

A laser ablation electron impact ionization time-of-flight mass spectrometer for analysis of condensed materials

F. Drewnick and P. H. Wieser

Citation: [Review of Scientific Instruments](#) **73**, 3003 (2002); doi: 10.1063/1.1490419

View online: <http://dx.doi.org/10.1063/1.1490419>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/rsi/73/8?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Laser ablation with resonance-enhanced multiphoton ionization time-of-flight mass spectrometry for determining aromatic lignin volatilization products from biomass](#)

Rev. Sci. Instrum. **82**, 033104 (2011); 10.1063/1.3563704

[A time-of-flight resonance ionization mass spectrometer for elemental analysis of precious metals in minerals](#)

Rev. Sci. Instrum. **73**, 4295 (2002); 10.1063/1.1518146

[Trace element analysis of precious metals in minerals by time-of-flight resonance ionization mass spectrometry \(TOF-RIMS\)](#)

AIP Conf. Proc. **584**, 46 (2001); 10.1063/1.1405582

[Repetitively sampled time-of-flight mass spectrometry for gas-phase kinetics studies](#)

Rev. Sci. Instrum. **70**, 3259 (1999); 10.1063/1.1149944

[A high resolution dual mass gate for ion separation in laser desorption/ionization time of flight mass spectrometry](#)

Rev. Sci. Instrum. **69**, 1661 (1998); 10.1063/1.1148823



A laser ablation electron impact ionization time-of-flight mass spectrometer for analysis of condensed materials

F. Drewnick^{a)} and P. H. Wieser

Institute for Physics, University of Hohenheim, D-70599 Stuttgart, Germany

(Received 1 March 2002; accepted for publication 9 May 2002)

Laser desorption/ionization (LDI) mass spectrometry suffers from poor reproducibility and a strong bias in representing the chemical composition of the sample in the mass spectra. In regard to develop laser mass spectrometry towards a quantitative analysis technique desorption and ionization processes should be separated. Here we describe a time-of-flight mass spectrometer (TOF-MS) with laser ablation and subsequent electron impact ionization (LA-EI-MS). Sample material is ablated by an Nd-YAG laser pulse ($\lambda=355$ nm, $E=0.5\text{--}35$ mJ, $\tau=9$ ns), which produces ions and neutrals in the ablation plume. After expansion, parts of the plume enter the EI ion source where neutrals are ionized by electron impact ($E_{\text{el}}=70$ eV). Ions are extracted from the ion source into the flight tube of the TOF-MS by applying a pulsed repeller potential. Depending on delay times between laser pulse and repeller pulse either neutrals or ions emitted from the sample were analyzed. Different mass spectra of the same sample are obtained in these two analyzing modes under the same irradiation conditions. With a relative standard deviation of 10% to 15%, reproducibility of mass spectra is significantly better in LA-EI-MS than in LDI-MS. © 2002 American Institute of Physics. [DOI: 10.1063/1.1490419]

I. INTRODUCTION

Laser desorption/ionization mass spectrometry (LDI-MS) is frequently used in the analysis of aerosol particles,¹ in trace analysis of metals and alloys, and in analysis of geological samples.² Due to the lack of the need for any sample preparation, this method is well suited for space applications as *in situ* planetary surface analysis.³ However, some of the major drawbacks of LDI-MS are its limited reproducibility and the strong bias in representing the chemical composition of the sample in the mass spectra due to large differences in ionization probability of different chemical species in the poorly understood desorption/ionization process.^{2,4}

Due to these limitations LDI-MS is mainly used for qualitative analysis such as characterization of individual aerosol particles.^{1,4} Extension to semiquantitative measurements is only possible for simple samples such as alloys⁵ or aerosol particles⁶ consisting of only few components with the introduction of relative sensitivity factors and normalization of the single spectra.

Better reproducibility and the possibility of quantitative analysis are achieved by separation of the ablation and ionization processes. Laser ablation of the sample material with subsequent ionization of the vapor in an inductively coupled plasma (LA-ICP-MS) or by resonant or nonresonant photoionization (REMPI, L2MS) have become powerful analytical tools for elemental and organic analysis of a wide variety of samples.^{7–11}

Another approach to overcome these limitations of

LDI-MS by separation of ablation and ionization processes with relatively low experimental effort is laser ablation with subsequent electron impact ionization of the vapor for mass spectrometry (LA-EI-MS). This combination was already used in the early days of laser mass spectrometry for analysis of several target substances as graphite, metals, and alloys.^{12–15} Later applications of this technique included the analysis of several dipeptides¹⁶ and caffeine, while for the latter electrons were generated by pulsed laser irradiation of a Ta wire.¹⁷ However, a systematic investigation of LA-EI-MS as an analytical tool has not been undertaken so far. Therefore, we developed a laser time-of-flight mass spectrometer, which allows laser ablation of solid materials and subsequent electron impact ionization of the vapor. This article describes its operation and first results achieved with this instrument varying the delay time between laser ablation and electron impact postionization.

II. INSTRUMENT DESCRIPTION AND PRINCIPLE OF OPERATION

An instrument schematic is shown in Fig. 1. The vacuum system consists of a sample transfer port (1), an ablation and ionization chamber (2), and the time-of-flight mass spectrometer (3). Each of these chambers can be separated by gate valves and are pumped individually by a turbo pump and a rotary pump.

The sample transfer port is used for rapid sample introduction into the vacuum. It is pumped by a 55 l/s turbo pump (Leybold) and a 2.4 l/s dual-stage rotary pump (Leybold). Evacuation to a pressure of 10^{-3} Pa is achieved in about 10 min. The sample is mounted on a 5 mm stainless steel sample carrier and is transferred into the ablation chamber

^{a)}Author to whom correspondence should be addressed; current address: Atmospheric Sciences Research Center, University at Albany, 251 Fuller Road, Albany, NY 12203; electronic mail: drewnick@asrc.cestm.albany.edu

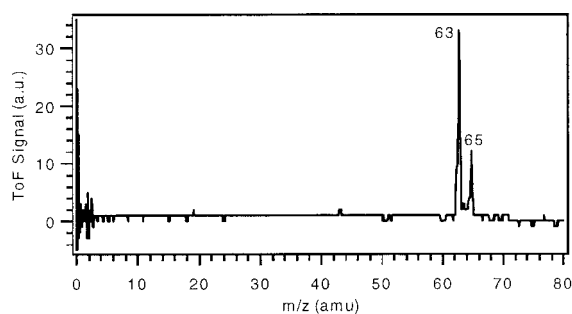


FIG. 3. Typical mass spectrum of a CuSO_4 sample with short delay time between laser ablation and injection into the flight tube. Only ions produced in the ablation process are analyzed, no electron impact ionization. Average of ten mass spectra.

taken under these conditions is shown in Fig. 3. Additional heating of the filament to produce a 70 eV electron beam does not change the mass spectra. Obviously no or only very few neutrals are present in the ionization region after this delay time.

Increasing the delay time between laser and repeller pulse decreases the intensity of the ion signals. At delay times of several hundred microseconds no ions can be detected anymore in the mass spectrometer with the electron beam off. After switching on the electron beam by heating the filament ion signals can be detected at these delay times; neutrals are present in the ionization region at this time after the laser pulse and are ionized by electron impact (LA-EI-MS). A typical mass spectrum of the same CuSO_4 sample as above, taken under these LA-EI-MS conditions is depicted in Fig. 4.

These observations lead to the conclusion that the LA-EI-MS instrument can be used in two analyzing modes by choosing appropriate delay times; an *ions mode* with short delay times of some tens of microseconds (no electron beam needed) and a *neutrals mode* with longer delay times of some hundreds of microseconds (electron beam needed for ionization of the neutrals).

As can be seen in Figs. 3 and 4, mass spectra recorded from the same sample under the same laser irradiation conditions are totally different in the two analyzing modes. In the ions mode only the copper isotope lines can be found in the spectra of the CuSO_4 samples. These spectra do not indicate any sulfate in the sample. In the neutrals mode the typical electron impact fragmentation pattern of water (m/z

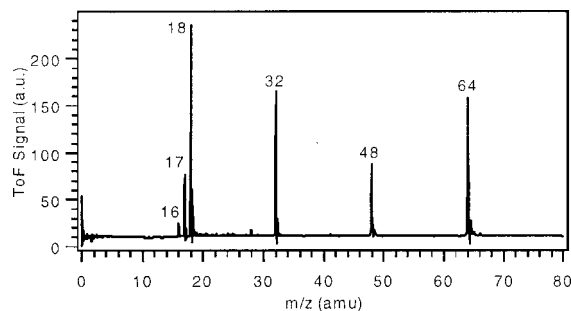


FIG. 4. Typical mass spectrum of a CuSO_4 sample with longer delay time $T_d = 1600 \mu\text{s}$. Under these conditions only neutrals ionized by electron impact are analyzed. Average of ten mass spectra.

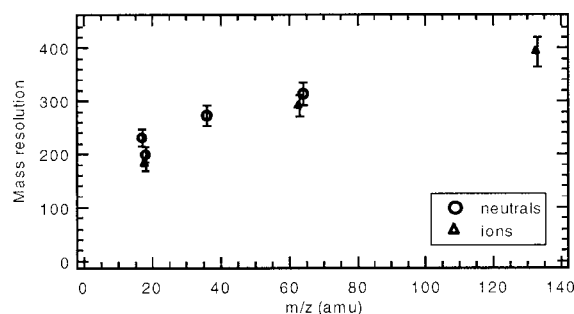


FIG. 5. Average mass resolution of lines depending on the ion mass.

$= 16 \text{ amu}:\text{O}^+$, $17 \text{ amu}:\text{OH}^+$, $18 \text{ amu}:\text{H}_2\text{O}^+$) and sulfur dioxide ($m/z = 32 \text{ amu}:\text{S}^+/\text{O}_2^+$, $48 \text{ amu}:\text{SO}^+$, $64 \text{ amu}:\text{SO}_2^+$) can be seen in the mass spectra. The two copper lines are missing completely in these spectra.

For a better understanding of the mechanisms leading to these different spectra in the two analyzing modes, a wide variety of standard samples will be analyzed. Obviously the ions emitted by the laser ablation process have a significantly larger velocity than the emitted neutrals. Future investigations on the velocity distribution will be done to provide additional insight in the processes going on at and after the laser ablation.

Resolution in time-of-flight mass spectrometry is mainly limited by the velocity distribution of the ions in direction of the flight tube and by the distribution of the ion positions at the moment of extraction into the acceleration field. Due to the orthogonal acceleration geometry of the vapor beam into the flight tube the velocity component in this direction is negligible. The distribution of the starting positions of the ions in the extraction field is determined by the width of the vapor beam and, therefore, by the diameter of the apertures between sample and EI source. Resolution is maximized in this kind of two-stage acceleration field at a certain ratio of the two acceleration voltages, depending on the geometry of the mass spectrometer.¹⁹

The mass resolution was determined for some ions of different masses as the average of the peak width (FWHM) of ten single spectra obtained under identical conditions. Uncertainty of these values is about 7%. As demonstrated in Fig. 5, the mass resolution is independent of the analysis mode and increases with increasing mass of the investigated ions. This is mainly due to the limitation of mass resolution by the finite sampling rate of the transient recorder (10 ns), which becomes less important at increasing flight times. Average resolution is between about 175 for very light ions and nearly 400 for ions with $m/z = 140 \text{ amu}$. This is sufficient to separate adjacent lines in the mass region of consideration.

For investigation of the reproducibility the peak area of several mass peaks was determined for a number (10–50) of single shot spectra received under identical analysis conditions. As a measure of reproducibility the standard deviation of the peak area σ_A divided by the mean peak area A was used. As shown in Table I relative uncertainty is in the range of 8% to 36% in the neutrals mode and in the range of 4% to 33% in the ions mode and thus significantly better than in conventional LDI-MS.

TABLE I. Reproducibility of mass spectra from a LA-EI-MS instrument in ions and neutrals mode.

Ions mode					Neutrals mode				
Sample	Ion (<i>m/z</i> /amu)	Number of spectra	Mean area (a.u.)	Reprod.	Sample	Ion (<i>m/z</i> /amu)	Number of spectra	Mean area (a.u.)	Reprod.
NaCl	Na ⁺ (23)	25	287	7%	FeCl ₃	H ³⁵ Cl ⁺ (36)	50	272	13%
		35	417	10%			50	305	8%
FeCl ₃	Fe ⁺ (56)	25	371	21%	NH ₄ Cl	NH ₃ ⁺ (17)	10	257	23%
NH ₄ Cl	NH ₄ ⁺ (18)	10	347	29%			10	297	19%
		10	178	19%			10	316	24%
CuSO ₄	Cu ⁺ (63)	10	170	33%	H ³⁵ Cl ⁺ (36)		10	372	17%
		10	328	6%			10	461	18%
		10	166	9%			10	428	20%
		10	531	4%			10	537	19%
CsCl	Cs ⁺ (133)	10	441	6%	CuSO ₄ [*] aq	H ₂ O ⁺ (18)	10	332	12%
		10	711	5%			10	406	36%
							10	197	12%
						SO ₂ ⁺ (64)	10	370	17%

The better reproducibility in the ions mode compared to conventional LDI-MS is probably due to the different irradiation conditions. In the ions mode of the LA-EI-MS instrument a larger area is irradiated by the laser pulse due to slight defocusing of the beam. This results in a smaller change of the target surface from shot to shot, yielding to a better reproducibility of the mass spectra.

IV. DISCUSSION

To overcome some of the limitations of conventional laser desorption/ionization mass spectrometry (LDI-MS) a mass spectrometer for laser ablation of solid samples and subsequent electron impact ionization of the vapor (LA-EI-MS) was developed. Solid sample material is ablated by an intense laser pulse of ~ 12 mJ pulse energy (resulting in an irradiation power density of about 7.5×10^8 W/cm²) and expands into the vacuum. Under the conditions investigated in these experiments ions and neutrals are produced in the laser ablation process. Due to the different velocities of the ions and neutrals they can be analyzed separately by applying appropriate delay times between laser ablation and extraction of the ions from the ion source into the flight tube of the time-of-flight mass spectrometer. The observed mass resolution of 175 to nearly 400, depending on the mass of the ions, is sufficient for separation of adjacent lines in the mass range of interest. Reproducibility of the mass spectra is significantly better than in conventional LDI-MS. Under optimal conditions relative uncertainties of less than 10% are observed.

The first results of the LA-EI-MS instrument presented here indicate that mass spectra recorded from the same sample under the same irradiation conditions contain totally different information using either the ions or neutrals mode.

Further systematic experiments with a wide variety of sample materials will be done to investigate the possibility of using LA-EI-MS as an analytical tool. Measurements of the velocity distributions of the neutrals and ions emitted by laser ablation should give more insight in the ablation/ionization process.

ACKNOWLEDGMENTS

The authors thank O. Eberwein and S. Husen for the technical support in building the LA-EI-MS apparatus and its electronics.

- ¹P. H. McMurry, *Atmos. Environ.* **34**, 1959 (2000).
- ²J. S. Becker and H. J. Dietze, *Fresenius J. Anal. Chem.* **344**, 69 (1992).
- ³W. B. Brinckerhoff, G. G. Managadze, R. W. McEntire, A. F. Cheng, and W. J. Green, *Rev. Sci. Instrum.* **71**, 536 (2000).
- ⁴M. V. Johnston, *J. Mass Spectrom.* **35**, 585 (2000).
- ⁵W. Mróz, A. Prokopiuk, B. Kozlov, T. Czujko, S. Józwiak, J. Krzywinski, M. P. Söckli, and C. Fehrenbach, *Rev. Sci. Instrum.* **71**, 1425 (2000).
- ⁶D. S. Gross, M. E. Gälli, P. J. Silva, and K. A. Prather, *Anal. Chem.* **72**, 416 (2000).
- ⁷J. S. Becker and H. J. Dietze, *Fresenius J. Anal. Chem.* **365**, 429 (1999).
- ⁸U. Boesl, *J. Mass Spectrom.* **35**, 289 (2000).
- ⁹R. Zenobi, *Fresenius J. Anal. Chem.* **348**, 506 (1994).
- ¹⁰U. Boesl, R. Weinkauff, C. Weickhardt, and E. W. Schlag, *Int. J. Mass Spectrom. Ion Processes* **131**, 87 (1994).
- ¹¹E. Woods, III, G. D. Smith, Y. Dessiatierik, T. Baer, and R. E. Miller, *Anal. Chem.* **73**, 2317 (2001).
- ¹²J. Berkowitz and W. A. Chupka, *J. Chem. Phys.* **40**, 2735 (1964).
- ¹³K. A. Lincoln, *Int. J. Mass Spectrom. Ion Phys.* **2**, 75 (1969).
- ¹⁴K. A. Lincoln, *Int. J. Mass Spectrom. Ion Phys.* **13**, 45 (1974).
- ¹⁵V. S. Ban and B. E. Knox, *Int. J. Mass Spectrom. Ion Phys.* **3**, 131 (1969).
- ¹⁶S. T. Fountain and D. M. Lubman, *Anal. Chem.* **65**, 1257 (1993).
- ¹⁷E. R. Rohwer, R. C. Beavis, C. Köster, J. Lindner, J. Grottemeyer, and E. W. Schlag, *Z. Naturforsch. A* **43**, 1151 (1988).
- ¹⁸O. N. Krokhin, in *Laser Handbook*, edited by F. T. Arecchi and E. O. Schulz-Du Bois (North-Holland, Amsterdam, 1972), pp. 1371–1407.
- ¹⁹W. C. Wiley and I. H. McLaren, *Rev. Sci. Instrum.* **26**, 1150 (1955).