



Afterglow of a microwave microstrip plasma as an ion source for mass spectrometry[☆]



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ARTICLE INFO

Article history:

Received 4 February 2014

Accepted 16 November 2014

Available online 22 November 2014

Keywords:

Microwave plasma

Hydride generation

Ambient desorption/ionization

Miniaturization

Volatile organic compounds

ABSTRACT

A microwave-induced plasma that was previously used for optical emission spectrometry has been repurposed as an afterglow ion source for mass spectrometry. This compact microwave discharge, termed the microstrip plasma (MSP), is operated at 20–50 W and 2.45 GHz in helium at a flow of 300 mL/min. The primary background ions present in the afterglow are ionized and protonated water clusters. An exponential dilution chamber was used to introduce volatile organic compounds into the MSP afterglow and yielded limits of detection in the 40 ppb to 7 ppm range (v/v). A hydride-generation system was also utilized for detection of volatile hydride-forming elements (arsenic, antimony, tin) in the afterglow and produced limits of detection in the 10–100 ppb range in solution. The MSP afterglow was found capable of desorption and ionization of analyte species directly from a solid substrate, suggesting its use as an ion source for ambient desorption/ionization mass spectrometry.

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1. Introduction

Rare-gas plasmas have a strong history as excitation/ionization sources for optical emission (OES) and mass spectrometric (MS) analysis. The most well known plasma source for elemental analysis is the radio-frequency inductively coupled plasma (ICP), developed in the 1960 s [1] and patented in 1969 [2]. Higher frequencies were also found useful for atomic analysis in the form of a microwave plasma, which operated at frequencies above 300 MHz, typically 2.45 GHz [3]. The microwave plasma has some advantages over an ICP, including its ability to be operated at moderate power levels and gas flows, even in helium.

Ambient desorption/ionization mass spectrometry (ADI-MS), begun with the introduction of desorption electrospray ionization (DESI) in 2004 [4], showcases the ability of traditional ionization sources to be used in alternative ways. In this case, it was found that the addition of an auxiliary gas flow around an electrospray ionization (ESI) [5] source could generate ions directly from a sample surface. As an extension of this thinking, an atmospheric-pressure glow discharge (APGD) was operated in the flowing afterglow mode and generated ions directly from a sample surface [6,7]. Similarly, a heater was added to a corona discharge to create the direct analysis in real time (DART) source [8].

An RF discharge was also modified by Kratzer et al. [9] to function as an ADI-MS source. From these examples, it seems inevitable that a microwave discharge would be applied to ambient mass spectrometry [10,11].

Miniaturization has increased the attractiveness of sources for use under ambient conditions. Examples include a liquid-sampling glow discharge [12], and a microfabricated atmospheric-pressure glow discharge [13]. A compact microwave plasma source would be particularly well suited for ADI-MS. Such a source, the microwave microstrip plasma (MSP), was introduced by the Broekaert group in 1999 [14,15] and improved in 2003 [16]. The source was used primarily for optical emission spectrometry (OES) of inorganic species, including the cold-vapor technique for the determination of mercury [17–19], hydride generation for the determination of arsenic and antimony [20,21], as a detector for halogenated hydrocarbons in gas chromatography [22], and for gas-phase bromine, chlorine, sulfur, carbon dioxide, and cyanide determination [23]. However, these applications all involved the introduction of sample material into the microwave discharge itself, which can perturb the plasma. In the present study, the afterglow of the MSP discharge is utilized for sample ionization and desorption in order to avoid plasma quenching and memory effects. Ambient desorption/ionization, exponential dilution, and hydride generation were all explored for sample introduction into the MSP afterglow and yielded attractive figures of merit.

2. Experimental

Fig. 1 displays a schematic diagram of the microstrip plasma (MSP) and a white-light image of the MSP at the inlet of an atmospheric-sampling mass spectrometer. All samples were introduced into the

[☆] This paper is dedicated to Nicolò Omenetto, on the occasion of his 75th birthday, in recognition of his outstanding contributions to the field of laser spectrochemistry and as an editor of Spectrochimica Acta Part B.

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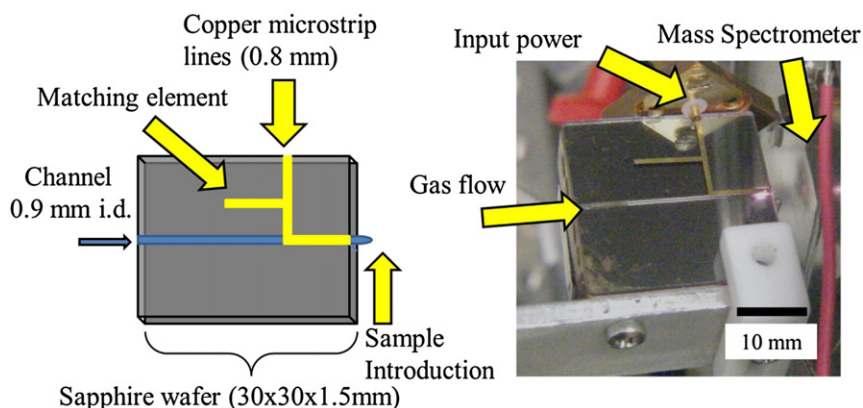


Fig. 1. Schematic diagram of microwave microstrip plasma (MSP) used in this work (left) and a white-light image of the source (right), which shows it sitting in front of the mass spectrometer. Scale bar represents 10 mm in image on right.

region between the MSP and the entrance orifice of the mass spectrometer. The distance between the microwave source and the inlet was varied to determine optimal placement, based on signal level, and was found to be 5 mm.

The MSP has been extensively described previously [14–16] but will be recapped here for clarity. A square piece of sapphire ($30 \times 30 \times 1.2$ mm) is used to support the MSP, with a 0.9 mm diameter hole through the center for gas delivery. Copper strips deposited on top (0.8 mm wide strip) of the plate distribute power for the discharge; a balancing arm was added for impedance matching. Power was supplied through a microwave power generator (Microtron 200, Electro Medical Supplies Ltd, Wantage, Oxfordshire, England) through a double-stub tuner (Model DSI09M, Weinschel Engineering, Gaithersburg, MD, USA), which was adjusted to keep reflected power below 5 W. The input line was terminated in a stub resistor (Model 8135, Bird Electronic Corporation, Cleveland, USA). All gases were ultra-high purity (99.999%, Air-gas mid-America, Bowling Green, Kentucky, USA). Helium flow was adjusted by a mass flow controller (MKS instruments, Andover, MA, USA). All analytes were reagent-grade.

A commercial time-of-flight mass spectrometer was used (LECO Renaissance®, LECO Corporation, St. Joseph, MI). Modifications to the instrument have been described in depth previously [24] but will be briefly covered here. A roughing pump was added to the first stage of the spectrometer along with an atmospheric-pressure interface, which consisted of a steel plate with a 250- μ m diameter aperture. An ion lens was added in the first vacuum stage to improve ion throughput into the second stage of the mass spectrometer interface.

A continuous-flow hydride-generation system was constructed according to previous experimental setups [25,26]. Sodium borohydride solutions stabilized with sodium hydroxide (both 1% in weight) were mixed with the analyte solution in a hydrochloric or nitric acid matrix (each 1 M); flow rates were controlled with a peristaltic pump (Gilson, Middleton, WI) into a mixing tee at a flow rate of 0.5 mL/min. To ensure complete mixing, a reaction coil was made from a 100-cm length of PTFE tubing. Liquid waste and analyte hydride passed into a gas-liquid separator that was filled with 2-mm diameter glass beads to increase the surface area and allow complete reaction to occur. A supplementary gas flow of helium at 50 mL/min was set by a mass flow controller (MKS instruments, Andover, MA, USA). The helium flow, which contained volatile hydride species, was introduced into the afterglow through a glass capillary (1 mm I.D.) positioned between the MSP and the inlet of the mass spectrometer. The position of the capillary was controlled with an x, y, z fiber-optic stage (Newport Corporation, Irvine, CA).

An exponential dilution chamber (EDC) [27] was also utilized to determine limits of detection for volatile organic compounds. The experimental setup has also been described previously [24]. In brief, a well-stirred 100 mL three-neck round-bottomed flask was used as the

dilution chamber, and helium flow through the flask was regulated by a mass flow controller (MKS instruments, Andover, MA, USA). The same glass capillary/stage setup used for hydride generation was employed to deliver the helium and analyte vapor to the optimized (based on signal level) position between the MSP and the mass spectrometer.

Headspace from volatile organic compounds (200–1000 μ g) was injected by means of a GC syringe into the round bottom flask. Based on the vapor pressure of the analyte, the amount injected, and the volume of the flask, an initial concentration was calculated. Then, from an exponential decay equation, the time domain signal was transformed into the concentration domain, to enable a calibration curve to be generated.

Powdered solid samples were introduced into the afterglow stream on melting-point capillaries (Chemglass Life Sciences, Vineland, NJ, USA) mounted on a custom-built stage (Newport corporation, Irvine, CA, USA). Simple mechanical abrasion was used to transfer small amounts (<1 mg) of material from a solid sample onto the melting-point capillary and into the MSP afterglow.

3. Results and discussion

Helium and argon were both used previously with the MSP. However, the current geometry of the MSP could be ignited only in helium. Examination of the chip showed significant erosion of the sapphire and copper at the exit of the strip. This erosion is believed to impact the chip's ability to sustain a discharge. Accordingly, helium was used for all studies reported here. The signal for the protonated water cluster

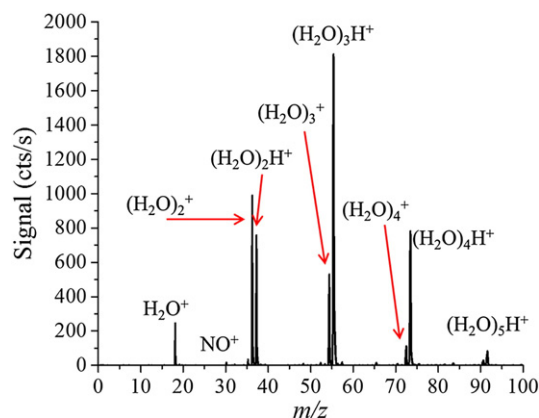


Fig. 2. Background mass spectrum from microstrip plasma, which demonstrates that the major ions are water clusters both ionized directly and protonated.

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