



Miniature mass spectrometer equipped with electrospray and desorption electrospray ionization for direct analysis of organics from solids and solutions

Ewa Sokol^a, Robert J. Noll^a, R. Graham Cooks^{a,*}, Luther W. Beegle^b, Hugh I. Kim^b, Isik Kanik^{b,**}

^a Department of Chemistry, Purdue University, West Lafayette, IN 47907, United States

^b Planetary Science, Jet Propulsion Laboratory, Pasadena, CA 91109, United States

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ABSTRACT

We report on the use of a small light-weight mass spectrometer (MS) for chemical analysis of organic material directly from solution or from the solid state with potential value in future planetary missions. The mass spectrometer used in the experiments reported here is handheld and controlled from a laptop computer through custom software. Detection and identification of small organic molecules, including some that might be prebiotics, was achieved using methods relevant to *in situ* and remote sensing applications. The miniature MS was equipped with a discontinuous atmospheric pressure interface (DAPI) and a home-built electrosonic spray ionization (ESSI) source. Aqueous solutions of molecules of interest were examined using the ESSI technique, while desorption electrospray ionization (DESI) was applied to examine solid samples. The system performance was characterized by direct analysis of analytes belonging to several compound classes including biotic and abiotic amino acids, purines, pyrimidines, nucleosides and peptides. Detection limits in the sub-ppm range for solutions were achieved with the atmospheric pressure sampling/ionization interface. Tandem mass spectrometry (MS²) was successfully applied to confirm trace detection of target compounds in mixtures. Multiple stage (MSⁿ) analysis, where $n = 3-5$, was employed for molecular structure confirmation and to demonstrate the high chemical specificity as well as the sensitivity of the instrumentation. The use of improved versions of this type of mass spectrometer on exploration missions could provide detailed chemical information on organic materials in physical states currently difficult to access. The high sensitivity and specificity, combined with rapid detection and the absence of requirements for sample preparation are encouraging features of the instrumentation.

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1. Introduction

The search for extra-terrestrial life features prominently in plans for planetary exploration, as exemplified in NASA's mission statement [1–3]. In line with this, we have been working to develop miniature mass spectrometers capable of providing high sensitivity and specificity in the detection of a wide variety of chemical and biological compounds. Simultaneously, we and others have been developing methods of ionization that can be adapted to direct analysis of condensed-phase samples using miniature mass spectrometers [4].

Mass spectrometry (MS) is capable of providing high sensitivity and selectivity in the identification and, with more difficulty,

quantitation of a wide range of chemical and biological compounds. Traditionally costly and cumbersome, it has been the subject of rapid recent development [5–9]. Several mass spectrometric systems have been successfully deployed in the field and a number of small instruments have progressed to the point of commercialization [10–13]. These mass spectrometers allow vapor analysis or the analysis of volatiles in aqueous solution and they employ standard electron ionization or chemical ionization methods together with gas or semi-permeable membrane interfaces [5]. Small mass spectrometers that allow direct chemical analysis of molecules in liquid and solid samples are much more rare and are only now becoming available, principally through the use of ambient ionization methods, in which samples are analyzed in the ordinary environment without preparation [14]. Here we explore the applicability of miniature mass spectrometers equipped with these types of ionization sources to the identification of such bio-organic compounds as might be encountered in the exploration of water-ice covered worlds and other extraterrestrial environments.

The partially ice-covered bodies Enceladus, Europa, Mars and from recent observations, the Moon [15], are the solar system locations thought to have the greatest potential as abodes for either

* Corresponding author at: Department of Chemistry, 560 Oval Drive, Purdue University, West Lafayette, IN 47907-2084, United States. Tel.: +1 765 494 5263; fax: +1 765 494 9421.

** Corresponding author. Tel.: +1 818 354 7233.

E-mail addresses: cooks@purdue.edu (R.G. Cooks), isik.kanik@jpl.nasa.gov (I. Kanik).

Table 1
Mini 10.5 mass spectrometer: performance and physical characteristics.

Characteristic	Mini 10.5 MS
Mass range/resolution	m/z 25–550 with unit resolution
Time for spectrum acquisition	1 s
Number of scans averaged (typically)	10
Data volume	120 kbits per spectrum
Mass (system)	~10 kg
Power consumption	50 W average

extant or extinct life. They are targets of interest because there is ample evidence for the presence of liquid water during at least some parts of their history [16–19]. For the Mars exploration program, a strategy of “follow the water” has dominated program planning for over a decade. Now that the history of aqueous processes is becoming better understood, the next step in this strategy would be to “find the carbon” referring to the discovery of organic biomarkers that may be present on Mars and elsewhere in the solar system where life may have existed [20]. Future missions to these objects will have to include instruments that can identify specific chemical compounds directly in the water, ice and soil.

In this context, one of a series of Purdue-built handheld mass spectrometers, the Mini 10.5 [21–26], was used for a systematic investigation of biomolecules, including biotic and abiotic amino acids, purines, pyrimidines, nucleosides and peptides. The miniature instrument was equipped with a discontinuous atmospheric pressure interface (DAPI) [27] to optimize delivery of externally formed ions into a small MS. A home-built electrosonic spray ionization (ESSI) source [28] was used to generate ions from organics in solution. The same ESSI ion source was used to examine solids samples in the desorption electrospray ionization (DESI) mode [29]. We seek to evaluate both sensitive detection of target molecules and specificity in making chemical assignments. Tandem mass spectrometry (MS/MS) was employed to achieve these objectives; it is highly desirable in the case of complex samples and also allows structural verification of target compounds detected at concentrations near the limit of detection (LOD).

2. Materials and methods

2.1. Mini 10.5 MS: instrument design

The Mini 10.5 is a hand-held mass spectrometer based on a rectilinear ion trap (RIT) [30] mass analyzer and aspects of its performance have been reported [21–26]. Table 1, summarizes performance and physical characteristics of this miniature mass spectrometer. The instrument features unit resolution, an upper mass limit defined by access to mass-to-charge ratio (m/z) of 550 Da/charge and detection limits for analytes in solution that range from high parts per trillion to low parts per million for favorable analytes. It is capable of performing multiple stage mass spectrometry experiments (MS^n) using waveform isolation and collision-induced dissociation (CID) of mass-selected precursor ions to generate product ions. All components, including the electronics and vacuum system, are assembled in an aluminum case of length: 34 cm, width: 22 cm and height 19 cm. The total weight of the instrument, including batteries, is 10 kg. The maximum power consumption, when both rough and turbo pumps are running and the RF is continuously being scanned to its maximum amplitude, is ca. 50 W; the instrument can be operated for 3–4 h on batteries, depending on the operating mode selected. The Mini 10.5 MS has a Windows operated on-board computer as well as wireless capabilities to allow communication with remote computers and with other Mini 10 series instruments [21]. The instrument is controlled by and data are processed using software (Version 2.2) from Griffin/ICx Analytical Instruments (West Lafayette, IN).

Mass analysis is performed using a quadrupole ion trap [31] configured in a simple rectilinear geometry (dimensions $x_0 = 5.0$ mm, $y_0 = 4.0$ mm, axial length $z_0 = 43.2$ mm) and operated in the mass-selective instability scan mode to generate mass spectra at a drive frequency of 1000 kHz and 250–4000 V_{0-p} . A supplementary AC signal at 350 kHz and an adjustable amplitude of 0.5–2.1 V_{0-p} , applied between the two x electrodes, allows resonant ejection during the RF mass-selective instability scan [21]. Ions are ejected in the order of increasing mass in the radial direction during the RF amplitude ramp, and then detected using a channeltron electron multiplier (Burle 5903, Burle Industries, Inc., Lancaster, PA) held at high voltage (–1300 to –1800 V, ca. 10^6 gain). Air is used as the buffer gas to cool the trapped ions prior to the mass scan and as the collision gas in the MS/MS experiments.

2.2. Sample delivery and ionization

The capillary inlet of the Mini MS was modified to incorporate a DAPI interface, which allows ions generated externally by atmospheric pressure ionization methods to be admitted into the ion trap in a pulsed fashion. This interface allows efficient sampling of ions from air into a system capable only of a low pumping speed. The discontinuous interface consists of two in-line stainless steel capillaries connected by a silicon tube that is physically pinched shut by a solenoid-operated pinch valve (model 390NC24330, ASCO Valve Inc., Florham Park, NJ). Ions, generated outside of the manifold, as well as surrounding gas from the atmosphere are drawn into the manifold while the pinch valve is held open [27]. The duty cycle for ion introduction is typically 1%, and is largely limited by the pumping speed of the vacuum system.

ESSI [28], a variant of electrospray ionization (ESI) [32], was used in order to produce ions from solution-phase samples. A home-built ESSI source, held at 3.5 kV potential, was operated using nitrogen nebulizing gas at a pressure of 120 psi. Solutions were introduced at a flow rate in the range of 3–5 $\mu\text{L}/\text{min}$. The choice of ESSI and the conditions used allowed the same device to be used to direct ionized solvent droplets at a surface and so perform desorption electrospray ionization (DESI). For these experiments, the capillary inlet was mounted on a movable bracket and tilted toward the surface being analyzed (the incident angle relative to the plane of the surface was 55° ; the take-off angle was 10°). Solvent droplets were propelled pneumatically and the sprayer was positioned 3 mm from the surface. The DESI source was held at 5.0 kV potential and operated using nitrogen nebulizing gas at a pressure of 150 psi. Spray solvents, either MeOH/ H_2O (50%, v/v) or acetonitrile, were introduced at a flow rate of 3 $\mu\text{L}/\text{min}$.

2.3. MS and MS^n experiments

Ions formed by ESSI or DESI were transferred through the DAPI interface into the mass analyzer where they are trapped while the co-introduced air and solvent vapors were pumped away. Once the pressure had dropped to levels at which mass spectra could be recorded [27], the trapped ions were manipulated using normal ion trap operations available in instruments capable of resonance ejection and mass-selective excitation. These capabilities allowed for tandem and higher-stage mass spectrometry experiments. Multiple stages of mass analysis and fragmentation were accomplished with the individual stages of dissociation and product ion selection being separated in time.

Single-stage MS experiments were conducted using a scan function consisting of four periods: (i) ion introduction (15–20 ms), (ii) pump down and ion cooling period (500–750 ms), (iii) mass analysis (60–100 ms), and finally (iv) a recovery period (200–250 ms). In the case of tandem MS experiments, ion introduction and cooling were immediately followed by two additional operations:

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