Figure A.7.6. Emission profile of an open wood fire, at the top of the fire, very thick smoke. hf06

Figure A.7.7. Emission profile of an open wood fire, at the bottom of the fire, where it burns well. hf07
A.8. Cigarettes

The yellow-colored particulate emission was particularly intense.

Figure A.8.1. Emission profile of a Philip Morris cigarette, freely burning.

Figure A.8.2. Emission profile of a Parisienne mild cigarette, freely burning.

Figure A.8.3. Emission profile of a Parisienne mild cigarette, freely burning.
Figure A.8.4. *Emission profile of a Philip Morris cigarette, exhaled.* kb01

Figure A.8.5. *Emission profile of a Parisienne mild cigarette, exhaled.* cf02

Figure A.8.6. *Emission profile of a Parisienne mild cigarette, exhaled.* cf03

Figure A.8.7. *Emission profile of a cannabis cigarette, exhaled.* ha01
A.9. Field blank

The field blank was carried along during the sampling of the residential heating systems, between January 11 and 13, 1999.

Figure A.9.1. Field blank. fb02
Appendix B: Elucidation of ambiguous peaks in aerosol mass spectra (c.f. Chapter 5)

The peaks at m/z = 194, 208, and 222 are commonly observed in the L2MS spectra of Diesel exhaust particles and in other L2MS spectra recorded from aerosol particles (Chapter 5). The assignment of these peaks to oxygenated PAHs rather than to partially hydrogenated alkylphenanthrenes is validated here. The determination is based on exact mass calculations for these peaks using six internal calibrants.
B.1. Introduction

The sequence of peaks at among others m/z = 194, 208, and 222 observed in the L2MS spectrum of Diesel exhaust particles (Figure 5.2.A) could in principle be caused either by partially hydrogenated alkylphenanthrenes (HAPhs) or by oxygenated polycyclic aromatic hydrocarbons (OPAHs) such as polycyclic aromatic ketones (PAKs) or polycyclic aromatic quinones (PAQs). The mass differences between these two classes of compounds caused by strongly varying numbers of hydrogen atoms are considerable, as shown by Table B.1. This makes it possible to distinguish between them by determining the exact mass of the peaks using a very accurate mass calibration.

<table>
<thead>
<tr>
<th>Number</th>
<th>Mass</th>
<th>OPAH</th>
<th>HAPh</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>194 Da</td>
<td>194.072616 Da C_{14}H_{10}O Anthrone Phenanthrone Methylfluorenone</td>
<td>194.109001 Da C_{15}H_{14} Dihydromethylphenanthrene</td>
</tr>
<tr>
<td>II.</td>
<td>208 Da</td>
<td>208.051881 Da C_{14}H_{8}O_{2} Anthraquinone Phenanthrenequinone</td>
<td>208.124651 Da C_{16}H_{16} Dihydromethylphenanthrene</td>
</tr>
<tr>
<td>III.</td>
<td>222 Da</td>
<td>222.067531 Da C_{15}H_{10}O_{2} Methylanthraquinone Phenanthrenequinone</td>
<td>222.140301 Da C_{17}H_{18} Dihydrotrimethylphenanthrene</td>
</tr>
</tbody>
</table>

Table B.1. Possible assignments for the ambiguous peaks detected from Diesel exhaust particles.

Determination of exact masses using TOF mass spectra is difficult, but has already been shown to be possible by Arnold and Reilly (1) among others. Several conditions have to be fulfilled by the mass spectra if a reliable exact mass determination is to be performed. In particular, the mass resolution must be as high as possible, the peaks must have a nice shape and not exhibit shoulders, and a large enough number of peaks must be present in the mass spectra that correspond to known compounds whose exact masses are known. The mass spectra recorded from Diesel exhaust particles (Figure 5.2.A and Appendix A.3) were found to meet the strict quality requirements. The natural and unquestionable presence of phenanthrene (Ph.), of C_n alkylphenanthrenes (APh.) with n ≤ 4, and of aluminum traces caused by the filter holder provided six peaks for the exact mass calibration.
Equation 2.4 is typically used for mass calibration in TOF mass spectrometers. However, its modified version Equation B.1 can sometimes exhibit a better correlation with the data.

\[ m/z = k \cdot \text{TOF}^2 + b \cdot \text{TOF} + a \]  

(Eq. B.1)

It is however important when using Equation B.1 to make sure that the fit keeps its physical relevance and does not deviate too strongly from the theoretically expected behavior described by Equation 2.3. Therefore, a fit using Equation B.1 is only appropriate if low values for the constants a and especially b are found.

### B.2. Results and discussion

Figure B.1 presents the results of the exact mass calibration from one of the twelve L2MS spectra recorded from Diesel exhaust particles. This spectrum was chosen because it exhibited the highest relative intensities of the peaks to elucidate. Although only this example is shown here, all of the other mass spectra led to the same conclusions. The top part of Figure B.1 displays the TOF spectrum as it was recorded. The peaks used for the mass calibration are marked with A-F and the ones to elucidate with I-III.

The middle part of Figure B.1 shows the expansion of the peaks of the TOF spectrum used for calibration. The dots represent the data points recorded with 5 ns sampling intervals by the digital oscilloscope. The solid lines are Gaussian fits that were used to determine the exact TOF for each calibration compound. Simply using the TOF corresponding to the data point with the highest signal intensity for each peak led to very close numerical values for the determination of the exact mass of the peaks to identify. A fit according to Equation B.1 was performed that yielded the values \( k = 0.13501 \text{Da/ps}^2 \), \( b = -0.0323651 \text{Da/ps} \), and \( a = 0.315699 \text{Da} \). The small values obtained for b and a validated the use of Equation B.1, and using Equation 2.4 again led to very close numerical values for the determination of the exact mass of the peaks of interest. The vertical bars in the middle part of Figure B.1 display the TOFs predicted for the calibration analytes using their known exact masses and the fitting parameters.
Figure B.1. Determination of the exact mass of three mass spectral peaks (I-III). A-F are the peaks used for the mass calibration. (A) TOF spectrum. (B) Magnified images around the calibration peaks. (C) Magnified images around the peaks to elucidate. For further explanations see text.
The bottom part of Figure B.1 shows the expansion of the three peaks to be elucidated in the mass spectrum calibrated using the fitting parameters. Again, the dots represent the experimental data points recorded with 5 ns sampling intervals and the solid lines Gaussian fits. The maxima of the Gaussian fits are located at 194.054 Da, 208.053 Da, and 222.065 Da. To allow a clear interpretation of these results, vertical bars were also drawn at the masses expected for the possible analytes that are listed in Table B.1. The mass difference between the masses of the two possible chemical formulas at both m/z = 208 and 222 corresponds to about one and a half digitalization points, that is to about 8 ns in the TOF spectrum. In these two cases, the experimentally determined masses differ by no more than 0.003 Da from the ones expected for OPAHs, but lie more than 0.07 Da below the ones expected for HAPhs. Therefore, these two peaks are unambiguously assigned to OPAHs. The elucidation of the peak at m/z = 194 is made somewhat more difficult by the smaller mass difference between the OPAHs and the HAPhs. The results, indicating a mass less than 0.02 Da below the one of the OPAHs and more than 0.05 Da below the one from the HAPhs however clearly demonstrate that this peak should be assigned to OPAHs as well.

B.3. References

Appendix C: Supporting data for the measurements over the course of single days (c.f. Chapter 6)

This appendix contains the complete experimental results on which Chapter 6 that describes atmospheric aerosol studies over the course of single days is based. The air pollutant concentrations and L2MS results that include S26 and the proportion of the signal intensities of selected masses relative to S26 are found here, for both sampling sites and for each one of the four summertime and four wintertime measurement days. The weather data recorded at the park site and the traffic numbers recorded at the street site are also enclosed for those days for which they were available.

Minor adjustments in the apparatus were occasionally required between sampling days that did not influence the quality of the data. However, this restricts the possibility to perform direct quantitative comparisons of the S26 intensity to within the following three groups of measurements: (i) June 1998 campaigns. (ii) July 1998 campaigns. (iii) January and February 1999 campaigns.
C.1. Street site, Tuesday, June 9, 1998

Figure C.1.1. Gas pollutants, street site, June 9, 1998.
Figure C.1.2. L2MS measurements, street site, June 9, 1998.
C.2. Street site, Sunday, June 14, 1998

Figure C.2.1. Gas pollutants, street site, June 14, 1998.
Figure C.2.2. L2MS measurements, street site, June 14, 1998.
C.3. Street site, Sunday, July 12, 1998

Figure C.3.1. Gas pollutants, street site, July 12, 1998.
Figure C.3.2. L2MS measurements, street site, July 12, 1998.
Figure C.4.1. Gas pollutants, park site, July 12, 1998.
Figure C.4.2. L2MS measurements, park site, July 12, 1998.
C.5. Street site, Wednesday, July 15, 1998

Figure C.5.1. Gas pollutants, street site, July 15, 1998.
Figure C.5.2. L2MS measurements, street site, July 15, 1998.
C.6. Park site, Wednesday, July 15, 1998

Figure C.6.1. Gas pollutants, park site, July 15, 1998.
Figure C.6.2. L2MS measurements, park site, July 15, 1998.
C.7. Street site, Sunday, January 24, 1999

Figure C.7.1. Gas pollutants, street site, January 24, 1999.
Figure C.7.2. L2MS measurements, street site, January 24, 1999.
C.8. Park site, Sunday, January 24, 1999

![Graphs showing gas pollutants at a park site on January 24, 1999.](image)

Figure C.8.1. Gas pollutants, park site, January 24, 1999.
Figure C.8.2. L2MS measurements, park site, January 24, 1999.
C.9. Street site, Thursday, February 4, 1999

Figure C.9.1. Gas pollutants, street site, February 4, 1999.
Figure C.9.2. L2MS measurements, street site, February 4, 1999.
C.10. Park site, Thursday, February 4, 1999

Figure C.10.1. Gas pollutants, park site, February 4, 1999.
Figure C.10.2. L2MS measurements, park site, February 4, 1999.
Figure C.11.1. Gas pollutants, street site, February 10, 1999.
Figure C.11.2. L2MS measurements, street site, February 10, 1999.
C.12. Park site, Wednesday, February 10, 1999

Figure C.12.1. Gas pollutants, park site, February 10, 1999.
Figure C.12.2. L2MS measurements, park site, February 10, 1999.
C.13. Street site, Sunday, February 14, 1999

Figure C.13.1. Gas pollutants, street site, February 14, 1999.
Figure C.13.2. L2MS measurements, street site, February 14, 1999.
C.14. Park site, Sunday, February 14, 1999

Figure C.14.1. Gas pollutants, park site, February 14, 1999.
Figure C.14.2. L2MS measurements, park site, February 14, 1999.
C.15. Weather, Sunday, July 12, 1998

![Graphs of various weather parameters over the day: Temperature, Pressure, Global and Balanced irradiance, Humidity, Precipitation, Wind direction, Wind speed, and Maximal wind speed.]  

Figure C.15.1. Weather, park site, July 12, 1998.

Figure C.16.1. Weather, park site, July 15, 1998.
C.17. Weather, Sunday, January 24, 1999

Figure C.17.1. Weather: park site, January 24, 1999.
C.18. Weather, Thursday, February 4, 1999

Figure C.18.1. Weather, park site, February 4, 1999.

Figure C.19.1. Weather, park site, February 10, 1999.
C.20. Weather, Sunday, February 14, 1999

Figure C.20.1. Weather, park site, February 14, 1999.

![Traffic numbers, street site, July 12, 1998.](image)


![Traffic numbers, street site, July 15, 1998.](image)


![Traffic numbers, street site, July 22, 1998.](image)
C.24. Traffic numbers, Thursday, February 4, 1999

![Graph showing traffic numbers for Thursday, February 4, 1999.]

Figure C.24.1. Traffic numbers, street site, February 24, 1999.

C.25. Traffic numbers, Wednesday, February 10, 1999

![Graph showing traffic numbers for Wednesday, February 10, 1999.]

Figure C.25.1. Traffic numbers, street site, February 10, 1999.


![Graph showing traffic numbers for Sunday, February 14, 1999.]

Figure C.26.1. Traffic numbers, street site, February 14, 1999.
Appendix D: Supporting data for the measurements over the course of a year (c.f. Chapter 7)

This appendix contains the complete experimental results on which Chapter 7 that describes atmospheric aerosol studies over the course of a year is based. The recoveries from the high volume filters of the analytes that compose S26 are given here for the five days where they could be determined. L2MS results that include S5 and the proportion of the signal intensities of selected masses relative to S5 are also found here for the four sampling sites and for both PM$_{10}$ and PM$_{2.5}$, together with the data for the PM, TC, EC, and OC concentrations. Finally, data on the the variation of the PM$_{2.5}$/PM$_{10}$ ratio during the year is enclosed.
D.1. Recoveries

The scaling factor is defined as the parameter to scale the highest value to 100% recovery. ●: Phenanthrene (178). ⊙: C₆-alkylphenanthrenes (192, 206, 220, 234). ■: PAHs (202, 216, 226, 228, 252, 266, 276, 278, 302, 326). ★: m/z = 231 family (231, 245, 259). ▲: Oxygenated PAHs (194, 208, 222, 236). ◊: Other peaks (218, 242, 254, 268).

**Figure D.1.1.** Recovery of the components of S26 on the high volume filter, Zurich, July 15, 1998. Scaling factor = 290.

**Figure D.1.2.** Recovery of the components of S26 on the high volume filter, Zurich, January 24, 1999. Scaling factor = 9950.
Figure D.1.3. Recovery of the components of S26 on the high volume filter, Zurich, February 4, 1999. Scaling factor = 4180.

Figure D.1.4. Recovery of the components of S26 on the high volume filter, Zurich, February 10, 1999. Scaling factor = 2880.

Figure D.1.5. Recovery of the components of S26 on the high volume filter, Zurich, February 14, 1999. Scaling factor = 3430.
D.3. Bern PM

Figure D.3.2. L2MS analysis of PM$_{2.5}$, Bern. Top: S5. Bottom: Percentage of m/z = 208, 252, and 268 in S5. Day #1: January 1, 1998. Day #366: January 1, 1999. Sampling was performed between February 1998 and January 1999.
Figure D.5.2. L2MS analysis of PM$_{2.5}$, Basel. Top: S5. Bottom: Percentage of m/z = 208, 252, and 268 in S5. Day #1: January 1, 1998. Day #366: January 1, 1999. Sampling was performed between February 1998 and January 1999.
D.7. Chaumont PM

Figure D.7.2. L2MS analysis of PM$_{2.5}$, Chaumont. Top: S5. Bottom: Percentage of m/z = 208, 252, and 268 in S5. Day #1: January 1, 1998. Day #366: January 1, 1999. Sampling was performed between February 1998 and January 1999.
Figure D.9.2. L2MS analysis of PM$_{2.5}$, Zurich. Top: S5. Bottom: Percentage of m/z = 208, 252, and 268 in S5. Day #1: January 1, 1998. Day #366: January 1, 1999. Sampling was performed between February 1998 and January 1999.
Figure D.10.1. PM$_{2.5}$/PM$_{10}$ distribution for S5 and its components, Bern.

Figure D.10.2. PM$_{2.5}$/PM$_{10}$ distribution for S5 and its components, Basel.
Figure D.10.3. PM$_{2.5}$/PM$_{10}$ distribution for S5 and its components, Chaumont. Day #1: January 1, 1998. Day #366: January 1, 1999.
Figure D.10.4. PM$_{2.5}$/PM$_{10}$ distribution for S5 and its components, Zurich. 
Appendix E: Cryogenic Sample Holder  
(c.f. Chapter 8)

An optimized procedure to freeze the water samples is described in Chapter 8. It simply makes use of the classical sample holder which is cooled in liquid nitrogen. The procedure that would have consisted of using a cryogenic sample holder developed during this thesis was rejected as it is more complicated. Nevertheless, this cryogenic sample holder offers unique properties and would be necessary to work at lower temperatures, for example for the analysis of liquids with a lower freezing point than water. For this reason, this Appendix describes the main features of the cryogenic sample holder and displays schematics of its components.

Unlike the conventional sample holder which simply consists of a stainless steel rod, the cryogenic sample holder is hollow and its cavity can be filled with a coolant such as dry ice or liquid nitrogen. It was designed with double walls separated by vacuum in order to isolate the coolant tank and hence slow down its volatilization. Different technical problems had to be solved to allow satisfactory results. (i) Since the sample is located at a potential of about 4000 V in the mass spectrometer, an electrical isolator had to be built between the tip where the sample is mounted and the coolant tank. Sapphire was selected because this material is one of the only ones that is simultaneously a thermal conductor and an electrical isolator. (ii) A screw made of an electrically isolating material had to be fabricated to hold the sapphire isolator between the tip where the sample is mounted and the coolant tank. Polycarbonate was selected because of its mechanical properties and because it is one of the only polymeric materials that can withstand very low temperatures. (iii) The two tubes used to create a cavity that can be put under vacuum are exposed to a temperature gradient of at least 100 degrees. To compensate for the thermal dilatation, a bellow had to be built in one of the tubes. (iv) No satisfactory way was found to generate a permanent vacuum between these two tubes. Therefore, the cavity was connected to a valve.
Figure E.1. General view of the cryogenic sample holder with its accessories (Scale 1:1). (A) Threaded cap. Samples are mounted by screwing it to the rod. (B) Rod. The black dots indicate welding between separately machined parts.
Figure E.2. Schematic of the components of the rod of the cryogenic sample holder (Scale 1:1). (A) Threaded tip, stainless steel. (B) Isolator, sapphire (Custom-made, Djeva, Monthey, Switzerland). (C) Rod tip, stainless steel. (D) External tube, stainless steel. (E) Bellow, stainless steel, (Modified FB-6510, Caburn, Glynde, UK). (F) Internal tube, stainless steel.
Figure E.3. Handle and plug for the cryogenic sample holder (Scale 1:1). (A) Plug, Teflon, retains the coolant in the cavity of the rod. (B) Handle, brass, can be screwed to the rod. (C) Allthread, used to move the plug forward as the coolant volatilizes.
Curriculum Vitae

Birth: La Chaux-de-Fonds, February 27, 1974

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1979 - 1983 : Primary school, Geneva and La Chaux-de-Fonds.


1987 - 1990 : High School, La Chaux-de-Fonds.

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