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# Laser Mass Spectrometric Analysis of Organic Atmospheric Aerosols. 1. Characterization of Emission Sources

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Carbonaceous aerosol particles stemming from combustion processes play a key role in air pollution. Major 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 task can be accomplished using two-step laser mass spectrometry (L2MS). Only small sample quantities are necessary, and the measurements can be 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.

## 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. This is usually achieved by analyzing tracer compounds specific to given emission sources. After sample collection on filters, various chromatographic methods are used for the quantitation of organic compounds and inorganic ions (4–12), while atomic spectroscopic methods allow the determination of the elemental composition (12–14). However, these techniques require a tedious and time-consuming sample preparation as well as the collection of relatively large sample quantities. This renders them less convenient for analyses at sites where aerosol concentrations may be low or the sampling time limited.

Hence, new methods are needed that make a more rapid identification of aerosol emission sources using smaller sample quantities possible. Two-step laser mass spectrometry (L2MS) (15–19) is a technique that allows chemical analysis within minutes, immediately after sampling, and without any sample preparation. These advantages combined with a sensitivity in the low attomole range for some analytes allow measurements of large numbers of samples collected over short periods of time. The principle of L2MS is the following: in the first step, an infrared laser pulse desorbs

intact neutral molecules from the surface of particles sampled on a filter. In the second step, a pulse from a tunable ultraviolet laser is used for resonance-enhanced multiphoton ionization (REMPI) of the desorbed species. This soft ionization scheme prevents fragmentation of the analytes. Mass analysis is then performed in a time-of-flight mass spectrometer. The mass spectra are dominated by intact parent ions of those compounds that strongly absorb the ultraviolet laser wavelength. In the case of atmospheric aerosols, these are aromatic compounds.

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 (11, 20–23). 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 is further validated for the reliable identification of different types of particle emission sources at sites of exposure in our companion paper (24).

## Experimental Section

**Sampling Apparatus.** Pieces of standard quartz fiber filter (Pallflex, Putnam, CT) of about 1 cm<sup>2</sup> area were mounted on custom designed filter holders (Figure 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 h in individual containers (13 mm diameter × 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 h before analysis. There were no discernible differences in their mass spectra.

**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 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 1. Two gasoline-powered cars with manual gears, one automatic gasoline-powered car, and one medium-duty Diesel truck were sampled.

Twelve residential heating systems were randomly selected within a 1 km<sup>2</sup> 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 at least partially prior to sampling.

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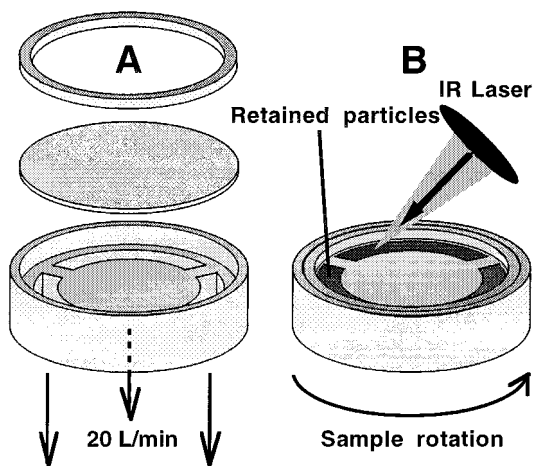


FIGURE 1. Custom designed filter holder used for both sampling and L2MS measurements. During sampling, the assembly is mounted at the end of a tube connected to a flowmeter and to a vacuum pump. (A) Expanded view before assembly of the holder, filter, and retaining ring. The air is pumped through the 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).

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

**L2MS System.** A home-built L2MS system was used that has been previously described elsewhere (15, 25). It was improved to allow for better mass resolution ( $m/\Delta m = 1200$ ) and improved shot-to-shot reproducibility. Only the main characteristics are given here. A CO<sub>2</sub> laser (Alltec 853 MS, Lübeck, Germany) was used for desorption. An optical parametric oscillator laser (MOPO-730D10, Spectra Physics, Mountain View, CA) tuned to 250 nm was used for positionization; this wavelength was found to be well-suited for the ionization of aromatic compounds of various sizes (16). 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 (16). A delay of 14  $\mu$ s between both lasers was found to yield maximal signal intensities. The ions were detected using a reflectron time-of-flight mass spectrometer (R. M. Jordan Co., Grass Valley, CA).

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 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 (16) were discarded. 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%.

## Results and Discussion

**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 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 (16). 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 208.124651 Da for hydrogenated C<sub>2</sub>-alkylphenanthrenes vs 208.051881 for OPAHs at the same nominal mass. The mass calibration was accurate enough to allow 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, ...). This finding is in good agreement with previous reports on the detection of large amounts of OPAHs in urban aerosol particles (26), especially from Diesel engines (11). It does not provide additional evidence for the presence of hydrogenated alkylphenanthrenes in Diesel exhaust particles (27) as suggested by other authors (28). It should also be mentioned here that the high sensitivity of L2MS for OPAHs has been demonstrated previously (29). The inset in Figure 2A shows how the relative intensity of selected peaks compared to the intensity of the dominant one at  $m/z = 206$  (C<sub>2</sub>-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 at the same time 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 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 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.

**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 ref 11 and with our own field studies (24). In the mass spectra, the dependence of the emission profile of the same vehicle on the driving cycle (Table 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

TABLE 1. Driving Cycles for the Characterization of Vehicle Emission Profiles

cycle	description	distance (km)	speed (km/h)	sampling duration (min)
idle 1	800 revolutions/min	0	0	1–10
idle 2	2000 revolutions/min	0	0	1–10
urban 1	slightly uphill, altitude difference 50 m, about five traffic lights	2.2	0–50	6–8
urban 2	slightly downhill, altitude difference 50 m, about five traffic lights	1.9	0–50	5–8
uphill	mountain road with curves, altitude difference 150 m	1.4	20–80	2–3
downhill	mountain road with curves, altitude difference 150 m	1.4	20–80	2–3
highway	flat	4.0	120	4
freeway	flat	1.5	80	1.3

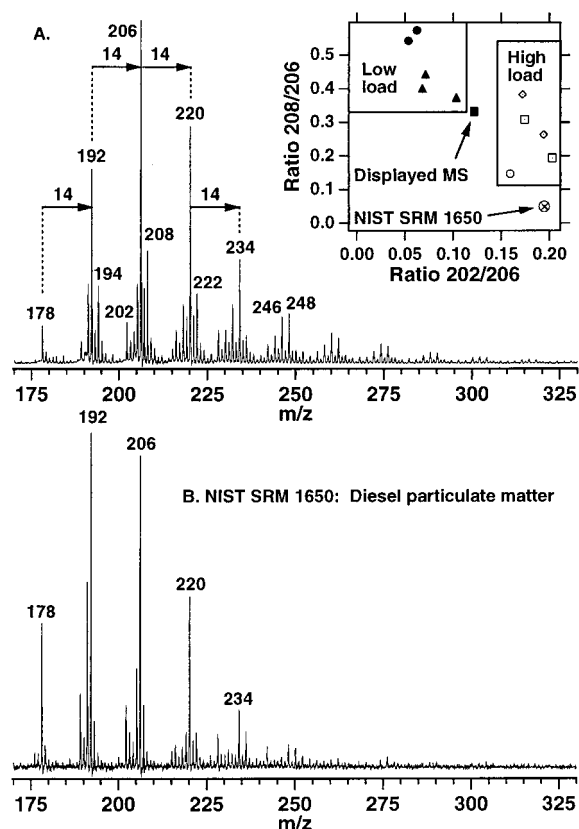


FIGURE 2. (A) Typical L2MS spectrum from particles emitted by a Diesel truck. Inset: an increased load on the truck engine enhances the formation of PAH skeletons, while a decreased load increases the formation of OPAHs. Both effects correlate. ▲: Idle 1 and 2 cycles. □: Urban 1 cycle (slightly uphill). ■: 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.

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 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 (11). Under certain driving conditions, a second pattern was also observed from gasoline engine exhaust in the higher mass range. Figure 3 (parts B and C) represents two cases with different intensities of this second

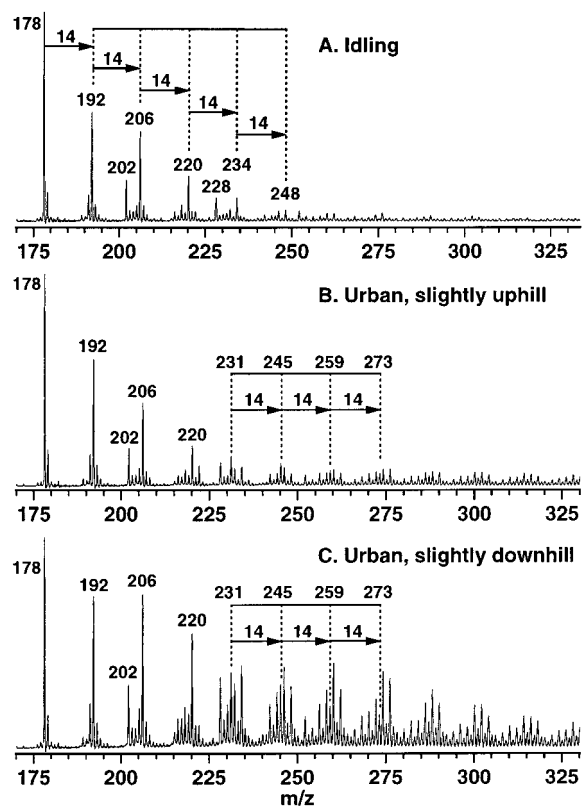


FIGURE 3. L2MS spectra from particles emitted by gasoline-powered cars. (A) Idle 1 cycle. (B) Urban 1 cycle (slightly uphill). (C) Urban 2 cycle (slightly downhill). Both traffic cycles (B) and (C) included a few stops at traffic lights during which the engine was idling.

pattern relative to the first one depicted in Figure 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 Figure 3 (parts B and C) 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 (30, 31), and kerogens (32). These compounds may survive the combustion process under certain driving cycles. Other possible assignments could be amino or cyano PAH derivatives (17).

**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



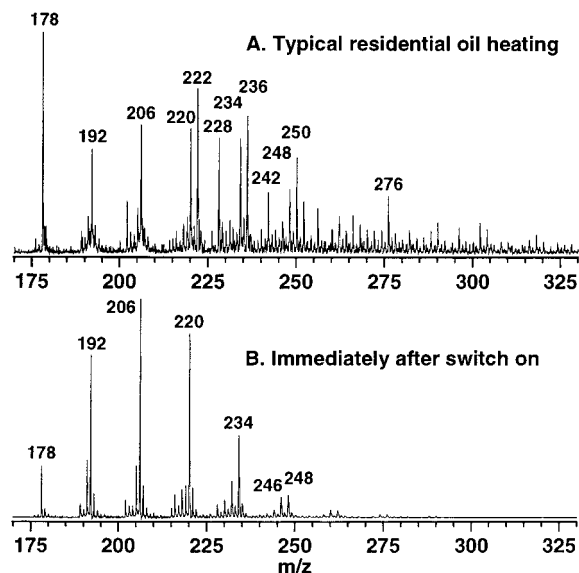


FIGURE 4. L2MS spectra of particles emitted by residential heating systems. (A) Extra-light oil heating, system was warmed. The total particulate emission is low. (B) Extra-light oil heating, immediately after switching the furnace on. The total particulate emission is orders of magnitude higher.

systems are known to have very low particulate emissions (33). 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 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 ( $m/z = 178, 202, 228, 252, 276, \dots$ ), by alkylphenanthrenes (192, 206, 220, 234, 248), and by alkylanthraquinones/alkylphenanthrenequinones OPAHs (222, 236, 250,  $\dots$ ). 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 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 4B than to the one of Figure 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.

**Wood Fires.** Figure 5 displays emission profiles for wood burning under different conditions. A striking feature is their

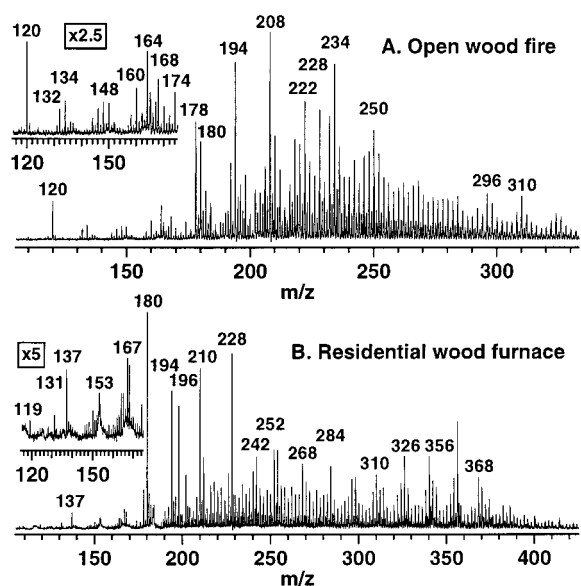


FIGURE 5. L2MS spectra of particles emitted by wood fires. (A) Open wood fire, fresh pine branches. (B) Residential wood furnace, dry beech logs.

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 5B) where dominant peaks were found even above 350 Da. Note that the heavier compounds are generally discriminated against in L2MS spectra due to reduced ionization efficiency (16). The especially high peak at  $m/z = 234$  ( $C_4$ -alkylphenanthrenes) in Figure 5A is very likely due to retene (1-methyl-7-isopropylphenanthrene), an isoprene derivative commonly used as a tracer for burning coniferous wood (21). The high amount of this  $C_4$ -alkylphenanthrene is particularly remarkable because the peaks for the other  $C_n$ -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 (21, 34). The comparison with these references allows one to tentatively assign the peak at  $m/z = 168$  to vanillic acid ( $C_8H_8O_4$ ), the one at  $m/z = 180$  to guaiacylacetone ( $C_{10}H_{12}O_3$ ), the one at  $m/z = 194$  to 3,4-dimethoxyphenylacetone ( $C_{11}H_{14}O_3$ ), 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 ( $C_9H_{10}O_5$ ), and the one at  $m/z = 210$  to 1-syringylethanone or 1-(3,4,5-trimethoxyphenyl)ethanone ( $C_{11}H_{14}O_4$ ).

**Cigarettes.** Figure 6 (parts A and B) displays 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 6A) and a freely burning cigarette (Figure 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 cannot simply be explained by contributions of the  $^{13}C$ -isotopomers. We believe that large amounts of N-containing heterocycles are present, conversion products

TABLE 2. Summary of the Main Features of the Sampled Emission Sources<sup>a</sup>

emission source	dominant peaks	ratio phen/ $\Sigma(C_n\text{-APhs})$	specific identification patterns
Diesel engine	$C_n\text{-APhs}$ ( $n \leq 5$ )	0.05–0.2	high proportion of $C_n\text{-APhs}$ ( $n \geq 2$ )
gasoline engine	Phen $C_n\text{-APhs}$ ( $n \leq 5$ )	0.4–0.8	peaks at $m/z = 231, 245, 259$
gas heating system	none	nc	
properly functioning oil heating system	weak particulate emission	0.4	high levels of alkylnthraquinones/ alkylphenanthrene-quinones OPAHs
poorly functioning oil heating system	Phen $C_n\text{-APhs}$ ( $n \leq 2$ )	0.8–(>1)	high proportion of $C_n\text{-APhs}$ ( $n \geq 2$ )
open wood fire	wide range	nc	retene ( $m/z = 234$ ) peaks in the range $m/z = 120\text{--}175$
residential wood furnace	$m/z = 180, 194, 196,$ 210, 228	nc	peaks at high masses ( $m/z = 326, 356, 368, \dots$ ) peaks in the range $m/z = 120\text{--}175$
cigarette	wide range	nc	small aromatic compds ( $m/z = 132, 146, 160, 182$ ) peaks in the range $m/z = 120\text{--}175$
cannabis	wide range	nc	cannabinol peak $m/z = 310$ peaks in the range $m/z = 120\text{--}175$

<sup>a</sup> Phen = phenanthrene, APhs = alkylphenanthrenes. The ratio phen/ $\Sigma(C_n\text{-APhs})$  was only calculated in the mass spectra where these peaks are dominant. Not calculated = nc.

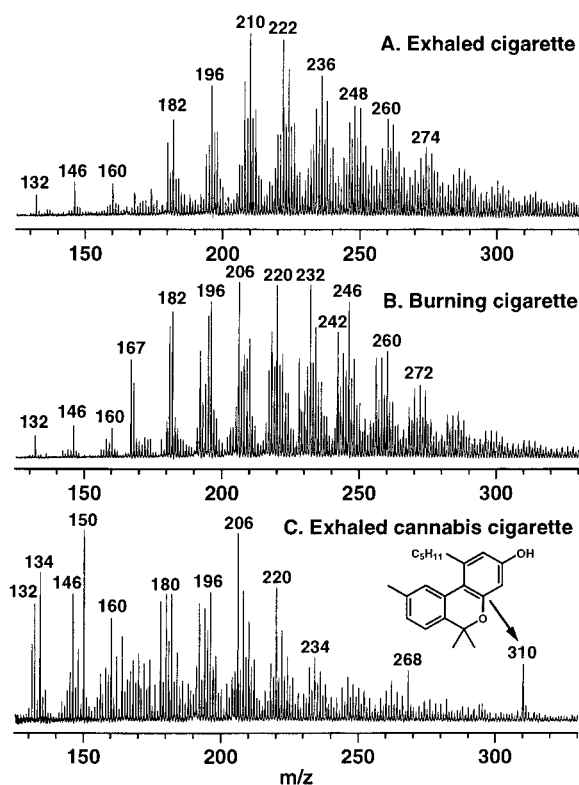


FIGURE 6. L2MS spectra of cigarette smoke particles. (A) Exhaled cigarette. (B) Burning cigarette. (C) Exhaled cannabis cigarette. The strong peak at  $m/z = 310$  is assigned to cannabinol (structure shown in inset).

of nicotine (20). 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 ref 20. 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 identify not only substance families such as "PAH skeletons", "alkylphenanthrenes", or "OPAHs" but also specific tracer compounds is further exemplified in Figure 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.

### Summary

The mass spectra displayed in Figures 2–6 whose features are summarized in Table 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 our companion paper (24).

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