

Switched Ferroelectric Plasma Ionizer (SwiFerr) for Ambient Mass Spectrometry

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We present the implementation of a switched ferroelectric plasma ionizer (SwiFerr) for ambient analysis of trace substances by mass spectrometry. The device utilizes the ferroelectric properties of barium titanate (BaTiO_3) to take advantage of the high electric field resulting from polarization switching in the material. The source comprises a [001]-oriented barium titanate crystal ($5 \times 5 \times 1$ mm) with a metallic rear electrode and a metallic grid front electrode. When a high voltage AC waveform is applied to the rear electrode to switch polarization, the resulting electric field on the face of the crystal promotes electron emission and results in plasma formation between the crystal face and the grounded grid at ambient pressure. Interaction with this plasma and the resulting reagent ions effects ionization of trace neutrals. The source requires less than 1 W of power to operate under most circumstances, ionizes molecules with acidic and basic functional groups easily, and has proven quite versatile for ambient analysis of both vapor phase and aspirated powdered solid samples. Ionization of vapor phase samples of the organics triethylamine, tripropylamine, tributylamine, and pyridine results in observation of the singly protonated species in the positive ion mass spectrum with sensitivity extending into the high ppb range. With acetic acid, deprotonated clusters dominate the negative ion mass spectrum. Aerodynamic sampling of powdered samples is used to record mass spectra of the pharmaceuticals loperamide and ibuprofen. Chemical signatures, including protonated loperamide and deprotonated ibuprofen, are observed for each drug. The robust, low power source lends itself easily to miniaturization and incorporation in field-portable devices used for the rapid detection and characterization of trace substances and hazardous materials in a range of different environments.

Ambient mass spectrometry has been defined practically as any method of ionization allowing for the sampling of analyte from a surface or ambient atmosphere without advance sample preparation, occurring at ambient pressure. There are a number of somewhat distinct methodologies for ambient mass spectrometry.

Several, such as desorption electrospray ionization (DESI),¹ are derived primarily from electrospray ionization (ESI). Others utilize laser desorption to volatilize the sample, including ambient pressure matrix-assisted laser desorption ionization (AP-MALDI).^{2,3} These methodologies are combined in hybrid techniques which utilize both ESI and MALDI for sample volatilization and ionization, including MALDESI⁴ and ELDI.⁵ Another category of prominent methods are electrical discharge or plasma based and include the low temperature plasma probe,^{6,7} direct analysis in real time (DART),⁸ and plasma-assisted desorption/ionization (PADI).⁹ In just the last half decade, the field of ambient mass spectrometry has grown from just a few to nearly 40 different techniques. Excellent reviews on the subject of ambient ionization which give a comprehensive listing of the ionization sources available for both surface sampling¹⁰ and ambient¹¹ mass spectrometry as well as ion mobility spectrometry¹² are available.

An ambient pressure pyroelectric ionization source (APPIS)¹³ for mass spectrometry based on pyroelectric lithium tantalate has been recently described. Owing to their noncentrosymmetric crystal structure, pyroelectric materials possess a spontaneous polarization P_s which changes in magnitude with temperature change. The lithium tantalate material used in the APPIS source is also ferroelectric, another property dependent on a noncentrosymmetric crystal structure. Ferroelectric materials are unique in that they have a spontaneous polarization which is electrically switchable. The net polarization of a substance is a consequence of crystal structure asymmetry leading to a net

- (1) Cooks, R. G.; Ouyang, Z.; Takats, Z.; Wiseman, J. M. *Science* **2006**, *311*, 1566–1570.
- (2) Laiko, V. V.; Baldwin, M. A.; Burlingame, A. L. *Anal. Chem.* **2000**, *72*, 652–657.
- (3) Laiko, V. V.; Moyer, S. C.; Cotter, R. J. *Anal. Chem.* **2000**, *72*, 5239–5243.
- (4) Sampson, J. S.; Hawkridge, A. M.; Muddiman, D. C. *J. Am. Soc. Mass Spectrom.* **2006**, *17*, 1712–1716.
- (5) Sheia, J.; Huang, M.; Hsu, H.; Lee, C.; Yuan, C.; Beech, I.; Sunner, J. *Rapid Commun. Mass Spectrom.* **2005**, *19*, 3701–3704.
- (6) Harper, J. D.; Charipar, N. A.; Mulligan, C. C.; Zhang, X.; Cooks, R. G.; Ouyang, Z. *Anal. Chem.* **2008**, *80*, 9097–9104.
- (7) Zhang, Y.; Ma, X.; Zhang, S.; Yang, C.; Ouyang, Z.; Zhang, X. *Analyst* **2009**, *134*, 176–181.
- (8) Cody, R. B.; Laramée, J. A.; Durst, H. D. *Anal. Chem.* **2005**, *77*, 2297–2302.
- (9) Ratcliffe, L. V.; Rutten, F. J. M.; Barrett, D. A.; Whitmore, T.; Seymour, D.; Greenwood, C.; Aranda-Gonzalvo, Y.; Robinson, S.; McCoustra, M. *Anal. Chem.* **2007**, *79*, 6094–6101.
- (10) Van Berkel, G. J.; Pasilis, S. P.; Ovchinnikova, O. *J. Mass Spectrom.* **2008**, *43*, 1161–1180.
- (11) Harris, G. A.; Nyadon, L.; Fernandez, F. M. *Analyst* **2008**, *133*, 1297–1301.
- (12) Guharay, S. K.; Dwivedi, P.; Hill, H. H. *IEEE Trans. Plasma Sci.* **2008**, *36*, 1458–1470.
- (13) Neidholdt, E. L.; Beauchamp, J. L. *Anal. Chem.* **2007**, *79*, 3945–3948.

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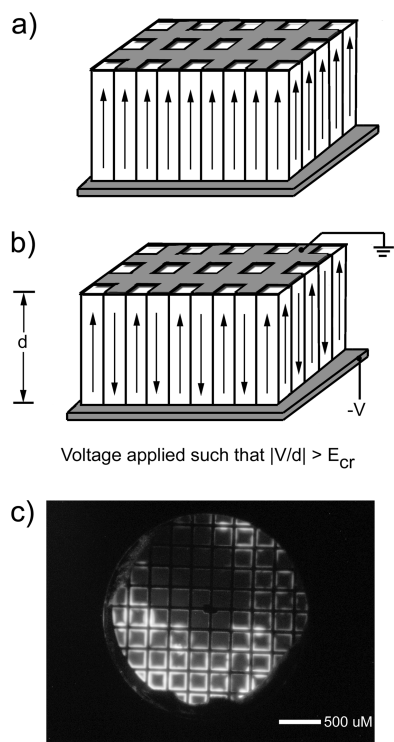


Figure 1. (a) Ferroelectric crystal with uniform polarization, where the polarization of all regions is identical. (b) Crystal with formed domains as a result of ferroelectric switching using a structured electrode. Domain walls, or boundaries between regions of opposite polarization, are formed. At the surface of the material, an electric field exists across the domain wall. (c) A 45 s exposure photograph of visible light from plasma arising near the grid when the polarization of a ferroelectric crystal is switched at ambient pressure.

dipole in the unit cell of the material. A material is uniformly polarized when all regions have the same polarization, as in Figure 1a. Because the material is ferroelectric, the polarization of any region can be changed by applying an electric field greater than the coercive field E_c . If a grid electrode is present, such as in Figure 1b, regions with different orientations of \mathbf{P}_s (termed ‘domains’) are formed. The coercive field varies from material to material and is dependent on the dielectric constant of the material in the direction of polarization as well as the bulk spontaneous polarization.

$$E_c = \frac{2}{3\sqrt{3}} \sqrt{\frac{\alpha^3}{\beta}} \approx 0.385\alpha P_s \quad (1)$$

Equation 1 is an expression for calculating the coercive field for a material, where $\alpha = 1/(2\epsilon_{ij})$, $\beta \approx \alpha/\mathbf{P}_s^2$, and ϵ_{ij} is the dielectric constant in the direction of polarization. Experimentally determined values for E_c are often 1 order of magnitude or more lower than calculated values, owing to physical processes occurring during domain wall formation, as discussed by Kim and co-workers.¹⁴ Experimentally, a coercive field of 20 kV mm⁻¹ is found for lithium niobate¹⁵ while a field

as little as 100 V mm⁻¹ is found for triglycine sulfate.¹⁶ Barium titanate (BaTiO₃) has a coercive field of approximately 500 V mm⁻¹.¹⁷

A plasma can arise on the surface of a switched ferroelectric material as a consequence of electron emission resulting from the large electric field created across domain walls when a switching electrode is nearby, as in Figure 1c. Ferroelectric electron emission is a well-known and well studied phenomenon¹⁸ that results in ionization of gases at both reduced (ultra high vacuum) and ambient pressures. Switched ferroelectric plasmas resulting from electron emission have been used previously in a number of applications,¹⁹ mainly involving high current electron emitters. Although several reports of ion production by switched ferroelectrics at reduced pressure have been published,^{20–23} ambient pressure plasma formation^{24–27} has not previously been used as a source of ions for ambient mass spectrometric analysis.

In the present work we describe a novel ion source for ambient mass spectrometry termed the switched ferroelectric plasma ionizer (SwiFerr), which utilizes the ambient pressure plasma resulting from a sample of barium titanate [001] whose polarization is switched by an audiofrequency electric field. The source can be applied in the field of ambient mass spectrometry as another tool for ionization at atmospheric pressure without using high power electrical discharges or radioactive materials, such as ⁶³Ni. Especially in the case of ⁶³Ni, the main obstacle for implementation is the handling and transport of radioactive materials, despite the simplicity of operation and sensitivity of that particular source. For the switched ferroelectric source described, high yields of both anions and cations are produced by the source and easily detected using an ion trap mass spectrometer. Vapor phase samples of amines and volatile acids result in detection of the protonated and deprotonated species, respectively, in the observed mass spectra. Aerodynamic sampling is employed to analyze powders of drug tablets of loperamide and ibuprofen. A peak corresponding to the active pharmaceutical ingredient for each drug is observed in the mass spectra. Pyridine is detected at concentrations in the low part-per-million range in air, suggesting that the ultimate sensitivity of the source is the high ppb range. Like other ambient ionization sources, the source also ionizes impurities commonly found in laboratory air, such as phthalates. Lastly, a detailed analysis of operating conditions to optimize sensitivity consistent with the goal of minimizing power consumption is presented. The low power consumption of the source suggests future incorporation into field portable instrumentation for

(14) Kim, S.; Gopalan, V.; Gruverman, A. *Appl. Phys. Lett.* **2002**, *80*, 2740–2742.
(15) Gopalan, V.; Mitchel, T. E.; Furukawa, Y.; Kitamura, K. *Appl. Phys. Lett.* **1998**, *72*, 1981–1983.

(16) Biedrzycki, K.; Markowski, L.; Czapla, Z. *Phys. Status Solidi A* **1998**, *165*, 283–293.
(17) Latham, R. V. *Br. J. Appl. Phys.* **1967**, *18*, 1383–1388.
(18) Rosenman, G.; Shur, D.; Krasik, Y. E.; Dunaevsky, A. *J. Appl. Phys.* **2000**, *88*, 6109–6161.
(19) Krasik, Y. E. *IEEE Trans. Plasma Sci.* **2003**, *31*, 49–59.
(20) Dunaevsky, A.; Krasik, Ya. E.; Felsteiner, J.; Dorfman, S. *J. Appl. Phys.* **1999**, *85*, 8464–8473.
(21) Sroubek, Z. *J. Appl. Phys.* **2000**, *88*, 4452–4454.
(22) Sroubek, Z. *Appl. Phys. Lett.* **2002**, *80*, 838–840.
(23) Chirko, K.; Krasik, E.; Felsteiner, J. *J. Appl. Phys.* **2002**, *91*, 9487–9493.
(24) Kusz, J.; Musielok, J.; Wanik, B. *Beitr. Plasmaphys.* **1982**, *22*, 381–386.
(25) Janus, H.; Kusz, J.; Musielok, J. *Beitr. Plasmaphys.* **1985**, *25*, 277–288.
(26) Biedrzycki, K. *J. Phys. Chem. Solids* **1991**, *52*, 1031–1035.
(27) Goly, A.; Lopatka, G.; Wujec, T. *J. Quant. Spectrosc. Radiat. Transfer* **1992**, *47*, 353–358.

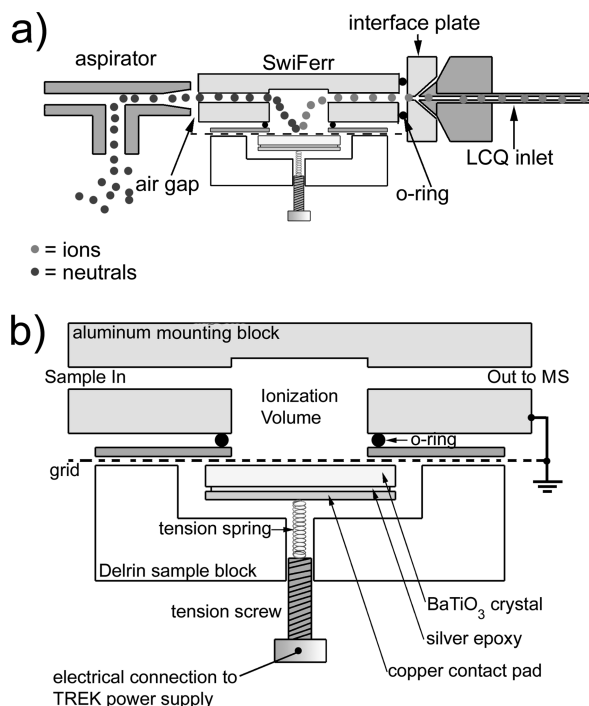


Figure 2. (a) Overview of the source arrangement in front of the mass spectrometer inlet. The source is attached to the atmospheric pressure inlet capillary using a machined interface plate. An air gap is maintained between the aspirator exhaust and source inlet. (b) Detail of the source. A $5 \times 5 \times 1$ mm sample of [001] barium titanate with contact pad attached is placed in a Delrin sample block, and a copper mesh grid and aperture plate are placed on top of the sample. The aluminum mounting block is isolated from the aperture plate by an O-ring. Electrical connections to the source are made using the tension screw (connection point for high voltage waveform) and the grid. When affixed to the mass spectrometer, the sample is drawn into the 'sample in' port, passed through the ionization volume where ionization occurs, and exits the source and enters the mass spectrometer. The grid and mounting block are maintained at ground potential throughout the experiment.

detection of hazardous materials and trace substances in a variety of different applications.

EXPERIMENTAL SECTION

Design and Construction of SwiFerr Ionizer. Figure 2a is an overview of the arrangement of the SwiFerr source with respect to the mass spectrometer inlet. The ion source is attached to the atmospheric pressure inlet of an LCQ Deca XP ion trap mass spectrometer using a machined interface plate. Vapor or aerosol samples are drawn into the source due to the gas flow induced by the atmospheric pressure sampling capillary being backed by vacuum. An air gap of 1–2 mm is maintained between the source sample inlet and aspirator exhaust so that the source is not pressurized when the aspirator is operated using compressed air. Figure 2b is a detailed schematic of the SwiFerr source. The device utilizes a $5 \times 5 \times 1$ mm sample of single crystal barium titanate oriented in the [001] direction with one face polished (MTI Corporation, Richmond, CA). Barium titanate has three phase transition temperatures, or Curie temperatures, and four phases, three of which are ferroelectric. Below 183 K, BaTiO₃ is rhombohedral, polarized along the [111] axis. From 183 to 278 K it is orthorhombic, polarized along the [011] axis. From 278 to 393 K, BaTiO₃ is tetragonal and polarized along the [001] axis,

and this is the orientation used in the current application owing to its intended use as an ionizer at ambient temperature and pressure. A contact pad comprising a 4.8 mm diameter disk cut from a 0.5 mm thick oxygen-free copper sheet is attached to the unpolished side of the crystal using silver conducting epoxy (MG Chemicals, Toronto, Ontario, Canada). A layer of silver epoxy achieving full coverage of the crystal face is first applied and allowed to cure before the contact pad is bonded using a second application of silver epoxy. The crystal with contact pad on one side is placed in a sample holder block machined from white Delrin, and a piece of woven copper mesh (0.230 mm diameter wire and 0.630 mm wire spacing) larger than the crystal surface area is placed on top of the face that does not have an electrode. An aperture plate (SS-PL-B-R187, Kimball Physics, Wilton, NH) is placed on top of the copper mesh. The aperture plate is vibrationally isolated from the mounting block using a silicone O-ring.

For detection of ions, a Thermo Scientific LCQ Deca XP ion trap mass spectrometer was used without modification other than the electrospray source being removed and replaced with the SwiFerr. Inlet capillary temperature was 40–70 °C, and the capillary was held at ground potential. To operate the source, an audiofrequency high voltage sine wave was applied to the rear electrode of the barium titanate sample by making an electrical connection to the tension screw, while the copper mesh and aperture plate were maintained at ground potential by making an electrical connection to the mesh electrode. The waveform was generated using a TREK PM101494A high voltage amplifier/generator (TREK Inc., Medina, NY) and can be varied in frequency from 0.1 to 10 kHz and in voltage from 0 to 20 kV p-p for testing purposes.

All chemicals were used as received, without further purification. Sample concentrations, when not specified, are unknown owing to the fact that the sample used was vapor resulting from the room temperature vapor pressure of the sample being tested, or aerosol particles in the case of sampled solids. For pharmaceutical sampling, a tablet of each drug was ground in a mortar and pestle before sampling. The tablets were commercial samples obtained from drug stores, rather than being pure samples of the active pharmaceutical ingredient purchased from a chemical supplier.

RESULTS AND DISCUSSION

Ambient Ionization of Vapor Phase and Solid Samples.

SwiFerr was used to ionize and detect a variety of samples ranging from organic vapors to samples of drug tablets. Both cations and anions are produced by the source, and the ion signal observed appears continuous when an ion trap mass spectrometer is used for detection. Figure 3a shows mass spectra of the amines triethylamine, tripropylamine, and tributylamine ionized by SwiFerr under ambient conditions. The samples were introduced as neat vapor at room temperature. Each amine was detected as a singly protonated quasimolecular ($M + H$)⁺ ion, owing to the basicity of tertiary amines. An aerodynamic sampling arrangement utilizing a pneumatic aspirator similar to that of Dixon²⁸ was used to sample powder from drug tablets. A tablet

(28) Dixon, R. B.; Sampson, J. S.; Hawkrigge, A. M.; Muddiman, D. C. *Anal. Chem.* **2008**, *80*, 5266–5271.

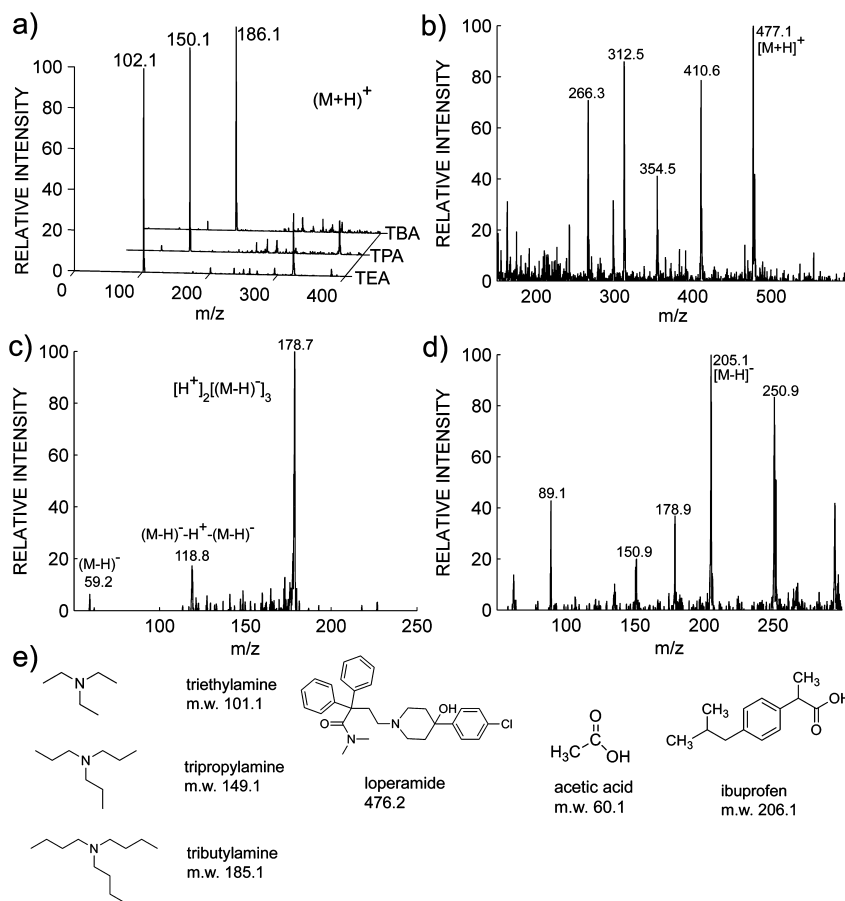


Figure 3. (a) Positive mode mass spectra of triethylamine, tripropylamine, and tributylamine ionized with SwiFerr. The singly protonated quasimolecular ion $(M + H)^+$ is observed for each amine. (b) Positive mode mass spectrum of a ground tablet of loperamide ionized with SwiFerr. Protonated loperamide is observed as the base peak in the mass spectrum, along with fragment ions of this species at lower m/z values. (c) Negative mode mass spectrum of acetic acid vapor obtained using SwiFerr. Monomeric deprotonated acetic acid (m/z 59.2) as well as the proton bound dimer (m/z 118.8) and trimer (m/z 178.7) are observed. (d) Negative mode mass spectrum of a ground tablet of ibuprofen ionized with SwiFerr. Deprotonated ibuprofen (m/z 205.1) is observed as the base peak in the mass spectrum. The peak at 250.9 is likely due to the tablet coating. (e) Structures and molecular weights for species in Figure 3a–d.

containing the pharmaceutical compound loperamide was crushed in a mortar and pestle and ground to a fine powder. The powder was aspirated into the SwiFerr source and the peak for loperamide was observed as the base peak in the mass spectrum (Figure 3b). Whether this is the result of particles interacting directly with the plasma or the detection of trace vapor phase species is not known. Like the vapor phase samples, loperamide also contains tertiary amine functionality and was detected as the singly protonated species in the mass spectrum. Figure 3c is an example of negative ion production with SwiFerr for a vapor phase sample of acetic acid. Deprotonated clusters of the acid dominate the SwiFerr mass spectrum. The drug ibuprofen was aerodynamically sampled and detected using SwiFerr in the same manner as loperamide, except that anions were analyzed. Ibuprofen was detected as the singly deprotonated species in the mass spectrum (Figure 3d) owing to the fact that it possesses carboxylic acid functionality. The ability of SwiFerr to ionize acids and bases by deprotonation and protonation, respectively, suggests chemical ionization as the chief ionization mode of the source. Reactant ions such as nitrate anion and hydrated protons are directly observed in experiments measuring ions resulting from the operation of the SwiFerr source in air (Figure 4). The observed reactant ions take part in proton transfer reactions which can

either deprotonate acids or protonate bases, and their presence indicates that the ionization mechanism operative in SwiFerr is ambient pressure chemical ionization, which is common for discharge based ion sources.

A variety of nontargeted ionic species are commonly observed with ambient ionization sources. Impurities in laboratory air are an often frustrating but sometimes convenient class of compounds which are ionized and detected using ambient mass spectrometry. An example class of compounds are certain phthalates which are commonly used as plasticizers in the manufacture of plastics and epoxies. Figure 5a is a mass spectrum of laboratory air, where the predominant peak in the spectrum is due to dibutyl phthalate. Figure 5b is a spectrum resulting from collisional activation of the mass peak in Figure 5a, and neutral losses positively identify the molecule as dibutyl phthalate.

Limit of Detection for Organic Vapors. Using the SwiFerr ion source implementation shown in Figure 2, the limit of detection (LOD) for pyridine was investigated using a sample of pyridine in nitrogen containing 6 Torr water vapor to enhance proton transfer chemical ionization. Pyridine concentration was varied using a model 1010 gas diluter (Custom Sensor Solutions, Oro Valley, AZ) which allows for dilution of a prepared mixture by a

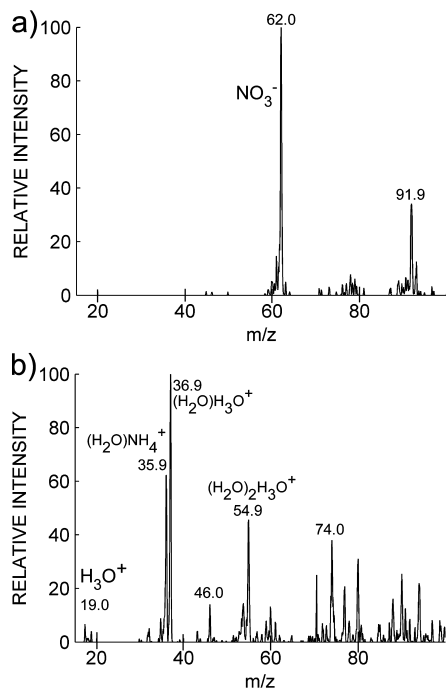


Figure 4. (a) Negative mode mass spectrum of reagent ions resultant from the operation of SwiFerr in air. Nitrate anion was observed and can take part in proton transfer reactions which ionize neutrals. The peak at m/z 92 may be due to $(\text{O}_2)\text{CO}_3^-$. (b) Positive mode mass spectrum of ions resultant from the operation of SwiFerr in air. Hydrated protons (clusters of neutral water molecules and hydronium ion) are present which can take part in proton transfer reactions which ionize neutrals. Peaks at higher mass are likely due to the ionization of impurities present in laboratory air.

factor of 2 to 50. In this case, a sample containing 50 ppm pyridine was prepared and mixtures containing from 25 to 1 ppm pyridine were available for analysis. Figure 6 is a mass spectrum of pyridine at a concentration of 4 ppm. Protonated pyridine appears at 80.1 m/z . Other peaks in the spectrum are trace impurities that do not result from ionization of pyridine. Detection of pyridine at 4 ppm with a signal/noise of approximately 50 indicates that the ultimate sensitivity of the ionizer in the present configuration is in the ppb range under optimal sampling conditions

Optimization of Parameters for Source Operation. Operation of ambient pressure ion sources with portable mass spectrometric instrumentation gives rise to a unique parameter space for their design and operation. Specific goals for components of miniaturized instrumentation include low mass, known scalability factors, good durability and lifetime, and minimized power consumption. Tolerance to pressure variations in the ion source, mechanical shock, and thermal cycling are also quite important. To in part investigate the suitability of the source for miniaturized instrumentation, power consumption of the source was studied by monitoring the rms current required for source operation at various operating frequencies concurrently with ion signal observed in the mass spectrometer. Monitor functions on the TREK supply provided readings of rms power as well as p-p voltage output. For a sample comprising laboratory air background, Figure 7 shows rms power consumption for source operation. More power is consumed during operation at higher frequencies with no increase in ion signal, indicating that the source operates more efficiently at lower frequency. The fact that the current flowing

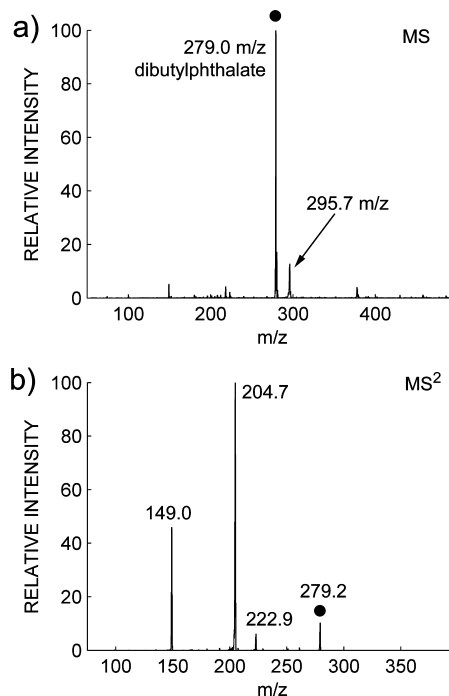


Figure 5. (a) Positive mode mass spectrum of laboratory air, with major constituent at 279.0 m/z . This is suspected to be protonated dibutyl phthalate, part of the phthalate class of impurities commonly found in laboratory air. The peak 17 amu higher is an ammonia adduct of this compound. (b) Collisional activation (MS^2) spectrum for the peak at 279 m/z . Neutral loss of 1-butene (56 amu) gives rise to the peak near 223 m/z , while loss of 1-butanol (74 amu) gives rise to the peak near 205 m/z . Sequential loss of n-butanol followed by loss of 1-butene (74 amu followed sequentially by 56 amu) gives rise to the peak at 149.0 m/z . These fragments are consistent with the dibutyl phthalate structure.

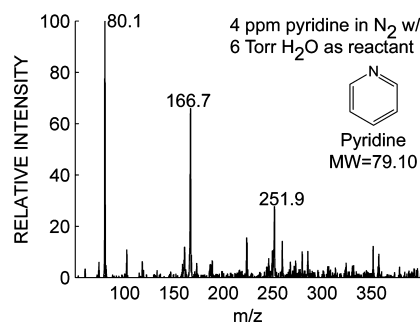


Figure 6. Positive mode mass spectrum of 4 ppm pyridine in nitrogen doped with water, obtained with SwiFerr. The observed signal-to-noise indicates that the ultimate sensitivity of SwiFerr is in the part-per-billion range. Other peaks in the spectrum are due to impurities in the sampling system.

in the circuit driving the switched crystal (and thereby power consumption by the source) increases with frequency is a result of the series RC nature of the circuit. The crystal itself has a characteristic resistance and capacitance which acts like a series RC element.

$$P = \frac{V_{\text{RMS}}^2}{\sqrt{R^2 + X_C^2}}, \quad X_C \equiv \frac{1}{\omega C} \quad (2)$$

Equation 2 is an expression for the power flowing in the circuit, where R is the characteristic resistance and X_C is the capacitive

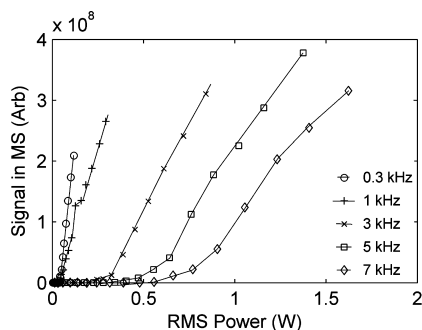


Figure 7. Plot of total signal observed in mass spectrometer for a sample of background lab air vs rms power for excitation of the crystal circuit at various frequencies. More efficient operation is obtained at lower frequencies.

reactance. Capacitive reactance X_C decreases with an increase in frequency, leading to a lower total impedance of the source $((R^2 + X_C^2)^{1/2})$ and increased current flow through the circuit element. Understanding the behavior of the SwiFerr source in the electrical circuit allows for the selection of optimal operating parameters with respect to power consumption and ion signal intensity. Since no gain in observed ion signal results from operation at higher excitation powers, we typically operate the source at a frequency of 1 kHz and adjust the peak-to-peak excitation voltage to a level which produces a satisfactory ion signal for each specific experiment (typically below 350 V rms). This corresponds to an ion source operating power of approximately 0.2 W for the present implementation of the SwiFerr plasma ionizer.

A common ion source for miniature analytical mass spectrometers has been electron impact, both from a thermionic emitter (hot filament) and more recently a glow discharge electron impact source (GDEI),²⁹ implemented on a field portable instrument. Unless carefully designed, thermionic devices often consume power greater than 1 W and suffer from fragility and susceptibility to shock loads. The GDEI source is greatly improved with respect to power consumption and mechanical integrity, but nonetheless requires a minimum nominal power of 300 mW for operation in an efficient, low power mode. This is comparable to the SwiFerr source. Other ion sources for miniature mass spectrometers, such as electrospray ionization, require both solvent and gas flow as well as high voltage above 1 kV DC.

Low power consumption is not the only motivating factor behind the design of the source. SwiFerr also is a low mass/volume device and should operate effectively over a wide temperature range, eliminating the requirement for temperature control of the ion source. The [001] ferroelectric phase of BaTiO₃

occurs between 278 and 393 K, allowing safe operation of the source between 278 K and about 330 K to avoid the upper Curie temperature of the material and phase transition. Lastly, the source is insensitive to atmospheric venting owing to the fact that it operates primarily at ambient pressure on Earth. There is no vacuum requirement for this source, in addition to no requirement for consumable liquids or gases. It operates in ambient air, with ion sampling into the instrument effected by the pressure differential between the ion source and mass analyzer.

CONCLUSION

A novel ion source for ambient mass spectrometry has been developed which utilizes the plasma formed on the surface of a switched ferroelectric material in contact with a grounded grid electrode for ionization of trace neutrals at ambient pressure, with good sensitivity and very low power requirements. Both anions and cations are observed from the same source arrangement due to chemical ionization because reactive chemical ionization agents of both polarities are produced by the plasma. Basic species such as triethylamine, tripropylamine, and tributylamine as well as the pharmaceutical loperamide were detected as singly protonated cations in the mass spectra. Acidic species such as acetic acid and the pharmaceutical ibuprofen were detected as singly deprotonated anions. In the case of acetic acid, proton-bound clusters of the anion were also detected. Sensitivity of the source to sample concentration was tested using a gas dilution method, and detection limits for pyridine were determined to be in the high ppb range, indicating suitability for use in a range of analytical applications. Lastly, electrical characteristics and power consumption of the source were analyzed. The source consumes less than 1 W of power under normal operation, which is unique for a plasma-based ionization technique. Power consumption varies with frequency as a consequence of the crystal appearing as a capacitive load in the circuit. As a result, operation at lower frequencies is desired when the minimization of power consumption is a goal.

ACKNOWLEDGMENT

This material is based on work supported by the National Science Foundation under grant number CHE-0416381. The authors also wish to acknowledge funding from the Beckman Institute at Caltech. E.L.N. acknowledges a Graduate Research Fellowship in Analytical Chemistry from Pfizer Analytical Research and Development, Groton, CT.

Received for review May 26, 2010. Accepted November 2, 2010.

AC1013833

(29) Gao, L.; Song, Q.; Noll, R. J.; Duncan, J.; Cooks, R. G.; Ouyang, Z. *J. Mass Spectrom.* **2007**, *42*, 675–680.