

A Glimpse into the Nature of Particles Created During Pulsed Laser Ablation of Arsenic Compounds in Ambient Gases

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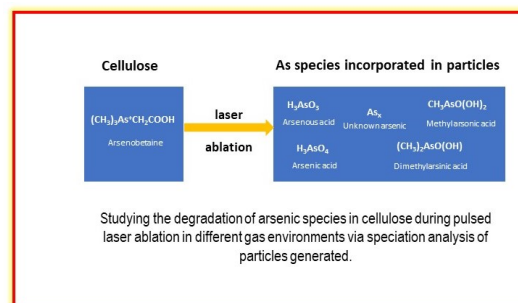
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ABSTRACT: The composition of particles resulting from pulsed laser ablation is not well understood, although it is anticipated that molecules from the ablated material undergo varying degrees of breakdown, depending on factors such as laser wavelength, energy, pulse width, matrix properties, and gas atmosphere. As reliable arsenic characterization and speciation techniques are available, a fundamental study was undertaken to shed light on the behavior of arsenic compounds (arsenic pentoxide, dimethylarsenic acid, and arsenobetaine within a cellulose matrix, along with pure elemental arsenic), using a pulsed 213 nm Nd:YAG laser and ablation in different gas atmospheres (He, Ar/CO₂ [99/1 %], Ar/O₂ [80/20 %], and O₂) at atmospheric pressure. The generated arsenic, collected in aerosol form on inline syringe filters (0.2 μm), was subjected to sequential dissolution, yielding water-soluble, HCl-soluble, and insoluble fractions. The water-soluble fraction was analyzed for arsenic species using chromatographic techniques in combination with element-specific detection. The analysis revealed that extremely complex processes take place during laser ablation, not only (partially) stripping organoarsenic species from their methyl groups and lowering the valence state, but also creating conditions for the synthesis of methylated arsenic species from arsenic pentoxide and generating more or less soluble nano/micro/macro particles for all arsenic compounds. These findings contribute to a more nuanced understanding of the multifaceted photochemical transformations that may occur during laser ablation of molecules.



INTRODUCTION

Laser ablation (LA) techniques have gained widespread popularity across various disciplines, including biological, biomedical, geological, and forensic sciences, in particular for the quantitative microanalysis of elements in solid samples. These techniques provide valuable insights into the distribution of molecules or nuclides, unraveling biogeochemical and physicochemical processes.^{1,2} Rasterizing with a pulsed laser beam across the surface of a sample releases material above a certain fluence threshold, which can then be analyzed for relevant information about molecules or nuclides using element-specific

detectors.³ When the laser interacts with the sample, the material ejected in the plume contains different types of species as a result of photochemical fragmentation:⁴ ions, neutral molecules, and (larger) solid particles. However, detection is primarily associated with measuring the total element content in these fragmentation products. This is performed either by mass spectrometry (ICP-MS) or optical emission spectroscopy (OES), following the high-temperature inductively coupled plasma (ICP) ionization or excitation of atoms in laser ablation-generated material.

This study exclusively investigates the laser ablation of arsenic compounds at atmospheric pressure, initially in a He atmosphere, the preferred carrier gas for analysis by LA-ICP-MS and LA-ICP-

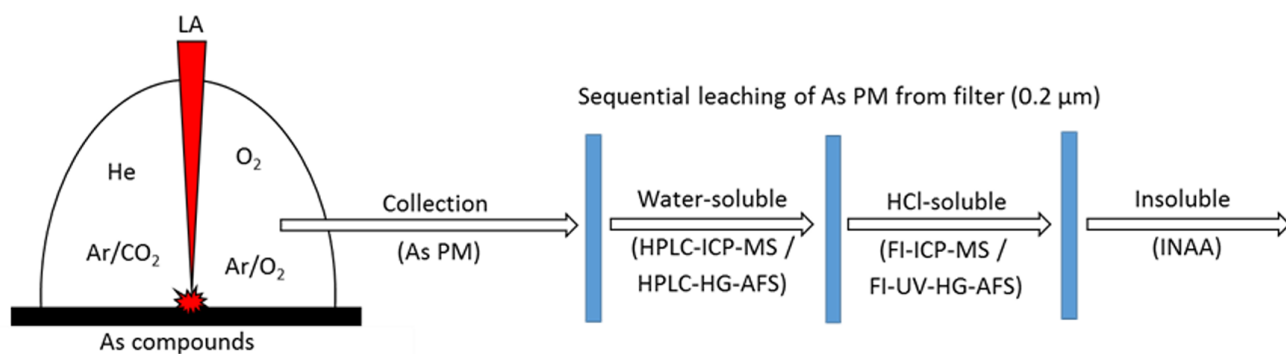


Fig. 1 Experimental workflow for laser ablation of As compounds (As(V), DMA, or AsB in cellulose and pure elemental As(0)) in different gas atmospheres (He, Ar/CO₂ [99/1 %], Ar/O₂ [80/20 %], or O₂, all Messer), followed by collection of particulate As matter (As PM), sequential extraction, and the analysis of the extracted fractions to determine the water-soluble As species, total HCl-soluble fraction, and insoluble fraction.

OES.⁵ In laser ablation, particles and compounds are formed by condensation in the vapor plume initiated by nucleation and subsequent coalescence and agglomeration.⁶ In general, the particles formed exhibit morphologies that can be classified as very fine round nanoparticles (< 20 nm), intermediate-sized nanoparticles (50–200 nm), and large, irregular microparticles (0.5–1.5 μm).⁷ Nano- and femtosecond lasers have different ablation and particle formation mechanisms, resulting in different particle size distributions and compositions.⁸ For conducting samples, such as alloys, nanosecond lasers may experience additional hydrodynamic sputtering (direct expulsion of the heated liquid phase) which results in bimodal particle size distributions.⁹ The composition of these smaller and larger particles is (slightly) different and can therefore lead to analytical anomalies (elemental fractionation), which are exacerbated by gravitational settling and the variable degree of ionization/excitation during ICP-MS/OES analysis.^{10–13}

Plasma chemistry constitutes a complex field of research¹⁴ primarily addressed through the simulation of laser ablation processes in the plume using molecular dynamics.¹⁵ This approach allows researchers to gain a deeper understanding of the underlying mechanisms at play.^{16,17} In general, bonds are broken when dissociation energies E (in eV) are lower than $h \cdot c / \lambda$, where h ($4.136 \cdot 10^{-15}$ eV·s) is the Planck constant, c is the speed of light ($3.0 \cdot 10^{17}$ nm·s⁻¹), and λ (in nm) is the laser wavelength. Photochemical dissociation processes are known to dominate for photon energies greater than 4.7 eV per photon,¹⁸ which translates to wavelengths less than 266 nm. Lasers with wavelengths below 266 nm dispense enough residual thermal energy after photolytic scission for thermally driven ejection of material. The exact composition of the particles produced during ablation can vary based on the laser ablation conditions, such as wavelength, energy, pulse width, and matrix properties, but also on the gas environment during ablation. These conditions can influence the degree of fragmentation via photochemical and photothermal bond-breaking processes, and are responsible for the composition

of the generated particles. The primary photochemical reactions that occur during laser ablation of cellulose include thermal degradation, resulting in the breakdown of the cellulose chains into smaller fragments and pyrolysis products, *e.g.*, furans, levoglucosan, and other small sugar-derived compounds, next to volatile organic compounds such as formaldehyde, acetaldehyde, acetic acid, and methanol.¹⁹ When cellulose is ablated in an oxygen atmosphere, it can produce CO and CO₂ through combustion reactions. To the authors' knowledge, no experimental research has been conducted on the composition of particles generated by laser ablation of cellulose doped with organoarsenic compounds. While one might anticipate the obliteration of organoarsenic compounds by powerful UV lasers, this study aims to demonstrate the extent to which these compounds can “survive” in the particles generated.

EXPERIMENTAL

For validation purposes, the experiments were performed independently in two laboratories (Laboratory 1 [Slovenia] and Laboratory 2 [Austria]) using the same laser ablation device under identical conditions, and complementary arsenic speciation setups (Laboratory 1 – HPLC-HG-AFS and Laboratory 2 – HPLC-ICP-MS). During the experiments, the need for further characterization led to additional leaching tests and residual arsenic analysis by instrumental neutron activation analysis (INAA), both performed only in Laboratory 1. Fig. 1 shows a schematic diagram of the workflow where it can be seen how four different arsenic compounds are ablated in different gas atmospheres, and the particles generated subjected to speciation analysis.

Preparation of samples. LLG plain disc filter paper (150 mm diameter; 100 % cellulose, ash content 0.06 %, Lab Logistic Group GmbH) was cut into strips (1×9 cm) and soaked for 1 h in stock solutions of arsenic compounds (Fig. S1) containing 1 g As L⁻¹

of either arsenate (As(V), Merck Titrisol standard solution), dimethylarsinic acid (DMA, Sigma-Aldrich) or arsenobetaine (AsB, synthesized in-house). Blank filters were soaked in ultrapure water. Filter strips were air dried and stored in plastic containers. For laser ablation, both ends of the filter paper were folded toward the center, resulting in three layers of paper. The folded filter was taped to a clean filter on all four sides. Elemental arsenic was used as a piece of crystalline arsenic (As(0)) and mounted on a glass slide with double-sided tape.

Laser ablation. Each LLG filter and the As(0) crystalline material were subjected to laser ablation at 213 nm (New Wave Research UP-213 laser ablation system) under the following conditions: fluence, *ca.* 1.0 J cm⁻²; beam diameter, 100 μm; scanning speed, 10 μm s⁻¹; repetition rate, 20 Hz; scan line length, 10 mm (for blanks, As(V), DMA and AsB) and 2 mm (for As(0)). The ablated material was transported out of the ablation cell with a carrier gas (0.95 l min⁻¹) and collected onto an inline syringe filter unit (Millipore PVDF membrane filter, 0.22 μm pore size, 25 mm diameter [Laboratory 1] or Bruckner Analysetechnik Nylon membrane filter, 0.2 μm pore size, 25 mm diameter [Laboratory 2]). The loaded syringe filters were stored at 4 °C for a short time (days). To prevent carry-over from one sample to another, the samples were ablated with blanks between each sample.

Arsenic speciation and total arsenic determination in eluates. Immediately prior to analysis, syringe filters with entrapped particles were leached with 0.8-1.0 ml ultrapure water to release water-soluble arsenic species. Anionic arsenic compounds were separated on an anion exchange column (Hamilton PRP-X100, 5 μm, 50 × 4.6 mm) under laboratory-specific separation conditions (15 mmol L⁻¹ KH₂PO₄, pH 6.1 at room temperature in Laboratory 1 and 20 mmol L⁻¹ NH₄H₂PO₄, pH 6.0 at 40 °C in Laboratory 2). The total arsenic concentration in aqueous leachates was determined by the flow injection (FI) method using either ultraviolet digestion - hydride generation - atomic fluorescence spectrometry (FI-UV-HG-AFS, Laboratory 1) or inductively coupled plasma mass spectrometry (FI-ICP-MS, Laboratory 2). Laboratory 1 performed additional leaching of the filters (to release recalcitrant arsenic) with 3 ml of 2.4 M HCl (for blanks and filters loaded with As(V), DMA, and AsB) or 2 × 3 ml of 2.4 M HCl (for filters loaded with As(0)). The insoluble, residual arsenic fraction on the inline syringe filters was analyzed by INAA.²⁰ Standard deviations were calculated from three parallel ablation runs, each analyzed by both laboratories.

RESULTS AND DISCUSSION

We can anticipate that laser ablation of organoarsenic compounds in cellulose may lead to the formation of arsenic-containing particles, volatile arsine or methylarsines, inorganic oxidation/reduction

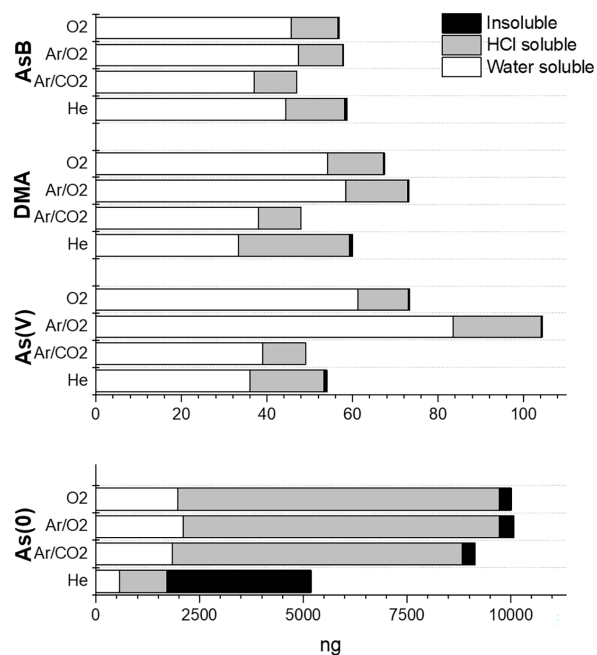


Fig. 2 Solubility of laser-induced particulate matter from ablation of different arsenic species in several gas atmospheres, collected on an inline syringe filter and fractionated into a water-soluble As fraction, an HCl-soluble As fraction, and an insoluble As fraction (note that the masses along the x-axis are different for the top three plots and the bottom plot). The data are also shown in Table S1, including their uncertainties.

products such as arsenite or arsenate, and fragmentation products. Gases produced from degradation of cellulose may react with any volatile compounds released from the organoarsenic compounds to form additional products. Below, the fate of As(V), DMA, and AsB in cellulose, and elemental As(0), upon pulse laser ablation in various gas atmospheres is investigated (see also Fig. 1).

Figure 2 shows that during laser ablation of As(V), DMA, and AsB in cellulose, the different gas atmospheres produce similar solubility fingerprints for the particulate matter collected on the inline syringe filters. The general trend is a water-soluble fraction of 55.4-83.5 %, an HCl-soluble fraction of 16.1-43.3 %, and a negligible insoluble fraction of up to 1.3 %. Fig. 2 also shows that ablation of As(0) in the different gas atmospheres results in approximately 100 times more particulate arsenic matter on the inline syringe filters than ablation of arsenic-saturated filter paper (with arsenic concentrations around 1,800 μg g⁻¹ As of As(V), DMA or AsB).

For laser ablation of As(0) in He atmosphere, the results show that the arsenic collected is slightly soluble in water (11.0 %) and HCl (21.9 %); the large insoluble fraction (67.1 %) shows a visible dark gray layer on the filter. This result is not unexpected, as the laser ablation process in a He atmosphere is inherently “reductive”, thereby facilitating the formation of As(0) particles. Since As(0)

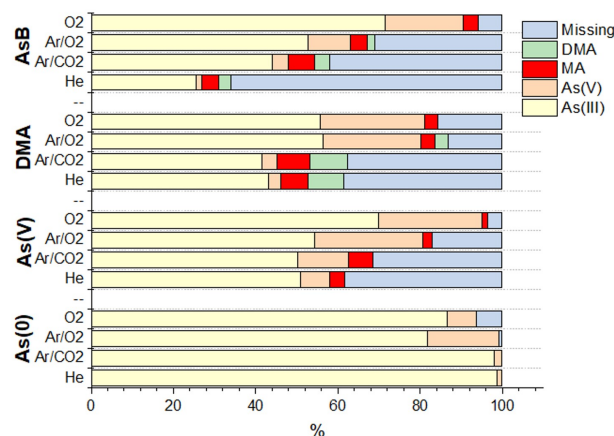


Fig. 3 Arsenic speciation results related to the water-soluble fraction from Fig. 1, i.e., populating the white bars in Fig. 2 with arsenic compounds. “Missing” is defined as the difference between total As and chromatographically identified As. The data are also tabulated in Table S2, including their uncertainties.

nanoparticles are water-soluble,²¹ the large insoluble As(0) fraction likely occurs in the form of larger micro/macroparticles. In contrast, ablation of As(0) in oxygen-containing gas-atmospheres yields nearly colorless inline syringe filters, indicating minimal formation of larger micro/macro particles, accounting for 2.9-3.5 % of the total collected particles. The remaining fractions are mainly water- and HCl-soluble, contributing around 20 and 77 %, respectively.

The speciation analysis results presented in Fig. 3 indicate that a considerable portion of the water-soluble arsenic produced during the laser ablation of As(V), DMA, and AsB in cellulose, under various gas atmospheres, is unaccounted for as it is “missing” from the overall totals. This “loss” is defined as the difference between total As and chromatographically identified As. “Losses” ranged from 3.6 % to 38.3 % for As(V), 13.1 % to 38.5 % for DMA, and 5.8 % to 66.1 % for AsB. The most significant arsenic “loss” occurred in the He reducing gas atmosphere, decreasing progressively with increasing levels of oxygen in the ablation gas. This suggests that the micro/macro particles collected on the inline syringe filters may have dislodged during leaching, ending up in the water-soluble fraction and subsequently being ‘filtered out’ on the (pre)column. Alternatively, laser ablation may have generated a so far unknown arsenic compound with strong retention on the analytical column. In contrast, laser ablation of As(0) in all gas atmospheres showed a markedly less significant effect, with only minor amounts (0.8 to 5.4 %) “missing” from the overall totals.

As the available oxygen in the ablation gas increases during ablation of As(V) in cellulose, a larger fraction of the particles undergo photooxidation, with the sums of As(III)+As(V) more or less increasing from 65.5 % (He) to 62.6 % (Ar/CO₂) to 80.6 %

(Ar/O₂) to 95.0 % (O₂). In all these cases, a minor percentage (1.4-5.9 %) of methylarsonic acid (MA) forms during laser ablation of As(V). The organoarsenic species DMA and AsB are almost completely scrambled during laser ablation, with small amounts of DMA (0.0-9.2 %) and no detectable AsB in the water-soluble fraction. For both DMA and AsB, it is evident that with increasing amounts of oxygen in the ablation gas, more As(III) + As(V) is formed, in unison with a decreasing amount of micro/macro particles “lost” on the (pre)column. These observations indicate that the wavelength of the 213 nm Nd:YAG laser (5.82 eV) not only facilitates the dissociation of existing bonds in organoarsenic compounds (with bond dissociation energies: As-As, 3.96 eV; As-O, 4.99 eV; As-H, 2.82 eV; As-C, 3.80 eV) but also initiates the formation of new bonds during the ablation of As(V), implying a synthesis process.

CONCLUSION

In conclusion, laser ablation of arsenic compounds (As(V), DMA, and AsB) in cellulose matrix under different gas atmospheres (He, Ar/CO₂ [99/1 %], Ar/O₂ [80/20 %], and O₂) led to the formation of particulate arsenic matter, comprising a mixture of arsenic species. A significant portion of the particulate arsenic matter is soluble in water and HCl, with the water-soluble fraction predominantly comprising As(III), indicative of reducing conditions within the ablation plume. With increasing oxidative gas atmosphere, a larger portion of the water-soluble arsenic transitions to inorganic As. None of the original molecular species “survive” when ablating DMA and AsB in oxygen atmosphere. A small amount of MA is formed during laser ablation of As(V) in the cellulose matrix. Laser ablation of elemental As(0) in a “reductive” He atmosphere yields mainly insoluble micro/macro particles, with the percentage dropping to about 3% in more “oxidative” gas atmospheres.

The fact that laser ablation of arsenic compounds results in a whole spectrum of arsenic species with incomplete conversion to inorganic arsenic, is an unexpected outcome of this work, warranting further research to elucidate the processes occurring in the laser ablation plume. Moreover, the findings offer supplementary evidence highlighting the difficulties related to precise calibration in studies utilizing LA-ICP-MS/OES analysis. Specifically, challenges arise from gravitational settling and insufficient ionization/excitation of atoms associated with particles.

ASSOCIATED CONTENT

Supporting information is available (Fig. S1, Tables S1 and 2).

AUTHOR INFORMATION



Johannes van Elteren received his PhD in Analytical Chemistry from Utrecht University (NL) in 1991. Subsequently, he held faculty positions at the University of Liverpool (UK), De Montfort University (UK), and Delft University of Technology (NL). Since 2002, he has been employed at the National Institute of Chemistry, Ljubljana (SLO), where he recently retired

as a research professor. While Johannes van Elteren has been active in various analytical disciplines, his research over the past 15 years has predominantly centred on the LA-ICP-MS technique with a specific focus on elemental imaging and nanoparticle analysis. He significantly contributed to advancing LA-ICP-MS imaging, particularly in terms of its fundamental aspects, thereby providing a deeper understanding of the parameters influencing the spatial resolution and mapping speed. Additionally, he played a pioneering role in developing the LA-single particle-ICP-MS technique for nanoparticle sizing and counting.



Walter Goessler received his MSc in chemistry in 1991 and his PhD in 1997 from the University of Graz in Austria. Thereafter he got a position as university assistant at the Institute of Analytical Chemistry at the University of Graz. After his habilitation in 2003 he was promoted to associate professor in Analytical Chemistry. In 2009, he established his

research group ACHE (Analytical Chemistry for Health and Environment). His research interest lies in speciation analysis, with a focus on arsenic. Current research topics include the transformation of arsenic from soil to biota, with a specific emphasis on mushrooms. Development of new methods for speciation analysis using different chromatographic systems and element-selective detection with ICPMS/(MS) are key competences in his research group. Walter Goessler is (co)author of over 360 articles in peer-reviewed journals with an h-index of 69 (Scopus).

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Notes

The authors declare no competing financial interest.

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