

Mass Spectrometry in the Home and Garden

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Abstract. Identification of active components in a variety of chemical products used directly by consumers is described at both trace and bulk levels using mass spectrometry. The combination of external ambient ionization with a portable mass spectrometer capable of tandem mass spectrometry provides high chemical specificity and sensitivity as well as allowing on-site monitoring. These experiments were done using a custom-built portable ion trap mass spectrometer in combination with the ambient ionization methods of paper spray, leaf spray, and low temperature plasma ionization. Bactericides, garden chemicals, air fresheners, and other products were examined. Herbicide applied to suburban lawns was detected in situ on single leaves

5 d after application.

Keywords: Household chemical analysis, Portable instruments, Tandem mass spectrometry, Organic analysis, Ambient ionization

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Introduction

A large number of chemical formulations are used daily for a wide variety of tasks by ordinary people. The manufacturer of these materials is subject to safety regulations but their use is largely uncontrolled. When questions arise regarding adverse effects, laboratory tests that are time consuming and expensive are normally required. This study seeks information on the applicability of small, portable mass spectrometers as a means of recognizing the presence of particular chemicals in products in the consumer environment. Attention is directed to qualitative analysis and to non-volatile as well as volatile compounds. The emphasis is on rapid and specific detection of key components in these products. Ambient ionization, the direct ionization of samples without work-up in their native environment, is particularly appropriate for these measurements. It provides the necessary speed of sampling and gener-

ates characteristic ions from most chemicals of interest [1]. When interfaced directly to a miniature mass spectrometer capable of tandem mass spectrometry, the chemical specificity needed for unambiguous detection is available [2]. Small ion trap mass spectrometers with discontinuous atmospheric pressure interfaces (DAPI) satisfy these requirements [3]. They are used here with paper spray and low temperature plasma, as well as leaf spray ionization. The two instruments used in this study, the Mini 10.5 and the Mini 12, are lab built instruments that have been described in the literature [4–6].

In situ analysis by mass spectrometry is not common and almost all such applications involve the analysis of volatile compounds, as noted in a recent review [7]. This is often done with a membrane introduction interface, which allows low molecular weight analytes to be measured from air and aqueous sample matrices. Membranes offer advantages of high sensitivity (with restricted analytes) although recent work has explored ways to lift some of these limitations [8]. Membranes offer many other benefits, especially when examining samples from complex matrices where they allow derivatization and pH adjustment [9, 10]. Examples of applications of membrane introduction include in situ analysis of contaminants in ocean water [11, 12], direct analysis of human breath [13],

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intravenous blood sampling [14], and on-line monitoring of bioreactors [15].

Ambient ionization [16–20] started with the development of desorption electrospray ionization (DESI), which was followed rapidly by several related techniques [21, 22]. DESI is a solvent-based technique that allows surface analysis in air [21]. Paper spray (PS) ionization, like DESI, is a spray-based ionization method. It is robust and simple to execute and is performed using a paper substrate cut to a point with application of the sample being followed by addition of solvent and application of a high voltage. Paper spray is suitable for both polar and non-polar analytes [23–25]. Another ambient ionization method used here is based on plasma ionization. Low temperature plasma (LTP) uses dielectric barrier discharge ionization generated by applying a high frequency potential across a hollow cavity containing a grounded electrode. A discharge gas, often helium, is used. This ion source consumes less than 5 W of power, making it amenable to portable mass spectrometers. The discharge can be used to interrogate a surface as well as to probe analytes in the gas phase [26, 27].

The need for in situ analysis has required robust mass spectrometers that operate in demanding environments and yet can make sensitive measurements. Harsh environments are not limited to outer space or underwater environments; in situ chemical analysis is also needed in many other locations, for example at crime scenes, and even in our homes [28–31].

Experimental

Instrumentation

Experiments were carried out using two mass spectrometers, the Mini 10.5 and the Mini 12, both built in-house. The Mini 10.5 weighs approximately 4 kg and was fitted with a DAPI pinch valve, which opens for 10–15 ms to allow ions to enter the mass spectrometer through a 15-mm steel capillary (i.d. 120 μm , o.d. 1.5 μm) and closes during mass analysis [32]. The pressure of the instrument increases to 10^{-1} Torr during ion injection and decreases to 10^{-4} Torr prior to mass analysis [3]. Because this instrument does not have the ability to operate in the negative polarity mode, the Mini 12 was used for such experiments. This latter instrument was equipped with a conversion dynode, which allows the user to analyze samples in either the negative or the positive ion mode. The mass resolution (FWHM) of both instruments is approximately $1m/z$. Both instruments consume 50 W and can operate for over 2 h on batteries. Tandem mass spectrometry was performed with two mass unit isolation and experimental conditions given elsewhere [2].

Ambient Ionization

The ionization source chosen for analysis was based on the sample of interest although for many samples the choice of source did not significantly influence the mass spectrum. Low temperature plasma (LTP), the dielectric barrier discharge ionization technique, used a high voltage AC potential (3 kV, ~ 2.5

kHz) to generate a plasma. Helium was used as the discharge gas although air or nitrogen could have also been selected to carry out the experiments at reduced sensitivity. The flow rate of the gas, measured with a variable flow rotameter, was maintained at 400 mL/min. The LTP source was constructed with 1/16" Swagelock T, fitted with the appropriate ferrules and nuts. Quartz glass with an i.d. of 0.75 mm and an o.d. of 1.5 mm, and a length of 90 mm was used as the dielectric barrier to which the AC signal was applied; a central needle constituted the ground electrode.

Paper spray was used as reported in the literature [23]. Whatman 1 filter paper, purchased from Sigma Aldrich (St. Louis, MO, USA), was chosen as the substrate to which the sample was applied. The filter paper was first cut into a triangle with a 40° angle and each side measuring approximately 1 cm. The sample was loaded by either wiping the surface or through wet deposition onto the paper. Following sample loading, 20 μL of methanol was added to the paper and finally 4 kV (DC) was applied via an alligator clip, and the sample was ionized and sprayed into the mass spectrometer.

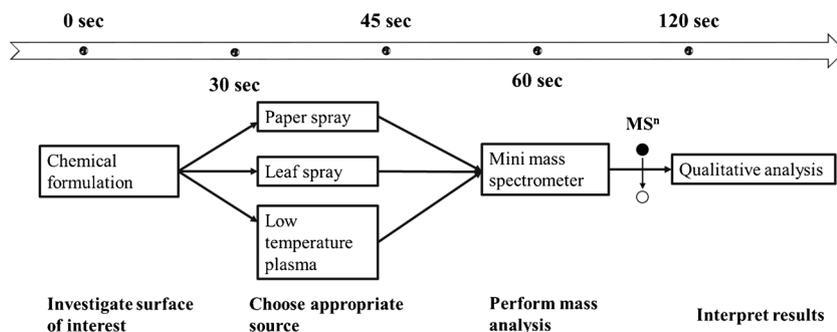
Leaf spray (LS), closely related to paper spray, involves cutting plant samples to create a sharp tip, applying high voltage and spraying endogenous phytochemicals directly from the plant material into the mass spectrometer. Experimental conditions were the same as for paper spray. Solvent can be applied to the surface of the plant in order to release exogenous chemicals on the plant surface. For some plant material such as grass blades, cutting the material to a sharp point was not necessary [33, 34].

Atmospheric pressure chemical ionization was also performed. This was done by applying a high DC potential to a needle creating a corona discharge at the tip. The electrical discharge triggers a chemical reaction cascade starting with ionized dinitrogen and yielding hydronium ions and other charged species that can ionize sample components by chemical ionization [35]. Once the discharge needle was placed 0.1 cm from the inlet of the mass spectrometer, the sample was moved towards the inlet and vapor phase sample-derived compounds were ionized.

Methods

All commercial products were used following label instructions. Aerosols could be analyzed directly in air, however to limit sample carry-over by exposure of the Mini MS to the aerosol, these samples were sprayed into small vials but still analyzed as aerosols. This method was shown not to enhance the sensitivity of the instrument; it simply prevented aerosols from lingering in the ambient environment. The general workflow of the experiments can be seen in Scheme 1. During the 5-d agrochemical study, four grass blades were interrogated each day and 15 measurements on each leaf were averaged to obtain each time point.

The mass spectrometer was carried into the field for the grass measurements, whereas the household chemicals were brought into the lab for the measurements.



Scheme 1. Experimental work flow

Chemicals

2,4-Dichlorophenoxyacetic acid, chlorothalonil, and benzalkonium chloride were purchased from Sigma Aldrich (St. Louis, MO, USA) as standards. All household and agricultural chemicals were purchased from Walmart Super Center (Lafayette, IN, USA). Brand names are deliberately omitted. [Supporting Information](#) contains table of all active chemicals examined in this paper.

Results and Discussion

Aerosols

Aerosols were sampled using low temperature plasma ionization. Among the compounds tested was a vanilla air freshener. Because these chemicals contain proprietary blends, it was difficult to identify all of the compounds; nevertheless, a peak at m/z 153 (Figure 1a) was observed and assigned to vanillin. Vanillin (MW 152) is a phenolic aldehyde commonly used as a component in air freshener because of its vanilla aroma. The identification was confirmed using MS/MS measurements made using the portable mass spectrometer, Mini 10.5. The ion of m/z 135 is a common fragment resulting from the loss of water from the ring of vanillin. The base peak, m/z 270, is believed to be a fragment of the stabilizer steartrimonium chloride. The peak at m/z 448 is an interferent from the polymer on the clamp assembly used to hold the LTP source in front of the instrument inlet.

A pet repellent containing the active ingredient 2-undecanone (MW 170) was examined in the positive ion mode. 2-Undecanone is frequently used as a perfume but because of its strong odor it can be used also as an insect or pet repellent. Pet repellents typically exist in volume concentrations of 1%–2% (v/v). The pet repellent was analyzed using multiple ionization methods but Figure 1b was produced using LTP. The spectrum shows protonated 2-undecanone at m/z 171; there is also a peak at m/z 189 corresponding to hydration of the protonated ion $[M + H + H_2O]^+$. The ion of m/z 341 was isolated and subsequently fragmented and the MS/MS spectrum confirmed that it was the protonated dimer of 2-undecanone rather than the molecular ion of another

constituent. The ion m/z 448 is related to the chemicals on the clamp assembly as already mentioned.

Bactericide

Glass surfaces were wiped with disinfecting wipes and then analyzed using paper spray. Quaternary amines are a common component in antibacterial agents that ionize very readily. Wet surfaces were analyzed by wiping Whatman 1 filter paper across the area of interest and then applying solvent and a high voltage. In the case of a surface that had dried between treatment and analysis, the filter paper was pre-wetted with 20 μ L methanol and then wiped. The results are nearly identical

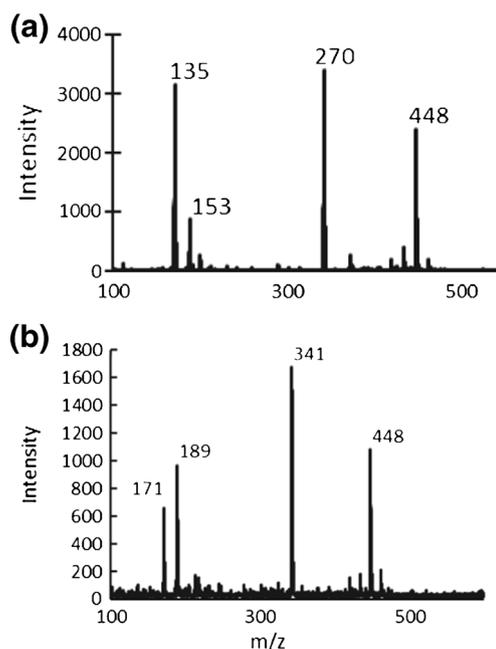


Figure 1. (a) Mass spectrum of vanilla air freshener analyzed by LTP in the positive ion mode. The protonated vanillin ion corresponds to the peak at m/z 153. A peak at m/z 135 results from the loss of the hydroxyl substituent as water; m/z 270 is believed to be a fragment of steartrimonium chloride. There is an interferent from the LTP holder at m/z 448. (b) Pet repellent analyzed by LTP in positive ion mode. The ion m/z 171 corresponds to protonated 2-undecanone at m/z 171

between the wet and dry surfaces, suggesting that analysis does not need to occur immediately after application. Figure 2a shows a full mass spectrum of disinfecting wipe residue from a glass surface. The spectrum includes two high abundance ions at m/z 332 and 364 corresponding to ionized benzalkonium with an alkyl chain length of 14 (benzyltrimethyltetradecylammonium) and 16 (benzyltrimethylhexadecylammonium) carbon atoms, respectively. There are a number of peaks that are not identified but attributed to the nondisclosed chemicals in the formulations and to degradation products from the benzalkonium ions. To confirm the identity of the 14-carbon chain benzalkonium species, MS/MS analysis (Figure 2b) resulted in a loss of toluene (92 mass units) to produce a fragment ion at m/z 240, which is the immonium fragment ion.

Bacteriostatic agents prevent the proliferation of bacteria and are commonly used to chemically treat water in humidifiers and as food preservatives [36, 37]. A commercial bactericide solution was diluted according to label directions (approximately 1000-fold), and 10 μL was spotted onto Whatman 1 paper with subsequent addition of 20 μL of methanol and analyzed by paper spray. This formulation is labeled as containing benzalkonium chloride as the active ingredient. The same major ions were observed as seen in the disinfecting wipe and MS/MS confirmed the assignment by comparison of the data with those for a standard solution of benzalkonium chloride. Although this chemical is highly effective, it is very toxic to fish, birds, and aquatic invertebrates [38].

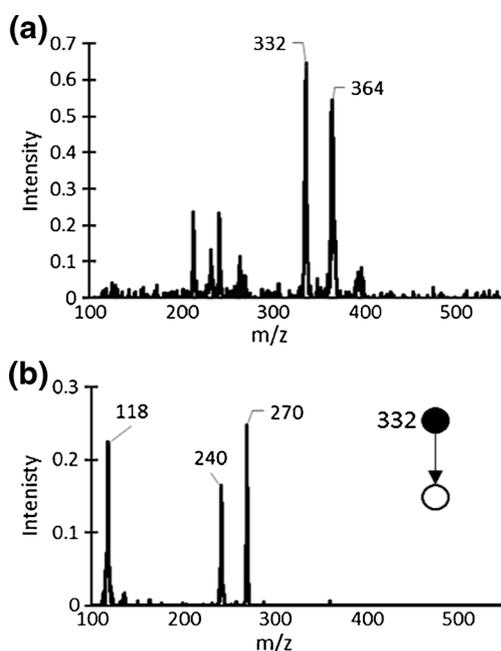


Figure 2. (a) Mass spectrum of disinfecting wipe using paper spray ionization in the positive ion mode. Ions m/z 332 and m/z 364 correspond to benzyltrimethyltetradecylammonium and benzyltrimethylhexadecylammonium cations. (b) MS² product ion spectrum of the precursor ion m/z 332. The peak at m/z 240 corresponds to the loss of toluene $[\text{M} + \text{H} - \text{C}_7\text{H}_8]^+$

Topical Solutions

A topical solution refers to any medication that is applied to a particular area of the skin. With portable mass spectrometers, one can analyze many compounds from a variety of substrates. To investigate this capability, the Mini 12 was used to interrogate human skin for two common chemical formulations, hydrocortisone cream and sunscreen.

Hydrocortisone was analyzed using paper spray ionization after the direct application of the ointment to the skin. To sample the skin, 30 μL of ethanol was applied to Whatman 1 filter paper and wiped across the area of interest. After sampling, 20 μL of ethanol containing 1% acetic acid (v/v) was applied as the spray solvent and then the high voltage was applied. An ion with m/z 363 $[\text{M} + \text{H}]^+$ was isolated and its MS² spectrum displayed several fragment ions, including that due to water loss from the hydrocortisone, m/z 345 $[\text{M} + \text{H} - \text{H}_2\text{O}]^+$, as well as the further dehydration products m/z 327 $[\text{M} + \text{H} - 2\text{H}_2\text{O}]^+$ and m/z 309 $[\text{M} + \text{H} - 3\text{H}_2\text{O}]^+$ (data shown in Supporting Information S2).

Another method to probe skin is to use chemical ionization to analyze the high vapor pressure constituents from a topical agent applied to the skin. Sunscreen was sprayed onto skin and analyzed directly using this method. The formulation chosen contains three active ingredients, avobenzone, octocrylene, and oxybenzone. Figure 3 shows a MS² product ion spectrum for protonated avobenzone, m/z 311. The single observed fragment ion at m/z 203 results from loss of a molecule of anisole from this precursor. Avobenzone was selected for isolation because it is in the lowest concentration of all the active ingredients in this formulation, to help demonstrate the sensitivity as well as the specificity of the methodology.

Agrochemicals

Agrochemicals are used on a global scale to fertilize crops, kill pests, maintain green lawns, and to increase yields. Field-deployable mass spectrometers allow their rapid analysis outside the lab, and the Mini 12 has been used to analyze crops after an application of herbicide. Both leaf spray and paper spray were utilized in studying agrochemical samples. 2,4-Dichlorophenoxy acetic acid (2,4-D, MW 220) is a common

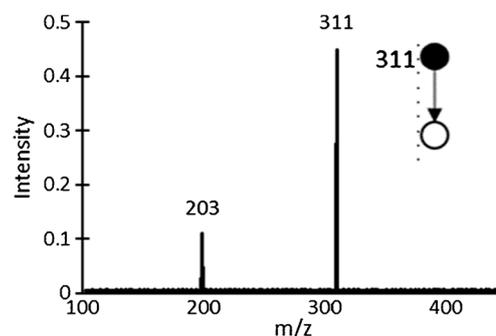


Figure 3. MS² spectrum of avobenzone collected in the positive mode using chemical ionization

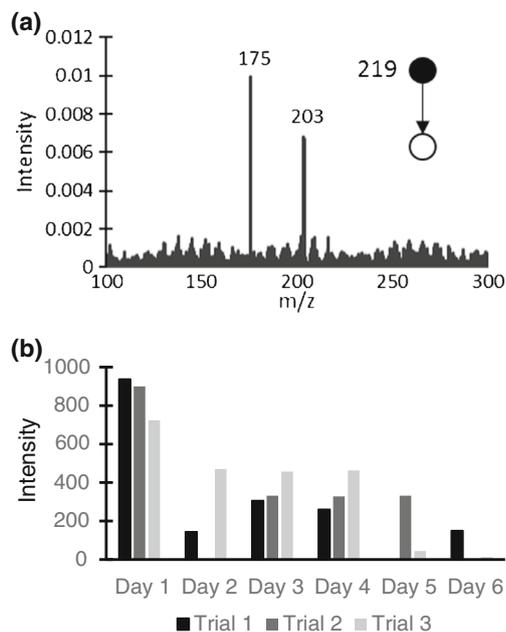


Figure 4. (a) MS² scan of 2,4-D using leaf spray in negative ion mode. (b) Plot of m/z 219 \rightarrow m/z 175 intensity over three 5-d replicates. Each data point represents the average of 15 MS/MS measurements made on each of four leaves, 15 times. Uncertainties (RSD) are 0.11, 0.53, 0.18, 0.24, 0.77, and 0.84 for d- 1 to d 6, respectively

herbicide that has recently received attention for its potential health effects on dogs [39]. The aim of this work was not to test these claims but to determine if a Mini mass spectrometer could detect small quantities of lawn chemicals in situ. Leaf spray was used to directly analyze grass from a lawn, post-treatment, and the portable instrument allowed herbicide detection for up to 5 d after the initial application. The estimated concentration of 2,4-D on d 1 was 0.15 g/m² assuming that there are 10,000 grass blades in a square meter. This approximates to 1.5 μ g of 2,4-D per blade of grass, assuming a uniform monolayer of grass on a lawn. For perspective, the recommended lawn application of 2,4-D is approximately 10 μ g/grass blade.

Experiments in the MS² scan mode allowed monitoring of the intensity of the signal due to the characteristic 2,4-D transition m/z 219 to 175, $[M - H]^- \rightarrow [M - H - CO_2]^-$. A typical product ion MS/MS spectrum which includes this transition is shown in Figure 4a, whereas Figure 4b shows the time-resolved ion intensity recorded over the course of a set of experiments. Each data point corresponds to five leaves, which were scanned 15 times and the data averaged. Some of the time points have rain labels because an in situ measurement was not possible on these days. Not surprisingly, there was a great deal of variability between the trials during this experiment, mostly from variability in sampling. However, the overall trend of decreasing 2,4-D signal as a function of time is clear. On the first day of the experiments, it is reasonable to assume that the chemicals being sampled are on the outside of the leaves but as the experiments progress the herbicide enters the leaves. Leaf spray is unable to plainly discriminate between exogenous and endogenous 2,4-D. To confirm that the suspected amount of 2,4-D was present on the leaves on d 1 as mentioned earlier, 1.6 μ g of herbicides was directly applied to the surface of a leaf and the 2,4-D intensity measured (average 750 arbitrary units). This gave good agreement with the results shown in Figure 4.

To expand the scope of the outdoor analysis, a fungicide containing chlorothalonil (MW 264) was applied to a maple tree. In contrast to the previous experiment, the leaves from the foliage needed to be cut to a point in order to be sprayed. Chlorothalonil exhibited limited solubility in ethanol, a common spray solvent for leaf spray so, instead, 15 μ L of acetonitrile (ACN) was applied. To detect the presence of fungicide, the ion m/z 266 was isolated and fragmented, which produced an ion at m/z 209. Figure 5 shows the MS² spectrum of a maple leaf recorded 3 d after the fungicide was applied. As one can see, it is nearly impossible to detect the presence of the fungicide from the single stage mass spectrum shown in the inset image. However, the signal

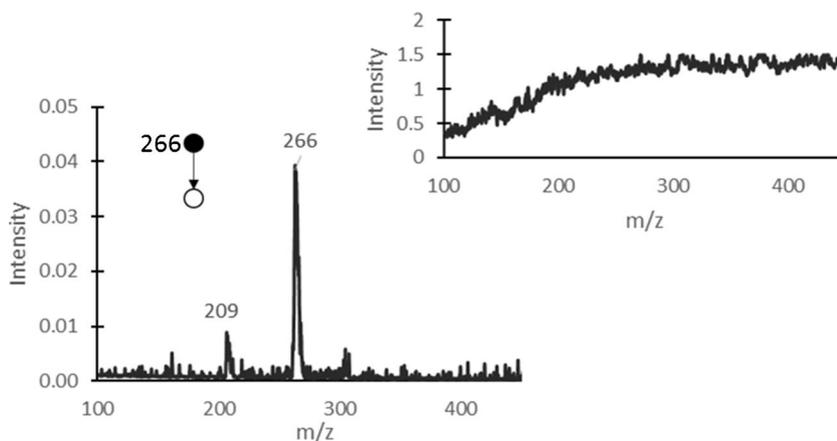


Figure 5. MS² of ion with m/z 266 recorded in positive mode. Inset image is a full scan acquired using leaf spray

can easily be discriminated from the noise by MS/MS, and this allows chlorothalonil to be detected up to 5 d after application.

Conclusion

We have demonstrated in situ chemical analysis of both volatile and non-volatile compounds using ambient ionization coupled with a portable mass spectrometer. The results presented in this article were recorded both indoors and outdoors. By using tandem mass spectrometry, it was possible to perform trace detection as well as bulk qualitative analysis quickly, from a variety of environments. The ability to quickly analyze substances allows high throughput chemical identification without expensive and time-consuming laboratory work. The miniature mass spectrometers performed well outdoors but will need improved cooling systems for operation under the highest heat/humidity conditions. Complex matrices, such as chemical formulations, skin, and agrochemicals, are easily analyzed using a single analytical instrument. A wide variety of ambient ionization techniques are applicable and vastly different sample types can be analyzed for a wide range of chemical compounds. This study shows that qualitative information can be gathered from full MS scans and that MS/MS capabilities help confirm identities of trace analytes.

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