Laser desorption and laser ablation Fourier transform mass spectrometry for the analysis of pollutants in complex matrices

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Introduction

The impact on human health of indoor and outdoor pollution is the subject of major interest and concern. Pollution is a generic term that covers the different releases into the environment of compounds having a negative and/or a toxic effect. Pollutants can be generated both by natural ways (e.g. volcanic eruptions) and by human activities, as for example through mining, energy production, industrial activities, human domestic activities or transport. To limit their impact on the environment, clean air acts have been adopted in industrial countries. Consequently, environmental pollutants need to be identified and measured. The main difficulties of their measurements are: first, the complexity of the associated environmental matrices; second, their low amounts; and third, the presence of different types of pollutants in the same environmental system.

Normalised methodologies have been adopted to characterise numerous organic and inorganic pollutants. They usually combine extraction, preconcentration and separation steps with classical techniques such as GC/MS (gas chromatography mass spectrometry), LC/MS (liquid chromatography mass spectrometry), UV/visible spectroscopy, atomic absorption or emission spectroscopy, or infrared spectroscopy for extractible and/or soluble pollutants. For insoluble pollutants, the use of X-ray fluorescence spectrometry or atomic emission or absorption spectroscopy after mineralisation, provides elementary analysis. Typically, one technique is dedicated to the analysis of a relatively small number of target compounds and the appropriate sample pretreatment steps (extraction, preconcentration and separation) may be time-consuming and may distort the composition of the sample being studied. From this analytical viewpoint it means that a long time period and a great variety of analytical techniques are required to cover the global composition of environmental samples. Consequently, analytical techniques that simultaneously analyse a wide number of compounds need to be considered. They have to be sensitive to the majority of compounds present in environmental samples and allow their identification. By using so-called "direct analysis techniques" to perform more quickly such analyses, sample treatments and separation operations may be avoided or reduced.

Mass spectrometry coupled with the laser ionisation technique, which ensures the direct characterisation of organic and inorganic compounds in the solid phase, may be one of these techniques.[1,2] In laser mass spectrometry, a laser beam is used to irradiate a solid sample. Depending on laser–matter interactions, some species are expelled into the gas phase from the sample surface.[3] They consist mainly of neutrals but ionised species are also formed. Both neutrals and ions are atomic or molecular species. Consequently, the analysis of such ions by mass spectrometry can be used to yield elemental and structural information on the sample under investigation. Depending on the laser irradiance in $\mathrm{W\,cm^{-2}}$ (energy per surface unit and time unit), two laser–matter interaction regimes have to be considered. At low irradiance: the laser desorption (LD) processes limit the amounts of matter expelled from the surface. The induced sample damage is generally not visible. As irradiance levels increase, the amounts of expelled species after laser irradiation increases and craters are formed at the surface of the sample. In addition, recombination processes may take place in the gas phase as a consequence of a high level of collisions. This regime is named laser ablation (LA). Both LD and LA may be used with mass spectrometry (MS) and allow a large range of compounds to be analysed. Detected ions are typically from the environmental matrix and/or from the compounds of interest, i.e. from

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the studied pollutants. Isobaric interferences may lead to significant difficulties for the ion assignment, especially as the mass of the ion increases. To obtain a global analysis of such samples, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) may present a better alternative to other instruments. It allows one to obtain higher mass resolution and higher mass accuracy than conventional mass spectrometers. These capabilities have been demonstrated particularly to resolve elemental composition of very complex mixtures such as petroleum.[4]

The principle of ion cyclotron resonance (ICR) is quite simple.[5] Ions trapped in a magnetic field adopt an orbital motion (cyclotron motion), the fundamental frequency ω of which can be calculated by the equation following:

$$\omega = \frac{q \times B}{m}$$

where q and m are the charge and the mass of the ion, respectively, and B is the magnetic field. After trapping in an ICR cell by means of magnetic and quadrupolar electrostatic fields, ions of the same mass-to-charge ratio are excited by a resonant excitation pulse into a coherent orbital motion at their specific cyclotron frequency. The excitation is then turned off. Ion clouds moving near the detection electrodes cause an image charge on these electrodes to balance the electric field induced by the periodic motion of the ions in the ICR cell. Depending on the circular orbit of the ions, the image charge oscillates at the resonant frequency of the ions and can be detected by a sensitive preamplifier setup. The accurate measurement of the frequency allows for both accurate mass measurement and the high resolution to be achieved. In practice, ion excitation is carried out by a sweep of a frequency range including the expected ion frequencies and the recorded signal is Fourier transformed to instantaneously get frequencies (then m/z ratio) of all the excited ions (broadband detection mode).

The aim of our work has been to advance the development of one instrument to be able quickly to get qualitative information on a larger range of pollutants in environmental samples. Here, we have evaluated the performance of FT-ICR-MS in LD and LA ionisation modes as a new approach to examine some organic and inorganic pollutants in various environmental matrices. More particularly, the broadband mode appears to be well suited to acquire a specific fingerprint, i.e. global composition of environmental systems. Two kinds of samples will be discussed. These will be those that are associated with various workplace atmospheres and then those that correspond to particulate matter associated with cigarette smoke.

Collection of the samples

Air samples of welding fume particles were collected from indoor facilities used for the construction of metal objects or from a painting hall for aircraft. Samples of the respirable dust fraction were collected at a flow of 60 L min^{-1}, using a cyclone. Dust particles are captured on a 50 mm diameter polyester membrane filter coated with Teflon®. The air sampling equipment was placed at fixed locations 1.5 m above the work floor and within 1 m of the welding process.

The cigarettes investigated were commercial products, which, according to the manufacturer, had a content of 8.0 mg of tar, 0.60 mg of nicotine and led to the production of 9 mg of carbon monoxide per cigarette. Two sample collection methods have been used in this study, as shown in Figure 1. Each cigarette is smoked at 1 puff/half minute, 2 s puff duration and 300 mL puff volume.

Method 1: mainstream cigarette smoke (MSS) of the cigarette is bubbled into successive 100 mL gas washing bottles. Each of these contains 50 mL of a 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) solution at a concentration of 10^{-4} mol L^{-1} in CH_2Cl_2. TCNQ allows charge transfer (C-T) complexes to be formed with PAH (polyaromatic hydrocarbons) compounds.[6]

Method 2: MSS particles are collected on extraction disks. These disks are made of 8 µm adsorbent particles (C_{18} silica, reverse phase) entrapped in a 500 µm thickness matrix of inert poly(tetrafluoro ethylene).

Instrumentation

Analyses were performed by using a laser microprobe FT-ICR mass spectrometer that has been described in detail elsewhere.[7,8] This instrument is a modified differentially pumped dual-cell Nicolet Instrument FTMS 2000 operated with a 3.04T magnetic field and coupled to a reflection laser interface. The ionisation step is performed using an ArF excimer laser (λ = 193 nm, pulse duration: 23 ns) for the study of organic compounds and a tripled Q-switch Nd-YAG laser (λ = 355 nm, pulse duration: 4.3 ns) for inorganic analysis. The diameter of the laser beam on the sample can be adjusted from five to several hundred micrometres, which corresponds to an irradiance ranging from 10^5 to 4×10^{10} W cm^{-2}.

Each FT-ICR mass spectrum results from an average of one hundred laser shots fired on consecutive spots of the sample to obtain an acceptable reproducibility on the ion relative abundance. Measurements are achieved with irradiance close to ~5×10^6 W cm^{-2} for the analysis of organics, whereas higher

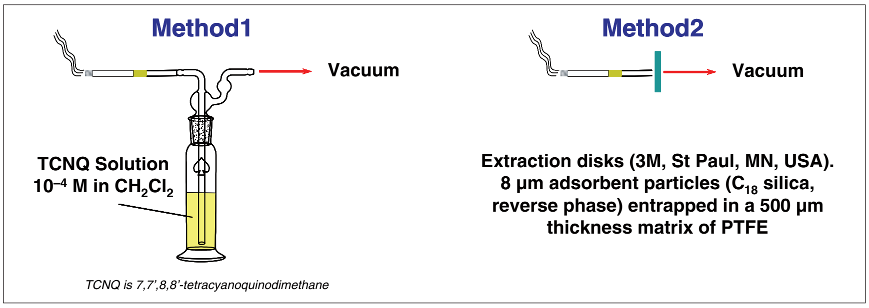

Figure 1. Methods used to collect mainstream cigarette smoke particles.

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Element	**ICP-MS Challenge**	**Traditional Technique**
Mercury	Poorly ionized and very low reporting requirements	Cold vapor AA or AFS
Arsenic	$ArCl^+$ and $CaCl^+$ interferences	GFAA or Hydride
Selenium	$ArCl^+$, $ArAr^+$ and S-based interferences	GFAA or Hydride
Sodium	High concentrations	ICP-OES

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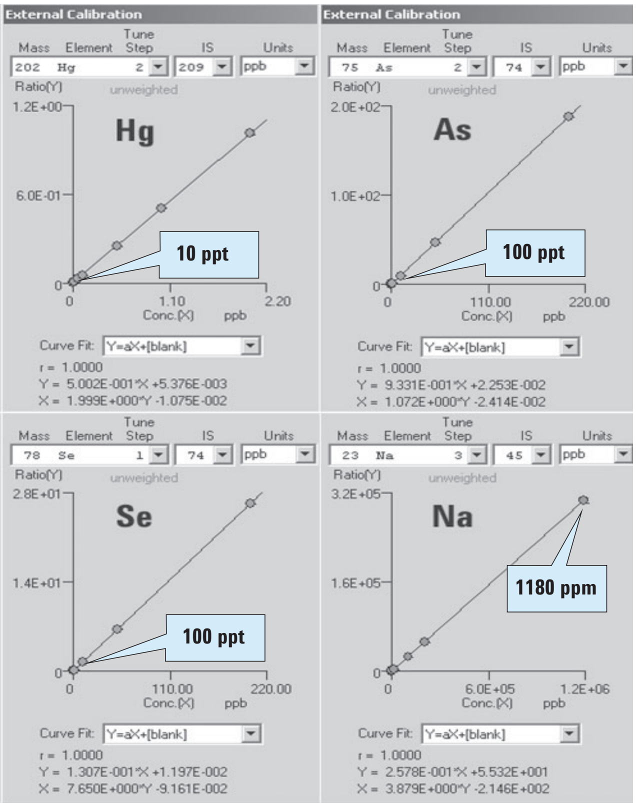

External Calibration

Mass: 202, Element: Hg, Tune Step: 2, IS: 209, Units: ppb

Curve Fit: Y=aX+[blank]

r = 1.0000
Y = 5.002E-001*X +5.376E-003
X = 1.999E+000*Y -1.075E-002

External Calibration

Mass: 75, Element: As, Tune Step: 2, IS: 74, Units: ppb

Curve Fit: Y=aX+[blank]

r = 1.0000
Y = 9.331E-001*X +2.253E-002
X = 1.072E+000*Y -2.414E-002

Mass: 78, Element: Se, Tune Step: 1, IS: 74, Units: ppb

Curve Fit: Y=aX+[blank]

r = 1.0000
Y = 1.307E-001*X +1.197E-002
X = 7.650E+000*Y -9.161E-002

Mass: 23, Element: Na, Tune Step: 3, IS: 45, Units: ppb

Curve Fit: Y=aX+[blank]

r = 1.0000
Y = 2.578E-001*X +5.532E+001
X = 3.879E+000*Y -2.146E+002

Figure 1. Calibration curves: Hg 10ppt - 2ppb, As 100ppt - 200ppb, Se 100ppt - 200ppb, Na 50ppb - 1180ppm.

Summary

With unmatched matrix tolerance, ability to simply remove interferences and wide dynamic range, the 7500ce sets a new standard for productivity in inorganic analysis.

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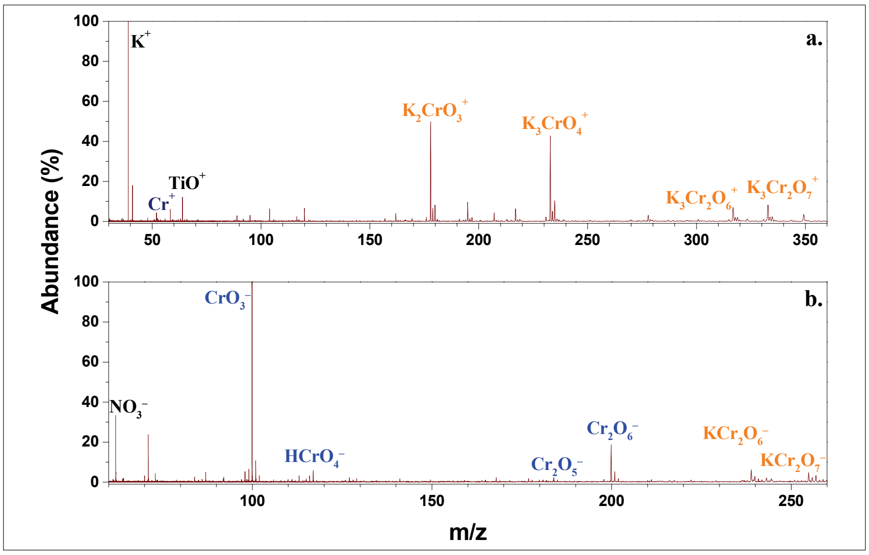

Figure 2. (a) Positive and (b) negative ion mass spectra of dust particles collected in a painting hall at an irradiance of 5×10^7 and 2.5×10^8 W cm^{-2}, respectively. Experiments are performed at the laser wavelength of 355 nm.

laser irradiances between ~10^7 and 10^8 W cm^{-2} are required to observe inorganic ions.

Dust particles collected in a painting hall for aircraft

Figure 2 shows the positive and negative mass spectra of dust particles collected in a hall where aircraft are painted. Whatever the ion detection mode, the main ionic species are associated with inorganic species. Only poorly abundant organic species are observed. In the positive ion spectrum [Figure 2(a)] two kinds of ions are observed. The first ions are atomic and yield elemental composition of dust particles. The abundance of these ions increases with the laser irradiance. At irradiance levels close to 10^{10} W cm^{-2}, they correspond to the base peaks of the mass spectra. Under these conditions K^+, Ti^+, Cr^+, Fe^+ and Zn^+ ions are observed. The second set of ions are ionic clusters and are detected intensely at low irradiance, close to their ablation/ionisation threshold, i.e. at this low irradiance value other ions are not observed. They consist mainly of associations between potassium, chromium and oxygen atoms: TiO^+, $K_2CrO_2^+$, $K_2CrO_3^+$, $K_3CrO_3^+$, $K_3CrO_4^+$, $K_3Cr_2O_6^+$ and $K_3Cr_2O_7^+$. Depending on the laser–matter interaction, these cluster ions are related to the molecular inorganic compounds present in the collected dust particles. Therefore, $K_xCr_yO_z^+$ ions are indicative of potassium chromate, potassium dichromate or chromium potassium alum. The analysis of these compounds allows us to clarify this analysis. The chromium potassium alum also leads to the detection by LA-FT-ICR-MS of cluster ions including sulphur atoms. Consequently, it is reasonable to consider that only potassium chromate or dichromate is present on the particles studied.

This conclusion is confirmed by the analysis of negative ions [Figure 2(b)]. First, no SO_x^- ions are detected. These species are indicative of sulphate or sulphite compounds and are systematically detected in their LA-FT-ICR-MS study. Second, potassium, chromium and oxygen in combination: $KCr_2O_6^-$ and $KCr_2O_7^-$, are also detected. Finally, the distribution of the intense chromium oxygenated species: CrO_3^-, $Cr_2O_4^-$, $Cr_2O_5^-$ and $Cr_2O_6^-$, is indicative of a hexavalent chromium compound. Indeed, the oxidation state of chromium could be identified by the methodology we published recently.[9] Depending on the ion intensity ratio $R=Cr_2O_4^-/Cr_2O_6^-$, trivalent and hexavalent chromium compounds can be distinguished. R is lower than 0.5 for Cr(VI) compounds and greater than 0.8 for Cr(III) compounds. R is equal to 0.031 ± 0.003 for the particles examined here. Consequently, chromium is hexavalent, which supports the presence of chromate or dichromate compounds in the dust particles investigated.

Welding fume particles from stainless steel industries

Figure 3 displays the mass spectra obtained from the study of welding fume particles at the laser ionisation wavelengths of 193 and 355 nm. Inorganic compounds were analysed *in situ* using 355 nm, whereas organic compounds, especially the investigation of PAH, require an additional treatment. 1.5 µL of a TCNQ solution (saturated solution in analytical grade methanol) is deposited on the filter to increase the sensitivity of PAH detection. Solvent is removed by evaporation at room temperature. Under these conditions, C-T complexes are formed and allow for the sensitive detection of PAHs.[6] The use of the 193 nm laser wavelength also ensures an increase in sensitivity.

At 355 nm in negative detection mode, the major detected ions are associated with inorganic compounds. They consist mainly of association between chromium or molybdenum atoms with oxygen. In addition, some ions containing fluorine are also observed. They are thought to result from recombination processes during or after laser irradiation between species expelled from the Teflon® filter and the dust particles. The distribution of $Cr_2O_4^-$, $Cr_2O_5^-$ and $Cr_2O_6^-$ cluster ions may be used to identify the nature of chromium present in the sample studied. The mass spectrum shown in Figure 3(a) has a $R=Cr_2O_4^-/Cr_2O_6^-$ ratio typical of a hexavalent chromium compound. This experiment has been reproduced 15 times on different locations of the filter. Six mass spectra correspond to anhydrous trivalent chromium and nine to anhydrous hexavalent chromium. Consequently, it is reasonable to consider for this sample that 40% of chromium is trivalent and 60% is hexavalent. In positive ions, the $K_3CrO_4^+$ ion is detected with poor abundance.

At the 193 nm wavelength, several PAH compounds are observed in the m/z 200–300 range. They are detected as odd electron molecular ions $M^{+\bullet}$, no fragmentation of either PAH protonated

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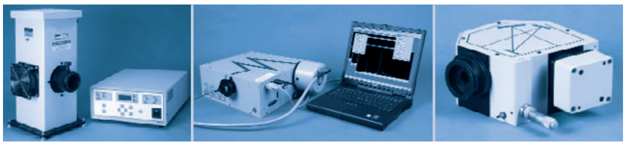

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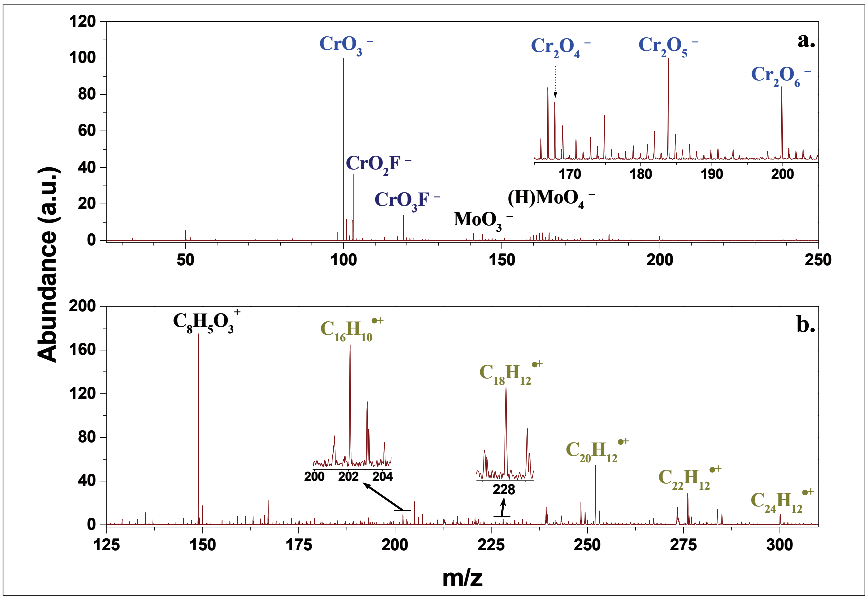


Figure 3. Analysis of welding fume dust particle: (a) LA-FT-ICR-MS in negative-ion mode with an irradiance of ~5×10^7 W cm^{-2} at the laser wavelength of 355 nm, (b) LD-FT-ICR-MS in positive-ion mode with TCNQ π-complexing agent at the laser wavelength of 193 nm with an irradiance of ~5×10^6 W cm^{-2}. The LA-FT-ICR-MS distribution of $Cr_2O_{4-6}^-$ ions are characteristic of hexavalent chromium compounds.

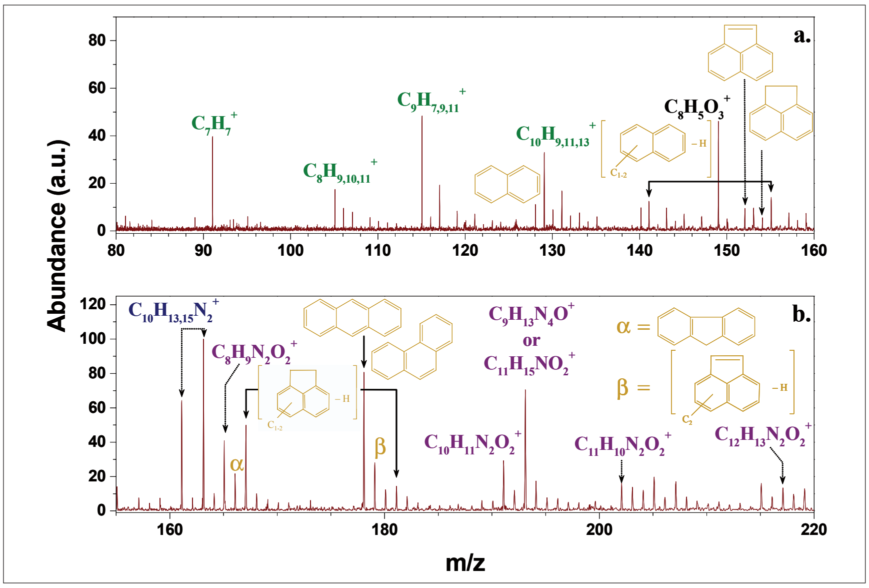


Figure 4. LD-FT-ICR-MS of MMS after bubbling in a 7,7′,8,8′-tetracyanoquinodimethane solution at a concentration of 10^{-4} mol L^{-1} in CH_2Cl_2. Measurement is performed in positive-ion mode with a power density of ~5×10^6 W cm^{-2} at the 193 nm laser wavelength in the (a) 80–160 and (b) 160–220 mass ranges.

or deprotonated molecules are observed. Pyrene and/or isomers are specifically detected at *m/z* 202. Chrysene and/or isomers are highlighted at *m/z* 228. The signal at *m/z* 252 is assigned to benzo[*a*]pyrene and/or isomers. Benzo(g,h,i)fluoranthene and/or isomers and coronene are also detected at *m/z* 276 and 300, respectively. In contrast to a previous study performed on diesel particle matter[6] alkyl-PAHs are not detected. Several other signals may be linked to several organic species such as phthalate compounds at *m/z* 149. Similar experiments have been performed without adding a TCNQ solution. In this case, the signal associated with PAHs decreases by a factor of between 2 and 10. The sensitivity increase appears to be higher for the smallest PAHs, which are known to be more volatile. The formation of C-T complexes allows the vapour pressure of PAHs to be decreased and consequently the PAH to be stabilised during analysis in the mass spectrometer.

Cigarette smoke particles

Method 1: Analysis of mainstream cigarette smoke after bubbling in TCNQ solution

Figure 4 shows the positive mass spectra of MMS obtained at low irradiance in the 80–220 *m/z* range. $C_xH_y^+$ hydrocarbon species and ions also including nitrogen and oxygen heteroatoms are observed. According to the mass resolution and the accurate mass measurement obtained under the experimental conditions used, part of the hydrocarbon species corresponds to carbon–hydrogen combinations related to PAH and alkyl PAH compounds. Naphthalene, acenaphthylene, acenaphtene, fluorene and anthracene (or phenanthrene) are more particularly detected as odd electron molecular $M^{+\bullet}$ ions at *m/z* 128, 152, 154, 166 and 178, respectively. Moreover, C_1-, C_2- and C_3-alkyl PAHs are also detected for naphthalene (*m/z* 141 and 155), acenaphthylene (only the C_2-compound at *m/z* 179) and acenaphtene (*m/z* 167 and 181). These species, which have an even *m/z* ratio correspond to $[M-H]^+$ or $[M-CH_3]^+$ ions of C_1-, C_2- and C_3-alkyl PAHs. Indeed, alkylated diaromatic and alkylated small size triaromatic compounds undergo under laser irradiation hydrogen or methyl elimination processes to form high stable tropylium analogue ions. Small hydrocarbon ions are also detected: at *m/z* 91 ($C_7H_7^+$ tropylium ion), 105/106/107 ($C_8H_{9,10,11}^+$), 115/117/119 ($C_9H_{7,9,11}^+$) and 129/131/133 ($C_{10}H_{9,11,13}^+$). These ions could be associated to the differently unsaturated hydrocarbons present in tar.

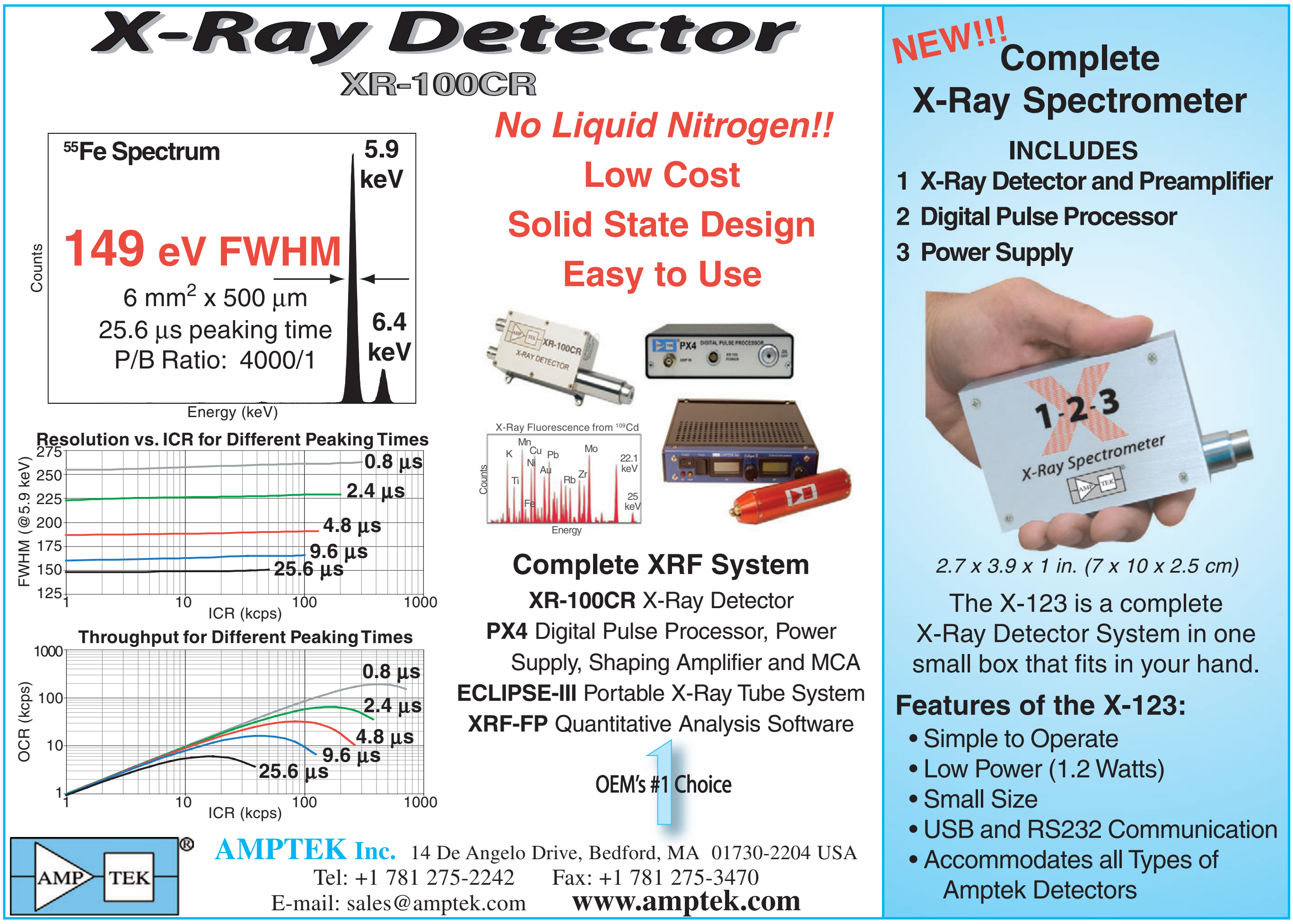
Species involving oxygen and nitrogen atoms are also detected. More specifically, nicotine pseudo-molecular $[M-H]^+$ and $[M+H]^+$ ions are observed at *m/z* 161 ($C_{10}H_{13}N_2^+$) and 163 ($C_{10}H_{15}N_2^+$), respectively. An intense ion is also detected at *m/z* 193. In spite of the high mass accuracy measurement obtained in the study (average error is close to 2 ppm) for this sample two assignments could be proposed: $C_9H_{13}N_4O^+$ (exact mass: 193.10839) and $C_{11}H_{15}O_2N^{+\bullet}$ (exact mass: 193.10973). The mass resolution required to distinguish both compounds is 145,000. Due to a lack of sensitivity in the very high-resolution mode, it was not possible to definitely assign the elemental composition and the structure of this ion. Nevertheless, $C_{11}H_{15}O_2N^{+\bullet}$ may be ascribed to a pyridine ring linked to an alkyl ester chain ($C_5H_4N–C_6H_{11}O_2$). $C_9H_{13}N_4O^+$ may correspond to the protonated ion of an amino derivate of N′-nitrosonornicotine (NNN), which is a tobacco-specific nitrosamine present in MSS. Finally, several $C_xH_yN_2O_2$ species are also detected at *m/z* 165, 191, 202 and 217.

Table 1. Assignment of positive ions detected between *m/z* 161 and 191 in the LD-FT-ICR-MS study of MMS particulate matter collected on an extraction disk with a power density of ~5×10⁶ W cm⁻² at the 193 nm laser wavelength.

Measured mass	Calculated mass	Error in ppm	Structure	Number of unsaturations	Mass resolution
171.116051	171.116826	−4.53	$C_{13}H_{15}^+$	6	12,411
172.111862	172.112075	−1.24	$C_{12}H_{14}N^+$	7	12,997
173.106520	173.107324	−4.65	$C_{11}H_{13}N_2^+$	7	10,877
173.132058	173.132476	−2.42	$C_{13}H_{17}^+$	5	11,712
175.122642	175.122974	−1.90	$C_{11}H_{15}N_2^+$	6	7936

Method 2: Analysis of mainstream cigarette smokes collected on extraction disks

When extraction disks are investigated at low irradiance close to ~5×10⁶ W cm⁻² numerous and large species up to *m/z* 700 are observed. Under these experimental conditions it is possible to obtain the fingerprint of MSS particulate matter. However, the large number of compounds present in cigarette smoke—up to 100,000—is expected to lead to significant isobaric interferences. Consequently, it is not always possible to definitely assign a formula to an observed ion. To ensure better analysis conditions, we increased the average mass resolution to about 10,000 for ions in the 160–250 *m/z* range. For example in the 171–175.5 mass range,



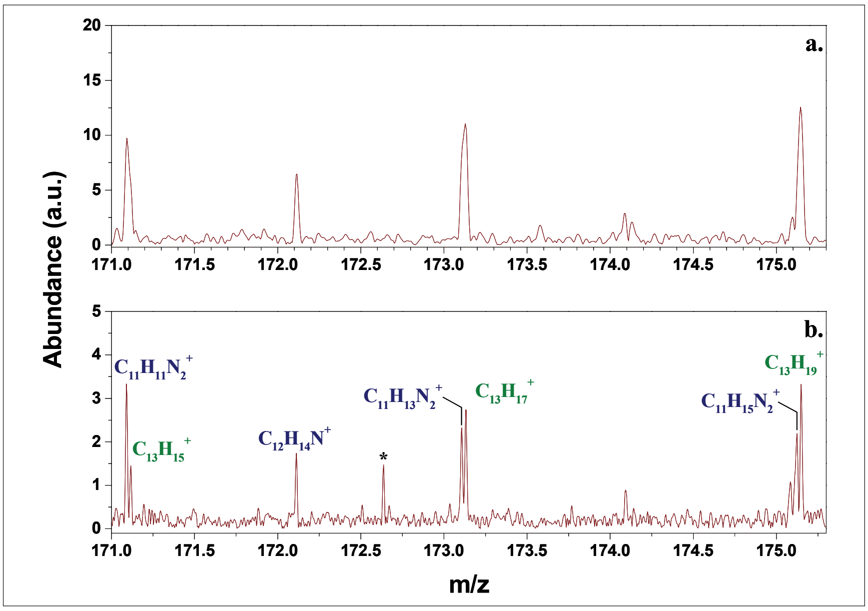


Figure 5. Positive LD-FT-ICR-MS of MSS particulate matter collected on an extraction disk (sample preparation method 2) obtained with an irradiance of ~5×10^6 W cm^{-2} at the 193 nm laser wavelength. Spectra are obtained under (a) medium and (b) high mass resolution conditions. See mass resolution in Table 1 and assignment in Figure 6. Asterisked ion corresponds to a foldover signal.

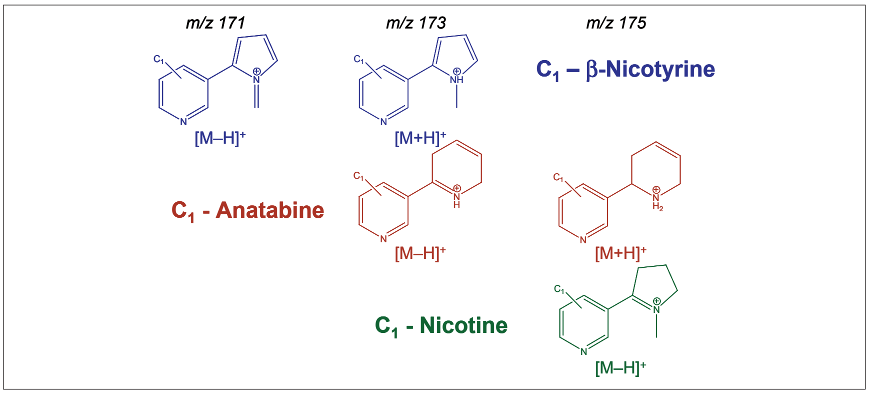


Figure 6. Assignment of positive ions associated to nicotine linked compounds observed in Figure 5.

Figure 5, isobaric interferences disappear at *m/z* 171, 173 and 175 (see Table 1). Thus, $C_{11}H_{11,13,15}N_2^+$ ions observed at *m/z* 171.091, 173.107 and 175.123, respectively, are distinguished from $C_{13}H_{15,17,19}^+$ ions detected at *m/z* 171.116, 173.132 and 175.148, respectively. $C_xH_y^+$ ions are thought to be from differently unsaturated alkyl chains of alkanes, fatty acids, aldehydes or ketones. Such compounds are present in the waxes of tobacco leaves or may be formed by pyrolysis of alkanes such as *n*-dotriacontane, a C_{32} alkane. $C_{11}H_{11,13,15}N_2^+$ ions are related to the $[M-H]^+$ and/or $[M+H]^+$ pseudo molecular ion of C_1-alkylated nicotine, anatabine, anabasine or β-nicotyrine (Figure 6). This latter compound is a degradation product of nicotine, which corresponds to the reduction of pyrrolidine ring into pyrrolic ring. Moreover, the $[M+H]^+$ ion of C_1-alkylated nicotine (or anabasine) is observed at *m/z* 177.138.

Conclusion

The results obtained by LA-FT-ICR-MS or LD-FT-ICR-MS for the study of various pollutants in very different environmental matrices clearly highlight the great capability of high-resolution mass spectrometry in combination with laser irradiation techniques for the study of very complex matrices. Moreover, these techniques can be used to study simultaneously organic and inorganic pollutants, thereby demonstrating the versatility of our approach. Finally, the limited pretreatments or the absence of pretreatments to obtain significant and valuable information offer a significant time saving. The choice of the appropriate laser parameters (irradiance and wavelength) as a function of the investigated pollutants ensures simultaneously that the compound of interest is extracted and ionised and allows its detection to be achieved by mass spectrometry. To increase further the potential of our approach, some improvements to our methodologies may be made. Isotopic dilution mass spectrometry (IDMS) could be used to enable quantisation. In addition, tandem mass spectrometry MS^n experiments could be performed to unambiguously identify the structure of detected ions. Finally, the use of an FT-ICR instrument fitted with a higher magnetic field would increase dramatically the accuracy of mass measurement, the mass resolution and the accessible range of measured masses.

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