

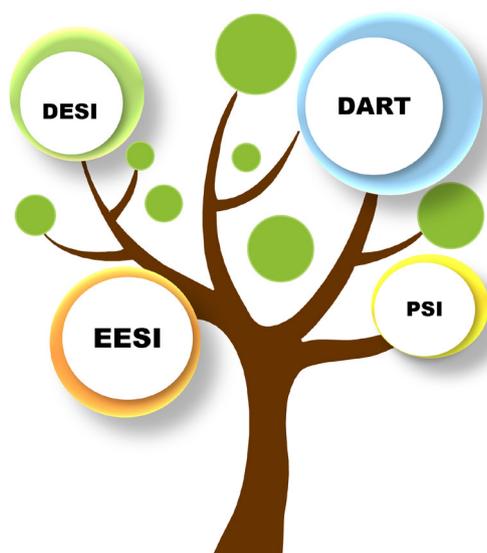
REVIEW

# Ambient Ionization Mass Spectrometry: Applications and New Trends for Environmental Matrices Analysis

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## AMBIENT MASS SPECTROMETRY METHODS



Since its introduction, ambient mass spectrometry methods have been demonstrated as potential approaches for a rapid and sensitive analysis of many compounds in complex matrices with a minimum or no sample preparation step performed. Some of these methods include low-cost devices and *in situ* methodologies that are included in the new trend of green analytical chemistry. The application of ambient methods for environmental analysis has been reported in the last decades for qualitative and quantitative analysis. This study aims to contribute with an overview of the 2016 to 2021 period of ambient mass spectrometry methods for applications in environmental analysis. In this context, this review reports especially applications for qualitative and quantitative analysis of contaminants using desorption electrospray ionization (DESI), direct analysis in real-time (DART), paper spray ionization (PSI), and extractive electrospray ionization (EESI) methods.

**Keywords:** Ambient mass spectrometry, Environmental, Green chemistry, Complex matrices, Environmental analysis

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## INTRODUCTION

The constant and technological progress of the industrial and agricultural sectors in recent decades has brought with it improvements over the obtention of products related to these sectors.<sup>1</sup> However, at the same time, the anthropogenic activity of humans in the environment because of these advances has also increased.<sup>2-4</sup> Currently, anthropogenic activities represent the potential of humanity to interfere with the natural balance of the environment.<sup>1</sup>

The monitoring of some compounds, especially those harmful to the environment, is a requirement for the control of the contaminants in environmental matrices. However, this monitoring is a challenge for analytical methods due to these contaminants in many cases being found at trace concentration levels and in the presence of endogenous compounds that act as interferents.<sup>5,6</sup> Thus, the development of analytical methodologies for the analysis of contaminants represents a promising approach for the adequate monitoring of contaminants.

During the last decades, analytical methodologies such as ambient mass spectrometry (AIMS) methods have been introduced, these methodologies can overcome the use of laborious sample preparation steps which demands time and uses considerable solvent volume. The development of AIMS methodologies with high sensitivity and selectivity, and devices capable of performing *in situ* analysis helps to overcome the sample preparation methods drawbacks. These AIMS methodologies and devices can improve the qualitative and quantitative information on many samples, such as environmental matrices.<sup>6</sup>

## AMBIENT MASS SPECTROMETRY (AIMS)

In general, electrospray ionization (ESI) represents an approach used to generate ions from the sample solution, especially for polar compounds.<sup>7</sup> Although ESI and other atmospheric pressure ionization (API) sources are capable to generate ions from many matrices, these traditional ionization methods still need an extensive sample preparation step before the analysis. These methods usually include the hyphenation of the mass spectrometer and a separation system, such as liquid chromatography (LC) and gas chromatography (GC).<sup>6,8</sup> On the other hand, AIMS methods allow the analysis of compounds in an open environment using minimal or no sample preparation, resulting in some devices that cover the trend of point-of-care (POC) analysis, which has been higher desirable by testing and diagnostics methods routine.<sup>7</sup> The literature methodologies reporting the use of techniques by AIMS have shown benefits in comparison with conventional ionization techniques, such as smaller sample volume requirement, little or no use of organic solvents, the elimination of the separation step by sample preparation, or chromatographic methods, and the improve of the method sensitivity and lower time of analysis.<sup>6</sup>

The AIMS concept was first introduced in 2004 by Cooks *et al.*<sup>9</sup> in which the use of desorption electrospray ionization (DESI) technique for the analysis of compounds present in tomato peel (*Lycopersicon esculentum*) and *Conium maculatum* seeds was reported. In this first application, it was proved to be an efficient approach for analysing the chemical profile and identifying the compounds present in the samples. In general, AIMS methods can be classified into two groups, that is spray-based (ESI-like) and plasma-based (APCI-like) methods. The spray-based approach includes the extractive electrospray ionization (EESI), easy ambient sonic-spray ionization (EASI), paper spray (PSI), probe electrospray ionization (PESI), and laser ablation electrospray ionization (LAESI) methods. In resume, this category involves momentum desorption, solvent extraction, and finally the ionization of the solution. The plasma-based methods include the direct analysis in real-time (DART), low-temperature plasma (LTP), dielectric barrier discharge ionization (DBDI), atmospheric pressure solids analysis probe (ASAP), and flowing atmospheric-pressure afterglow (FAPA). This category uses an electrical discharge between two electrodes in a gas flow to make the ionization of the target analyte (s).<sup>6</sup>

Since its introduction, AIMS techniques have brought great advances in the development of analytical methods, involving some fast and sensitive methodologies for a wide variety of analytes in different matrices, especially for environmental analysis (Figure 1) and (Table I).<sup>8,9</sup>

The upward trend in AIMS-related research can also be seen on platforms such as the Web of Science. The reports in such platforms have shown the increasing on the publications related with ambient mass spectrometry. Following this trend, applications of AIMS methods in environmental sciences has also been pointed out as an interesting field to the application of such methods and devices (Figure 2). Considering this, a discussion of the publications from the period of 2016-2021 on some AIMS methods for environmental matrices is presented in this revision study, as well as the trends for the future of the ambient methods for environmental analysis.

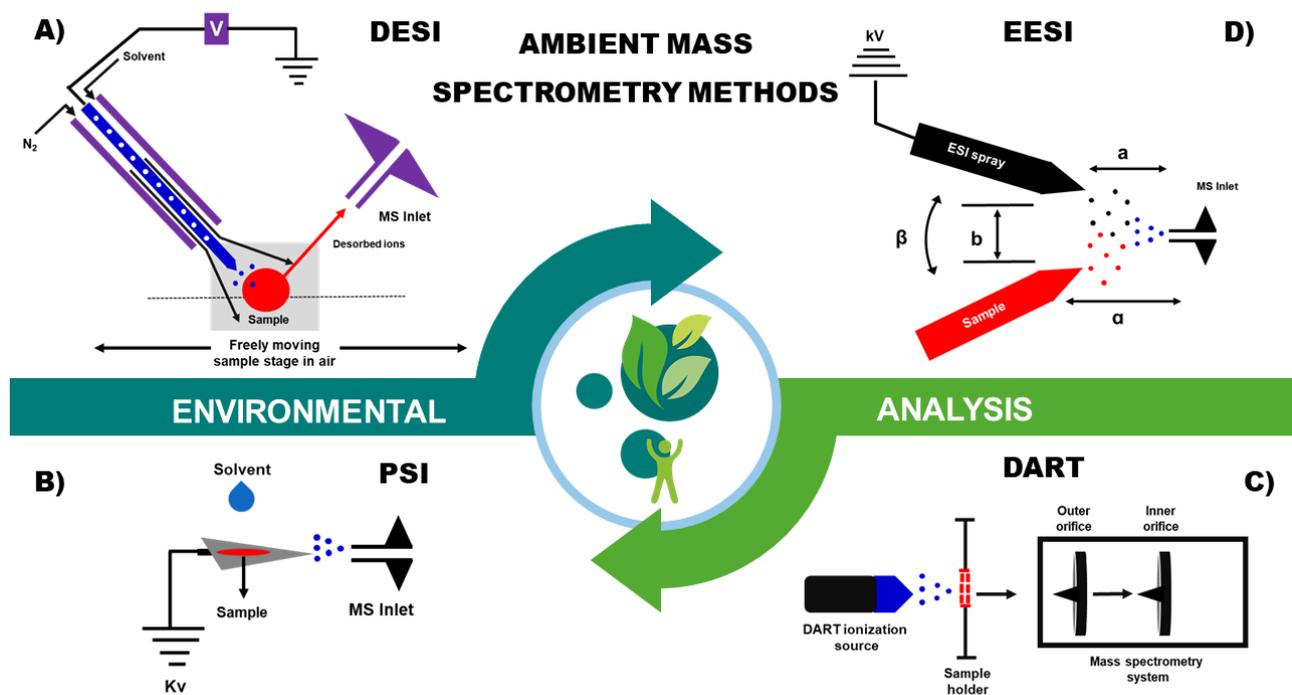


Figure 1. Ambient mass spectrometry techniques combined with environmental analysis.

**Table I.** Methods described in the literature using ambient mass spectrometry applied to environmental analysis

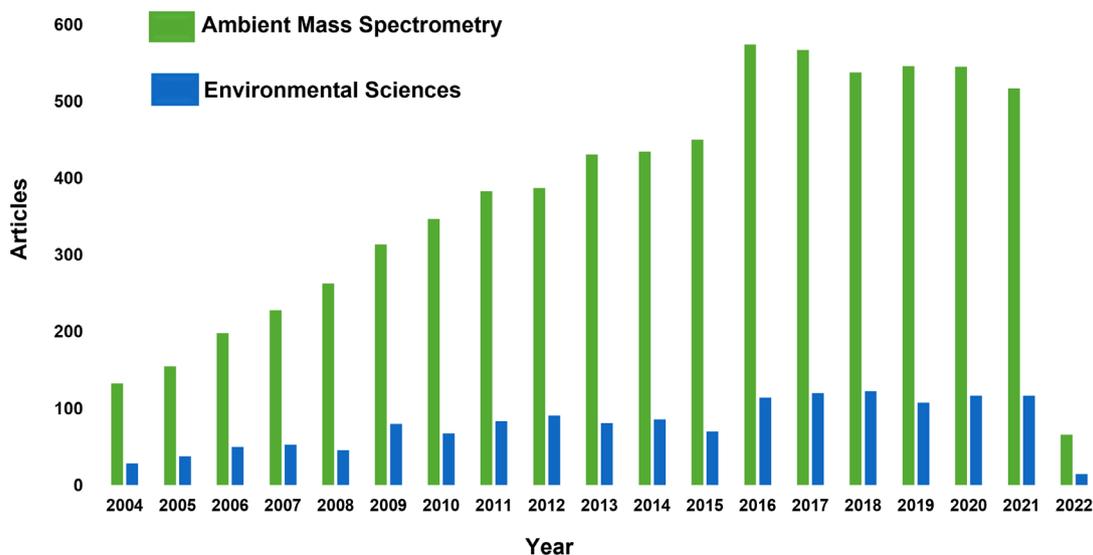
Analyte(s)	Sample	Analytical Methodology	LOQ	LOD	Recovery (%)	Ref.
Perfluoroalkyls	Plants	DESI-MS HAS EDS	0.3-0.5 ng g <sup>-1</sup>	0.09-0.15 ng g <sup>-1</sup>	87.5-114.9	12
Dimethoate, trifloxystrobin, and tebuconazol	Olive and vine leaves	DESI-MS	50.0-150.0 ng g <sup>-1</sup>	15.0-50.0 ng g <sup>-1</sup>	-	13
32 pesticides	Fruit	DESI-MS	-	1.0 pg mm <sup>2</sup>	88.0	14
Ionic liquids	Fish	DESI-MS	-	-	-	15
Duomeen O (n-oley <sup>1</sup> ,3- diaminopropane)	Industrial waters	PSI-MS/MS	-	< 0.1 pg	-	16
Acephate Cyazofamide Chlorpyrifos	Tomato peel	PSI-MS	0.03 mg g <sup>-1</sup>	0.01 mg g <sup>-1</sup>	90.4-96.4	17
Bisphenol A and S	Thermal paper	PSI-MS	87.0 ng g <sup>-1</sup> / 13.0 ng g <sup>-1</sup>	5.0 ng g <sup>-1</sup> / 1.9 ng g <sup>-1</sup>	92.0 - 109.0	18
Metaldhyde	Water	PSI-MS/MS	-	0.05 ng mL <sup>-1</sup>	-	19
Microcystins	Water	PSI-MS	3.0 µg L <sup>-1</sup>	1.0 µg L <sup>-1</sup>	77.0 - 103.6	20
Tetrabromobisphenol A	Tap water Springwater Lake water	SPME-PSI-MS	0.001 µmol <sup>-1</sup>	-	95.1 - 101.6	21
U, Bi, Pb, Cd, Fe and Zn	Cotton	PSI-MS	-	94.0 ng	-	22

(To be continued in the next page)

**Table I.** Methods described in the literature using ambient mass spectrometry applied to environmental analysis (Continuation)

Analyte(s)	Sample	Analytical Methodology	LOQ	LOD	Recovery (%)	Ref.
Phenoxy-carboxylic acids	Environmental waters	DART-MS	-	0.5-2.0 ng L <sup>-1</sup>	79.9-119.1	23
Triazine Herbicides	Tap water, pool, and lake	DMSPE-DART-MS	-	1.6-152.1 ng L <sup>-1</sup>	87.5-115.0	24
Phthalic Acid Esters	Environmental water	SSE-DART-MS	-	0.1-0.9 ng L <sup>-1</sup>	82.8-119.0	25
Microplastics and Nanoplastics	Natural waters	DART-MS	100.0 pg L <sup>-1</sup>	30.0 pg L <sup>-1</sup>	60.0-70.0	26
Pesticides	Surface water	SPME-TM-DART/MS	0.1-5.0 µg kg <sup>-1</sup>	-	-	27
Pesticides	Lettuce and celery	QuPPE-DART-HRMS	50-190.0 µg kg <sup>-1</sup>	20.0-60.0 µg kg <sup>-1</sup>	71.0-115.0	28
Steroid hormone	Residual water	DART-MS	-	2.5 ng L <sup>-1</sup>	-	29
Trimethyl phosphate	Residual water	DART-MS/MS	50.0 pg mL <sup>-1</sup>	0.05-100.0 ng mL <sup>-1</sup>	88.0-107.6	30
Organic UV filters	Environmental water	DART-MS	-	40.0 ng L <sup>-1</sup>	-	31
Glycosides	Tobacco Leaves	DART-MS	0.05-0.1 µg mL <sup>-1</sup>	0.02-0.05 µg mL <sup>-1</sup>	-	32
Tetrabromobisphenol A	Wastewater, river water and tap water	EESI-MS	-	0.05-4.6 µg L <sup>-1</sup>	-	33

**DESI-MS:** Desorption electrospray ionization-mass spectrometry; **HAS-EDS:** transmission electron microscopy equipped with energy-dispersive spectroscopy; **PSI-MS:** Paper spray ionization mass spectrometry; **PSI-MS/MS:** Paper spray ionization-mass spectrometry tandem; **SPME-PSI-MS:** Solid-phase microextraction-paper spray ionization-mass spectrometry; **DART-MS:** Direct Analysis in Real-Time – Mass Spectrometry; **DMSPE-DART-MS:** Dispersive Magnetic Solid-phase Extraction - Direct Analysis in Real-Time - Mass Spectrometry; **SSE-DART-MS:** Sorbent and Solvent co-enhanced - Direct Analysis in Real-Time - Mass Spectrometry; **SPME-TM-DART-MS:** Solid Phase Micro Extraction - Transmission Mode - Direct Analysis in Real-Time - Mass Spectrometry; **QuPPE-DART-HRMS:** Quick Polar Pesticides Extraction - Direct Analysis in Real-Time - High-Resolution Mass Spectrometry; **DART-MS/MS:** Direct Analysis in Real-Time – Mass Spectrometry tandem; **EESI-MS:** extractive electrospray ionization mass spectrometry.



**Figure 2.** Publication numbers per year, using ‘Ambient Mass Spectrometry’ and ‘Environmental sciences’ as search words. Publication until Feb 2022. Source: www.webofscience.com

### ***Desorption electrospray ionization desorption (DESI)***

DESI technique was developed by Cooks *et al.* in 2004.<sup>34</sup> DESI belongs to the family of AIMS techniques and mass spectrometry imaging (MSI). In MSI analysis, chemical images are generated by plotting the signal intensities of the analyte of interest in a 2D or 3D space corresponding to the area of the sample that was analysed (Figure 1A). Through the application of DESI technique, it is possible to locate the spatial distribution of certain compounds in a sample of interest.<sup>35</sup> Because of the speed, sensitivity, and the possibility to perform *in situ* analysis, DESI technique has been highlighted as a potential approach to the development of surface analysis studies.<sup>36</sup>

In DESI ion desorption process, a primary spray is formed, with electrically charged solvent drops (less than 10  $\mu\text{m}$ ),<sup>37</sup> under high pressure of an inert gas jet in high-velocity (about 100  $\text{m s}^{-1}$ ) that reaches the sample on a glass slide.<sup>38,39</sup> This impact creates a thin layer of solvent that results in a solid-liquid extraction of the sample.<sup>39</sup> Then, the desorption of the analyte(s) occurs due to the shock of the primary spray. A secondary spray is formed containing the sample, and the analytes are then attracted to the mass spectrometer inlet.<sup>40</sup> The ionization of the technique creates single or multiple ions, in a mechanism exactly of what is observed in an ESI interface.<sup>41</sup> In this technique, changes in spray solvents are used to obtain good sample selectivity in a non-destructive way.<sup>42</sup>

The application of DESI in imaging analysis allows the visualization of biomolecules from a sample surface.<sup>43</sup> The MSI approach has been highlighted in literature to be mainly performed in the study of the chemical profile of many biomolecules, such as metabolites,<sup>44</sup> lipids,<sup>45</sup> and proteins.<sup>46</sup> In DESI-imaging, an unidirectional scan on the x-axis of the sample is performed, in which each line on the x-axis results in a mass spectrum. The sample is located on a moving platform on the y-axis, enabling the next row to be parsed.<sup>47</sup> It is important to emphasize that this movement is repeated, the analytes of the next lines are not unduly removed, leading to the loss of information. The total area of the sample is divided into pixels. The distance between lines on the y-axis corresponds to 1 pixel and is the same distance on the x-axis. This distance corresponds to a spatial resolution that normally ranges from 150  $\mu\text{m}$  to 250  $\mu\text{m}$ . As desorption occurs continuously, it is necessary that the surface of the sample be smooth and flat, with no irregularities, after analysing the x and y axes, the generated spectra are merged to produce the images.<sup>48,49</sup>

The desorption efficiency of the analyte(s) is intrinsically linked to the optimization of some parameters in the geometric position of the DESI. The parameters that most influences the analysis are the angle of

incidence, which is the angle formed by the spray on the sample, the angle of ion collection, the distance between the sprayer and the surface, and the distance between the surface and the MS inlet, as shown in Figure 3.<sup>50</sup>

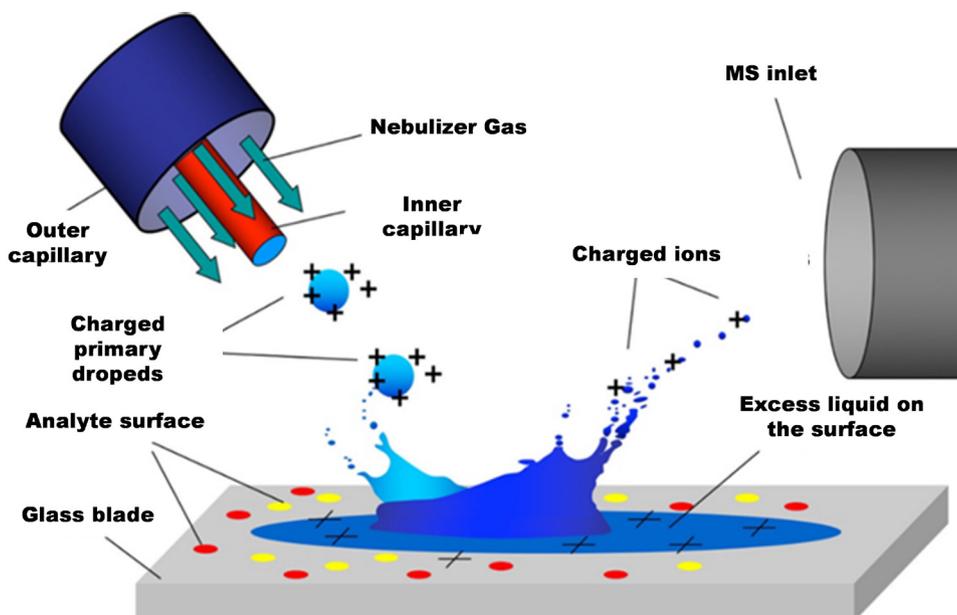


Figure 3. Scheme for geometric optimization of DESI.

Furthermore, the composition of the spray solvent is also a fundamental parameter for DESI desorption and ionization mechanism. The effect of the solvent on signal intensity and the resolution was extensively studied by Green *et al.*<sup>51</sup> The most used solvent composition is methanol and water, however, there are other solvent reported that include methanol (MeOH), acetonitrile (ACN), ethanol, dimethylformamide (DMF), among others.<sup>52</sup> Solvent optimization improves ionization efficiency and the method sensitivity.<sup>51</sup> Other parameters must be optimized for each sample, these parameters include the pressure of the nebulizing gas and the conditions in the mass spectrometer, all these parameters are directly linked to the obtained response.

DESI technique is widely used for biological samples, mainly for brain tissue in clinical case studies.<sup>38,53–55</sup> However, the literature points out the application in forensic chemistry,<sup>56</sup> metabolomics,<sup>57</sup> food,<sup>14</sup> and environmental analysis.<sup>12</sup>

Recently, Wang *et al.*<sup>12</sup> verified the absorption potential of perfluoroalkyl substances (PFASs) in plants using desorption electrospray ionization-mass spectrometry (DESI-MS) and transmission electron microscopy equipped with energy-dispersive spectroscopy (TEM-EDS). Within the PFASs group, perfluorooctanoic acid (perfluorooctanoic, PFOA) and perfluorooctane sulfonic acid (perfluorooctane sulfonic, PFOS) are the most representative substances, which present great risks of contamination to the environment and living beings. For the DESI-MS analysis, eight wet plants were submitted to hydroponic experiments (soilless cultivation technique) to visualize their distribution at tissue and cell levels. These plants were incubated for 1 month with PFOA and PFOS solutions washed with deionized water and divided into roots, stems, and leaves. The optimized DESI parameters were optimized, and results showed that the PFASs accumulated in the plants represented 1.67-6.7% of the total mass added to the hydroponic systems, and PFOS accumulated mostly in the roots (48.8-95.8%), while the PFOA was stored mainly in the aerial part (29.3-77.4%). DESI-MS and TEM-EDS analysis showed that PFASs were transported from the hydroponic root solution via both apoplastic (through cell walls and/or intercellular spaces) and symplastic pathways (through plasma membranes or via plasmodesma). Thus, DESI-MS and TEM-EDS

techniques demonstrated to be efficient approaches applied to visualization, tracking, absorption, and transport of PFOS and PFOA in plants.

DESI technique was also used as an interface in the analysis of the pesticides dimethoate, tebuconazol, and trifloxystrobin in olive and vine leaves by Rocca *et al.*<sup>13</sup> This study aimed to assess the exposure of workers during the application of these agrochemicals on crops, as evidence suggested serious adverse effects and chronic occupational exposure. The compositional mixture of the solvent used was methanol/water (80:20 v/v). This mixture showed great efficiency in the desorption of these analytes in the leaves of olive trees and vines. The three pesticides were analysed and validated using figures of merit. The validation showed weakness in intra-day precision, in which field analyses required more repetitions for reliability, which could suggest disadvantages in quantitative assays by DESI-MS. In addition, the actual monitoring of samples was close to the last point of the calibration curve, showing an excessive concentration of pesticides in the leaves. Although the DESI-MS methods had shown lower precision in the quantitative assay, the developed method showed advantages such as low solvent consumption (less environmental impact), absence in sample preparation, and reduced analysis time.

Gerbig *et al.*<sup>14</sup> applied DESI technique to detect 32 pesticides in nine different fruit samples. The surface of these fruits was pressed into glass slides to promote the passage of these pesticides onto a flat surface. The method showed great potential for quick and simple screening of food items. This was demonstrated using real samples taken from routine controls. Thus, it was also shown that DESI-MS could perform non-destructive actions in qualitative and semi-quantitative measurements. Although quantifying directly from the sample surface has limitations, the concentrations determined were in the same order of magnitude as the reference values and served as an indicator for deciding whether the product should be reanalyzed by another analytical method.

An approach to the toxicity of ionic liquids in zebrafish was reported by Perez *et al.*<sup>15</sup> The authors found after the images of these fish using DESI, that the liquid AMOENG 130 accumulated in the central and respiratory nervous system and could pass through the blood-brain barrier (“filter” formed by cells and nervous tissue). This was the first report on the use of the image produced by DESI to determine the distribution and metabolism of an ionic liquid in an aquatic vertebrate and demonstrated the potential of this technique to monitor other micropollutants in aquatic vertebrates.

### **Paper Spray ionization (PSI)**

PSI technique was first introduced in 2010 by Cooks *et al.*<sup>22</sup> This AIMS method as the name suggest, uses a paper with a triangular shape connected to a macroscopic sharp tip.<sup>58,59</sup> The ionization of the analytes occurs after the application of the sample on the center of the paper’s surface with later application of a voltage (2 to 5kV),<sup>60</sup> finally the application of an acid or basic solvent onto the paper promotes the desorption of the analytes, this process leads to a generation of a Taylor cone spray which is taken towards the mass spectrometer inlet (Figure 1B).<sup>61</sup> The analysis is performed in two modes, positive and negative, according to the properties of the target analyte(s).<sup>62,63</sup> The ionization efficiency of the analyte(s) is intrinsically linked to its physicochemical characteristics, an effective interaction between the target analyte and the paper substrate, and the optimization of some fundamental parameters, promotes a more sensitive method and a better analytical performance.<sup>64,65</sup>

Among the main parameters to be evaluated, the paper substrate and the solvent must be considered to obtain a high sensitivity methodology.<sup>61</sup> The solvent must dissolve the compound of interest in the paper substrate to its greatest extent via capillarity, moving it to the tip of the triangular paper. The spray solvent has the function of extracting and solubilizing the analyte of interest. The choice of solvent is critical in the development of the method.<sup>66</sup> Due to the porous nature of the paper substrate, it can retain or not elute the analyte throughout the paper. Changing solvents can influence on method detection limits. Aqueous solvents improve surface tension and spray stability, while chlorinated solvents proved to be efficient in increasing the corona discharge voltage potential.<sup>67</sup>

Different substrates can offer specific results, as they can have different composition, thicknesses, and porosity, contributing to hindering the effectiveness of ionization and the flow of analyte throughout the paper. The chromatography paper and filter paper are the most commonly used materials; however, the modification of the paper can be performed according to the analysis objectives.<sup>62</sup> Thinner papers with smaller pore diameters, in general, tend to reduce the analyte flow throughout the paper, which could increase the ionization efficiency.<sup>68</sup>

Another important parameter to be evaluated for the efficiency of spray formation, but sometimes neglected, is the angle of the tip of the paper concerning the MS inlet source. Signal intensity, spray current and electric field are dependent on the paper angle. Based on the usually applied electric field, the literature pointed out that the most used angle has been 30°. In addition to this, paper substrates can be laser cut, with this approach it is possible to obtain correct angulation and reproducible construction.<sup>62</sup> To obtain good results with this technique, in addition to the mentioned factors, it is also necessary to evaluate other factors that may influence, such as the sample volume the distance between the spectrometer inlet capillary and the tip of the paper, which in general, will also depend on the ionization ratio of the analyte of interest.<sup>58</sup>

Since its introduction, the technique has been widely used in many fields, such as in the clinical,<sup>69,70</sup> forensics,<sup>67</sup> foods,<sup>71</sup> and environmental.<sup>19</sup>

Jjunju *et al.*<sup>16</sup> reported the analysis of aliphatic primary alkyl corrosion inhibitor amines in water samples reacting PSI experiments using an LTQ Orbitrap Exactive instrument. To prove the analytical performance of the method, the PSI-MS method was applied in three different water samples including feedwater, condensate water, and boiler water from large medium pressure. The method was capable to achieve a low limit of detection (LOD) of 0.1 pg with reproducibility less than 10%. The MS/MS of the Duomeen O molecule at the LOD concentration eliminated the matrix effect of the water samples providing to be a potential qualitative approach to corrosion inhibitor amines in water samples analysis.

The indirect contact with toxic substances is one of the most concerning about human health, especially those with the capacity of being retained in environmental compartments.<sup>72</sup> Concerning this, Bernardo *et al.*<sup>18</sup> described the use of PSI-MS for the detection and quantification of bisphenol S (BPS) in three different commercially brands of thermal papers. The analytical performance of the method showed a LOD as low as 5 ng g<sup>-1</sup> with recovery values ranging from 92.2 to 109.04%. The quantification of BPS in the three papers showed values ranging from 1.36 to 6.77 µg L<sup>-1</sup>. According to the authors the developed method was comparable to conventional analysis such as LC-MS and GC-MS reported in literature for BPS analysis. Due to this, the developed PSI-MS method was pointed out as a promising approach to replace some conventional methods of determination of BPS and without any sample preparation.

Rodrigues *et al.*<sup>73</sup> in 2020 reported a PSI-MS methodology for the steroid hormones (levonorgestrel and algestona) determination in wastewater samples analysis. The authors described the paper modification with a paraffin barrier on the triangular paper. This simple modification improved the analyte flow throughout the paper and resulted in a better spray stability, according to the authors. The ionization conditions of the analytes involved the use of a spray voltage of 3.5 kV and collision energy of 35 eV. The performance of the proposed methodology was evaluated through the figures of merit, reaching the low limit of quantification (LOQ) below to 2.3 µg mL<sup>-1</sup> and LOD below to 0.7 µg mL<sup>-1</sup>, in addition recovery values ranging from 82 to 102%. According to the obtained results, the modification with paraffin described led to an increase in the sensitivity of the technique.

Recently, PSI-MS soil analysis was reported by Dowling *et al.*<sup>74</sup> for the detection of pharmaceuticals, drugs, and hydrolysis products of chemical agents used in weapons. The voltage for both analytes was optimized separately, being used about 4.5 kV for drug analysis and 4.0 kV for hydrolysis products of chemical agents. As could be seen, the voltage is optimized according to the analyte structure and physicochemical properties, the better MS response is chosen considering not only the analyte response but also equipment integrity. According to the authors, the methodology reported an alteration for soil analysis, which is usually performed by obtaining the crude soil extract after many sample preparations steps.

Soil analysis by PSI-MS was also reported by Liu *et al.*<sup>75</sup> in which they described the quantification of tetrabromobisphenol A (TBBPA) in soils and sediments. The analysis was performed together with an internal standard enriched with a stable isotope (<sup>13</sup>C<sup>12</sup>-TBBPA) for the quantification of the target analyte. Better results were obtained by the voltage used of -2 kV, the vertex angle of 30°, base length 14 mm, and lateral length 29 mm. The chosen distance between the tip of the paper and the mass spectrometer inlet was 6 mm. Among the analysed solvents, methanol was chosen as the best for extracting and transporting solvents. This study demonstrated an alternative to improve the quantitative performance of the PSI-MS methods using an internal standard compound. Under these conditions, it was obtained a linear range of 0.1-100 mg L<sup>-1</sup> (R<sup>2</sup> = 0.9975) and recoveries values between 90.4%-101.1%, being possible to compare with other conventional methods.

In 2017, Kotthoff *et al.*<sup>76</sup> also performed the analysis of TBBPA in sediment samples using liquid chromatography coupled with atmospheric pressure photoionization tandem mass spectrometry (LC-APPI-MS/MS) and obtained recoveries values ranging from 71.5 to 112.5% for sediments. In comparison with methodologies applying separation steps such as chromatography, the methodology applied by Liu *et al.*<sup>75</sup> showed similar or higher recovery values, in addition to having presented an analysis time of 1 minute for each sample. Differences in results compared to other methods can be attributed to the correlation of the internal standard of the isotope method. Without sample purification and chromatographic separation, the method achieved high sensitivity and low analysis time, which was shown to have great potential for routine analysis of emerging contaminants in soil samples.

The analysis of samples from some animals is an alternative to identify the effect of bioaccumulation in the environment, in which some compounds with an accumulating potential are retained in animals, especially those of aquatic origins, such as fish and some vertebrates. Having this in mind, Chun Wei *et al.*<sup>77</sup> reported the modification of a paper with graphene oxide and nylon membrane for the analysis of malachite green and its metabolites in freshwater fish. The modification of the paper with graphene and the nylon membrane led to a strong interaction between the electrons of the π-π bond of graphene oxide with the conjugated in-plane π electrons of the rigid triphenylmethane backbone of the malachite green, in addition to the strong electrostatic interaction between the hydrogen bonds of the malachite green molecule and the graphene oxide, favoring the interaction between them. As a result, in tests with aqueous solutions, more than 98% malachite green was adsorbed onto the modified paper. The analysis of fish tissue samples showed that a concentration of 0.65 µg kg<sup>-1</sup> was obtained, which met the minimum performance limit (2 mg kg<sup>-1</sup>) proposed by the European Commission to determine the sum of malachite green and its metabolite green leucomalachite in food products.

Another paper modification was proposed in 2019 by Zargar *et al.*<sup>78</sup> in which the modification of a porous graphene paper with a molecularly imprinted polymer (MIP) was described for the analysis of the pesticide propoxur in samples of tap water and water from crops through the source by mobility spectrometry ionic (IMS). The application of MIP was intended to offer greater selectivity for the target analyte, thus the pesticide itself was used as a template during the synthesis of MIP and later electroplated on the surface of the graphene paper. The modification of the paper led to obtaining a LOD of 0.3 ng mL<sup>-1</sup> and a recovery ranging from 94 to 102%. Through the proposed methodology, the authors stated that compared to other methods described in the literature, the PSI method proved to be fast and effective in analysing the target analyte. The modification with the polymer MIP generated greater selectivity for the pesticide propoxur, increasing the sensitivity of the analyte for the detection technique, which compensated the non-selectivity of the IMS analysis.

### **Direct real-time analysis (DART)**

The AIMS method known as DART was introduced by Cooks *et al.* in 2005,<sup>79</sup> months after the introduction of DESI. The technique was introduced with the main focus on performing rapid analyses at ambient pressure, belonging to the class of AIMS techniques based on plasma ionization.<sup>80</sup> In DART the ion source can be used to analyse solid liquid, and gaseous samples.<sup>81</sup> In a few words, DART ionization uses heated

metastable gas atoms that are capable to desorb and then ionize the target analyte(s).<sup>82</sup> DART ionization process is performed in the presence of an inert gas (usually helium or nitrogen) in a discharge chamber leaving the species in an excited (metastable) state, resulting in a flow of plasma gas.<sup>83</sup> Upon leaving the chamber, the metastable species encounter the sample, and the desorption and ionization of the analyte(s) occur, which is directed to the mass spectrometer inlet (Figure 1C), the ionization of the sample can generate positive and negative ions. When applied in positive ion mode, metastable species collide with atmospheric water molecules producing hydronium (Penning ionization) and subsequently, the ionization of the analyte occurs. In contrast, in the negative ion mode, clusters of negative ions composing water and oxygen molecules react to form negative ions of the analyte.<sup>80,83</sup>

The optimization of the DART method involves the study of the ionization gas applied (He or N<sub>2</sub>) and its temperature, the distance between the gas output of the ionization source and the sampling hole of the mass spectrometer, the electrical potential responsible for producing a glow discharge and the gas flow.<sup>83</sup>

According to Sisco and Forbes,<sup>82</sup> although nitrogen can also be used as the ionization gas, helium is the most commonly used in DART analysis. This preference of helium instead nitrogen is because of its energy to ionize water of the metastable atoms. In positive mode, the ionization mechanism is driven by the ionization of water in the atmosphere. The ionization mechanism can be seen in Equations 1–4 as follows:



Robert *et al.* reported that the DART/orifice distance and the grid potential are parameters with significant influence on method efficiency, in which, the reduction of this distance and the increasing the potential from 250 V to 650 V, leads to an increase of the relative abundance of O<sub>2</sub><sup>+</sup>• in the background mass spectrum of real-time direct analysis-mass spectrometry. Thus, these conditions benefit the formation of molecular ions, these parameters can be optimized and adjusted to the desirable conditions, in which the non-optimization of these parameters can lead to the two simultaneously ionization in the method (by proton transfer or by penning).<sup>84</sup>

Since the introduction of the DART technique in 2005, the literature has been reporting some applications in many scientific fields, such as food,<sup>85</sup> agriculture,<sup>28</sup> forensic,<sup>86</sup> clinical analysis,<sup>87</sup> and environmental analysis.<sup>88</sup>

In 2020, Nicolás Zabalegui *et al.*<sup>89</sup> reported the development of an analytical method based on a direct transmission mode analysis system in real-time quadrupole time-of-flight mass spectrometry (TM-DART-QTOF-MS) coupled with multivariate statistical analysis for the analysis of existing organic compounds in seawater samples in the surface microlayer (SML) and underlying water (ULW) collected on the Cape Verde Islands. The analysis involved the use of He as an ionizing gas at a temperature of 300 °C, in the negative ionization mode. The transmission mode geometry TM-DART was implemented as an optimization, which established a distance of 2.5 cm from the source, which allowed the analysis of samples in continuous flow and minimization of the risk of cross-contamination. From the methodology applied using DART, the authors found the possibility of differentiating the SLM and ULW samples through the chemical profile of both. In addition, the study pointed out that fatty acids, halogenated compounds, and organic compounds containing oxygenated boron were present in SML samples and could participate in photochemical reactions at the ocean air-water interface. According to the authors, one of the advantages of applying DART technique instead conventional electrospray methodologies for seawater analysis was to minimize the high salts concentration levels in the sample to MS analysis, not requiring desalination, which could result in a change of the matrix.

The analysis of microplastics in environmental water samples was recently described by Zhang *et al.*<sup>88</sup> For the analysis of microplastics, the samples were initially prepared, being heated by a ramp, starting at 50 °C and reaching 600 °C for 6 min. The products generated from this heating were taken to ionization by DART using helium as the reagent gas, a voltage of 350 V and heating of 300 °C, and analysis using the Orbitrap mass spectrometer. The application of the methodology for the analysis of microplastics led to the identification of plastics with different chemical profiles, and possibly from different origins, in which resulted in a mass spectrum exhibiting about ~ 10,000 discrete peaks, corresponding to plastic additives released by thermal desorption and degradation products of polymer generated by pyrolysis. Through the application of statistical data analysis, the chemical profile of plastics could be differentiated by creating a fingerprint for the analysis of each type of plastic.

Still on analysis of aquatic environments, Nei *et al.*<sup>90</sup> reported the use of DART-MS to estimate the concentration of histamine and 1,8-diaminooctane in fish fillets. The use of the DART-MS analysis method was applied to test the target analytes presented in 165 samples. According to the authors, the detection sensitivity was influenced by the temperature of the gas heater, and the temperatures between 350 and 450 °C resulted in larger and more defined peak areas. In addition, the matrix effect also affected and demonstrated by the recovery values of the developed method, (151.5 and 619.9%), in which, according to the authors, future studies would be necessary to reduce the matrix effect. However, the study proved to be a possible approach for analyzing mainly histamine, since it is a biogenic amine responsible for cases of food poisoning.

Emmons and Gionfriddo<sup>91</sup> reported a strategy to minimize one of the limitations of ambient mass spectrometry, which is the appearance of transient microenvironments (TME), that occur mainly in analyses that are carried out in variable and non-ideal conditions. For the study, the authors reported the use of solid-phase microextraction (SPME) with DART-MS coupled to a thermal desorption unit (TDU) for the analysis of pesticides and drugs from surface water. However, for more precise analysis, a new SPME geometry, SPME-Arrow shape, was used, which presented a greater improvement on extraction phase volume compared to conventional SPME fiber. This instrumentation used was an optimization of the conventional parameters of the DART technique. Furthermore, other parameters that were optimized regarding the ionization source were the localization of the TDU-DART device in the inlet of the mass spectrometer and the plasma temperature. During the analysis, three positions were tested: first in full contact, then a distance of 5mm, and finally 10mm. Meanwhile, for each position, the plasma was at different temperatures: 300, 350, and 450 °C, respectively, being capable to quantify the analytes in the range of  $\mu\text{g L}^{-1}$  with a time analysis of 5 minutes. The authors concluded that this study proved to be quite satisfactory, allowing further expansion of AIMS analysis into more complex samples and in unconventional environments, where the use of TDU-DART provided rapid and reliable on-site quantification.

### **Extractive electrospray ionization (EESI)**

Before being known as extractive electrospray ionization, the EESI technique was first introduced as fused droplet electrospray ionization (FD-ESI) in 2002 by Shiea *et al.*<sup>92</sup> as an approach for the analysis of peptides and proteins. After this first introduction, the technique underwent extensive studies by other research groups, especially by Cooks *et al.*<sup>93</sup> In 2006 the technique was finally known as EESI, whose first application was in the analysis of biological matrices, reporting a methodology without any previous sample preparation.<sup>94</sup> The ionization mechanism involves the instrumental configuration using two sprays, one containing the solution for electrospray formation and connected to an energy source for the application of voltage, and the other spray with a neutral analyte solution. Then the two sprayers are placed in a certain position to form two converging streams (Figure 1D). In the gas phase, the particles containing the neutral analyte collide with the charged electrospray droplets, through this collision the analyte is extracted from the neutral drop to the charged electrospray drop forming the ions that are taken to the mass spectrometer inlet and then analyzed.<sup>11,93,94</sup>

As previously described, the system involves the use of two sprays that collide with each other. Thus, the parameters to be optimized for a better ionization efficiency involve the study of the formation of the two sprays.<sup>95</sup> In this context, the angles between the two nozzles ( $\beta$ ) and between the nozzle containing the neutral analyte and the inlet of the mass spectrometer ( $\alpha$ ) should be optimized, being generally adjusted to  $60^\circ$  and  $150^\circ$  respectively. In addition to the angles, the distance between the two sprayers ( $b$ ) and the inlet of the mass spectrometer ( $a$ ) must be optimized to favor ionization, usually using distances of 0.5-20 mm and 3-15 mm respectively. In addition to these parameters, the flow of the sprayers must be controlled to favor an efficient collision between the charged spray and the neutral sample droplets.<sup>6,81</sup>

Despite having been introduced for the analysis of biological matrices, since its creation, the technique has been used in different scientific fields, such as cosmetic analysis,<sup>96</sup> drugs,<sup>97</sup> and also in the application in the environmental analysis.<sup>6</sup>

Recently, Giannoukos *et al.*<sup>98</sup> reported the use of the real-time detection of metals and trace elements in the production of biogas from the anaerobic digestion of manure and mixed organic sources, using an extractive electrospray ionization source coupled with time-of-flight mass spectrometry analysis (EESI-TOF-MS). The method optimization included the study of how the biogas interacted with the charged droplets of the spray. This study involved the evaluation of different proportions of  $N_2$  (1/2, 1/5, and 1/10) as biogas diluent and  $N_2$  flux. The optimization of the gas proportion and flow parameters led to the use of a 1:5 mixture of biogas:  $N_2$  and a flow of  $1.5 \mu\text{L min}^{-1}$ . Through the methodology, it was possible to compare the percentage of removal of 14 metals in installed adsorbent materials dedicated to the removal of organic contaminants. EESI quantification found that about 64% (for Cu), 60% (for Fe), 62% (for Zn), 36% (for Cd) and 100% (for Pb) were removed from the raw biogas. The application of the methodology proved to be an effective tool for monitoring the removal of metals in raw biogas, also assisting in the creation of cleaning and filtering protocols.

Although AIMS methods are not normally performed after some previous sample preparation, in some cases the application of a sample preparation step before the AIMS analysis can lead to an increase in the technique's sensitivity to achieve better analytical performance. In 2020, Liu *et al.*<sup>99</sup> described the use of internal extractive electrospray ionization (IESSI) ionization for the analysis of 15 organophosphate class pesticides (OPPs) in environmental water samples after enrichment by  $\text{Fe}_3\text{O}_4\text{-ZrO}_2$  particles. The application of the material as a sample preparation step led to the removal of interfering agents present in the environmental samples and the concentration of OPPs. The proposed methodology showed LODs in the range of 0.14 to  $16.39 \text{ ng L}^{-1}$  and recovery values in the range of 85.4 to 105.9%. The application of EESI allowed the analysis of 15 pesticides in an analysis time of 1 min. The results showed that the application of a rapid pre-sample preparation can increase the sensitivity of the EESI technique, including high sensitivity, fast analysis, and selectivity for the detection of OPPs in environmental water samples.

Another application of previous sample preparation before analysis by EESI was described in 2018 by Kou *et al.*<sup>100</sup> in which the use of molecularly imprinted polymers and IEESI tandem analysis of fluoroquinolones (FQs) in environmental water samples was reported. The authors chose to use the MIP in a  $0.22 \mu\text{m}$  filter, in which the water samples were eluted, and through a selective polymer interaction process, the FQ molecules were retained, and by applying electrospray as an elution solution, target analytes were eluted into the mass spectrometer inlet. Under the optimized conditions, the methodology offered LOD values ranging from 0.015 to  $0.026 \mu\text{g L}^{-1}$  and recovery values from 91.14 to 103.60%. Although systems by AIMS do not normally use any previous sample preparation, the use of MIP's in this study allowed analyses by IEESI in shorter times.

The analysis of pesticides in honey samples was described by Deng *et al.*<sup>101</sup> the authors reported the use of the neutral desorption-extractive electrospray ionization (ND-EESI) for the determination of organophosphate insecticides and two types of carbamate insecticides in commercial samples of honey without any previous sample preparation. The application of the methodology for the analysis of pesticides proved to be efficient for the determination of the analytes with LODs ranging from 1.16 to  $4.18 \text{ ng g}^{-1}$  and recovery values between 87 to 114.98%. The effect of the matrix on the analytes was the

parameter that most influenced the determination of pesticides. Of the five pesticides studied, only one (chlorpyrifos-methyl) had an average matrix effect on signal suppression, the others were not affected by the sample, this effect was attributed to the interaction of the pesticide with the sample. However, the proposed methodology using neutral desorption sampling gas to gently impact a surface led to a lower ion suppression which decreased the matrix effect observed for chlorpyrifos-methyl and improved real-time detection of other analytes in the sample without prior sample preparation.

In 2020, Gao *et al.*<sup>102</sup> applied EESI for the analysis of the chemical profile of nectar and honey samples from three citrus species. The analysis was performed by extractive electrospray ionization high-resolution mass spectrometry (EESI-HRMS), the results showed the presence of 12 polyphenols and 8 amino acids, while analysis by high-efficiency-detection liquid chromatography by ultraviolet (HPLC-UV) showed the presence of 9 polyphenols. Statistical analysis showed that the profile of the nectar samples was similar to each other, in the same way as the honey samples. However, through the results, it was possible to distinguish the nectar and honey samples by the differences between chemical composition. Compared to the HPLC-UV analysis, the EESI analysis showed greater detail in the presence of chemical components in the samples, without needing any separation step or previous sample preparation. According to the results, the EESI technique could not only be used for quantitative methods, but also for qualitative methods, especially for the differentiation of sample chemistry, through fast and sensitive methodologies.

## NEW TRENDS FOR AIMS METHODS IN ENVIRONMENTAL ANALYSIS

### ***Application of sample preparation methods for AIMS analysis***

The combination of an adequate sample preparation with AIMS methodologies shown as an interesting tool either for sampling or to improve the selectivity and sensitivity of the MS analytical methods. In 2016, Fang *et al.*<sup>103</sup> reported on a review study, strategies, and applications of the SPME technique in association with AIMS methods. According to the authors, this combination can offer the opportunity for direct sampling and direct analysis of trace analytes in biological, environmental samples, forensics, food, small individual organisms, and even single-cell samples under open and environmental conditions.

The protective mask has become a reality for everyone, since 2019 due to an infection disease, known as COVID-19. Having this in mind, in 2020, Yuang *et al.*<sup>104</sup> reported the use of SPME fiber-containing different coatings (Polydimethylsiloxane, Polydimethylsiloxane /divinylbenzene, Carbon/ polydimethylsiloxane, and Carbon/polydimethylsiloxane/ divinylbenzene) into a face mask to *in vivo* sampling the aerosol of exhaled air by patients with the aim to screening the chemical profile of this aerosol by DART-MS. For this purpose, two SPME fibers were inserted into a face mask, after the sampling, one fiber was used for recording the full spectrum, the other was used to perform MS/MS analysis.

The related study showed a potential of sampling by SPME in the mask was appropriate to assess the chemical profile of breathed air. So, despite having been applied to the analysis of drugs, the authors point out that the methodology can be applied to other analyses that are directly linked to the respiratory quality of human beings. Thus, sampling by SPME and analysis by AIMS in an environmental context, can be used for the analysis of contaminants in the air, especially in large cities, to carry out the monitoring of these compounds in the daily life of large urban centers.

Another application of SPME containing a matrix-compatible coating together with DART-MS was reported in 2019 by Gómez-Rios *et al.*<sup>27</sup> for the analysis of pesticides in surface water. All the sampling processes of the SPME were performed in less than 3 min, after the sampling, the SPME fiber was placed at the DART inlet, and the analysis was performed in 4 min, showing the speed of the methodology. The applied methodology was capable to obtain LOQ's values of 0.1-5  $\mu\text{g Kg}^{-1}$  for the 19 pesticides studied. The analysis offered the profile of pesticides in the samples, in addition to allowing their quantification in 2-minute per sample.

The application of the SPME technique directly to environmental samples was reported by Deng *et al.*<sup>105</sup> in which the authors described the coupling of SPME with ambient mass spectrometry ion source using a surface coated wood tip probe for ultra-trace perfluorinated compounds (PFCs) in water samples

analysis. The authors reported the modification with n-octadecyldimethyl[3-(trimethoxysilyl)propyl] ammonium chloride on the surface of a sharp wooden tip via silanization. The wooden tip is a desirable substrate for AIMS analysis due to its porous and hydrophilic properties. When applied some solvent and voltage, the material becomes conductive, and then an electrospray is generated. Furthermore, because of the of hydroxyl groups abundance, the material becomes an ideal candidate for the functionalization and modification of its surface. The optimized methodology presented LODs and LOQs values for PFCs analysis of 0.06-0.59 ng L<sup>-1</sup> and 0.21-1.98 ng L<sup>-1</sup> respectively. For last, quantification of real samples was performed by isotope internal standard calibration curve method or isotope dilution method, the results showed a range of PFCs from 0.95 to 15.95 ng L<sup>-1</sup> for lake water, 0.55 to 20.1 ng L<sup>-1</sup> for river water, 0.78 to 12.8 ng L<sup>-1</sup> for whole blood, and 68.6 to 562.1 ng L<sup>-1</sup> for milk samples showing its higher concentration of PFCs.

### ***Electrospray laser ablation ionization (LAESI) applied for environmental analysis***

The electrospray laser ablation ionization (LAESI) technique was introduced in 2007 by Nemes and Vertes.<sup>106</sup> The ionization consists in two-stage process.<sup>107</sup> In the first stage, it is created a fine mist of neutral droplets that is generated from the sample by contact with a pulsed mid-infrared (IR) laser, adjusted to the O-H stretch adsorption (2.94 μm). The ionization of the desorbed analytes from the sample is performed in the second stage, in which the interaction of the charged spray (ESI source) with the desorbed analytes promotes the ionization of the analyte(s) present in the sample (Figure 4A).<sup>6,92,107,108</sup> The eminent advantage of the technique is its ability to access more internal compounds in the sample and not just compounds present on the surface such as DESI. Thus, the LAESI technique brings the formation of chemical images as a function of depth (x, y, and z), due to IR laser ablation.<sup>108</sup> Since its introduction, the technique has been widely applied especially for cell and tissue analysis,<sup>109,110</sup> with few recent applications reported for analysis in environmental matrices.

In 2014, Beach *et al.*<sup>110</sup> described the analysis of the neurotoxin domoic acid (DA) in crustaceans by LAESI-MS/MS. The analysis of the muscle tissue of the crustacean samples compared with reference materials, led to the obtainment of a detection limit of 1 mg kg<sup>-1</sup> and recovery values close to high-performance liquid chromatography-spectrometry methods of tandem masses (HPLC-MS/MS) (103-123%) in addition to analyses with times of up to 10 s for each sample. In the same year, Nielen and Beek<sup>111</sup> described the use of the Laser-ablation electrospray ionization-mass imaging (LAESI-IMS) to investigate the potential of the technique for obtaining macroscopic and microscopic images of pesticides, mycotoxins, and plant metabolites in rose leaves, orange and lemon fruits, ergot bodies, cherry tomatoes, and corn kernels. With the application of the technique, it was possible to quantify the analytes on the surface and inside the samples through laser penetration in contact with the different matrices, performing not only 2D images but also 3D images. The application of the technique in both studies showed the potential of the LAESI technique to carry out the mapping not only on the surface but also inside different samples with an environmental focus, in fast methodologies, and without sample preparation.

Recently, Vaz *et al.*<sup>107</sup> described the use of (LAESI imaging) to investigate the diffusion of the mycotoxin patulin from rotten to healthy areas of fruits. Although, this can be considered a food analysis, the environmental concerning of mycotoxins in food samples is due to its high toxicity in lower levels of concentration. Also, according with Escrivá *et al.*<sup>112</sup> due to the bioaccumulation of such secondary metabolites, they can cause their carry-over in animal fluid, organs and tissues, and consequently reach and affect human health. For the study, Vaz *et al.*<sup>107</sup> used slices of mold-infected and uninfected (control samples) apples and strawberries. The application of an infrared laser beam (2.94 μm) resulted in the ablation of the analytes. The application of LAESI as capable to achieve a LOD of 50 ng mL<sup>-1</sup>. The visualization of the patulin was observed in all infected fruits in both diseased and healthy areas, these results suggested the diffusion of patulin from the mold-infected area.

Although there are not many works in the literature reporting the LAESI technique for environmental analysis, recently, Maloof *et al.*<sup>113</sup> described a literature review on the use of chemical imaging techniques

for environmental analysis, among them, the LAESI technique was discussed and showing possible trends for the technique that should be taken into account in this review.

The analysis of rocks and other environmental solids has always been considered a challenge, due to the difficulty of working with such matrices. However, imaging techniques such as LAESI have been proving to be an alternative to solve this problem. The analysis of rocks and other solid particles in the environment can provide important information, especially about where they were collected. Having this in mind, Gundlach-Graham *et al.*<sup>114</sup> reported the use of the low-dispersion laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) for the analysis of metals in rock samples. The application of the technique showed a resolution of ~10  $\mu\text{m}$ , proving to be effective for evaluating the chemical profile of environmental rocks.

The potential of this technique for environmental science lies in its functioning, allowing the analysis not only of the surface but also of the interior of the sample, which is a possible approach for the analysis of contaminants in difficult-to-work environmental matrices, such as rock samples. Furthermore, compared to other techniques based on electrospray, such as DESI, for example, the application of LAESI makes it possible to obtain 2D and 3D images, which makes it even more feasible to study the chemical profile of complex samples.

### **Perspectives in environmental analyses using the Nano-DESI technique**

Another approach that has a few reports in the application in environmental analysis is Nano-DESI. This technique was first reported in 2010 by Roach *et al.*,<sup>115</sup> in which the conventional DESI resources are used, with some modified configurations. In summary, a solvent bridge is formed between two capillaries, and the surface is then analysed. One of the capillaries is responsible for providing the solvent for the extraction of analytes onto the surface. The second capillary promotes the transport of the solution containing the extracted analytes to the mass spectrometer inlet, through nano-spray self-aspiration (Figure 4B).<sup>116,117</sup> This technique has been constantly improving, showing until now high resolution and sensitivity, providing spatial distribution of surfaces analysed in great detail. The technique has been constantly improved showing resolutions of 200  $\mu\text{m}$  and 20  $\mu\text{m}$  for biological matrices and good sensitivity, providing adequate spatial distribution of surface analytes.<sup>118</sup>

Yin *et al.*<sup>119</sup> developed a Nano-DESI methodology, that happened the instrument fabrication to the processing of the obtained data, resulting in more sensitive and quantitative images of lipids and metabolites in biological matrices. A resolution better than 10  $\mu\text{m}$  was possible by acquiring 104.400 pixels. The method for quantification was based on the use of internal standard and signal normalization to minimize the matrix effect, common in quantitative image analysis. The use of the internal standard and normalization requires special care, errors may represent inappropriate behavior of the analytes and may compromise the developed methodology. These advances show a great contribution to imaging via Nano-DESI, but the use of other complementary techniques such as HPLC may be necessary.

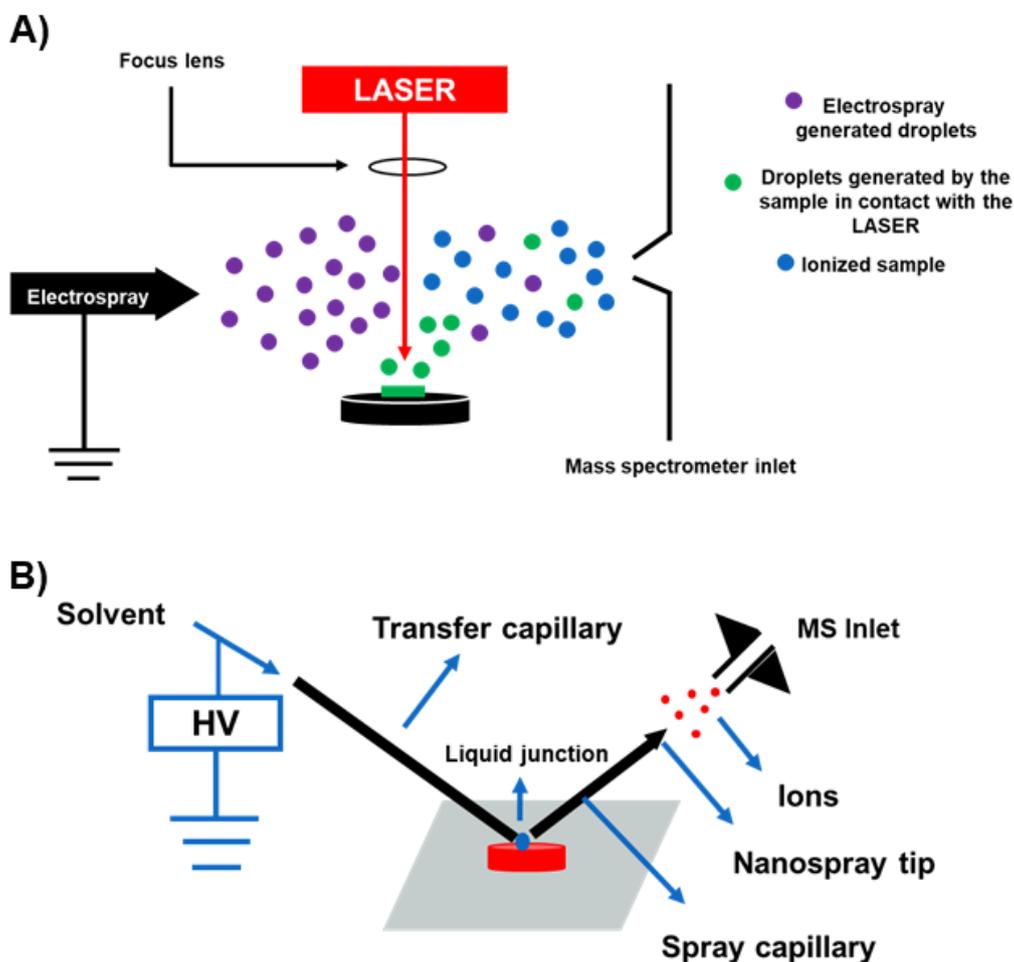
Like DESI, Nano-DESI can be applied in several areas, such as crude oil analysis,<sup>120,121</sup> analyses in biological matrices,<sup>122,123</sup> bacterial characterization,<sup>124</sup> pharmaceutical,<sup>125</sup> among others. Despite its wide application, its use in environmental matrices is few reported in the literature. In this context, approaches that integrate this area can be widely studied using this technique.

In 2014, Laskin *et al.*<sup>126</sup> analysed the molecular composition of organic matter in soil samples using the Nano-DESI technique. In this study, it was possible to molecularly characterize these samples without prior sample preparation, in short analysis time, high sensitivity, and low sample consumption. Nano-DESI made up the need for laborious extraction of organic matter from the soil, which usually uses large volume of organic solvents.<sup>127</sup> For these analyses, approximately 10 ng of organic mass was used, showing the effectiveness of this technique in an environmental matrix.

In summary, Nano-DESI is under constant development showing distinct applications to a wide range of analytes in different matrices. Having this in mind, the potential of application of this technique allows analyses with minimal or no sample preparation, low solvent consumption, low sample quantity, high

sensitivity, low analysis time, and better image resolution. Studies involving environmental matrices (ore, wood, rocks, pollutants, plants, among others) can help to unveil environmental states if better explored. Finally, the approximate ability to quantify analytes on a surface via Nano-DESI may open new doors for routine methods in the expression of pollutants in plants, for example.

As it was possible to observe, AIMS techniques also present the possibility of optimizing their resources, whether in the development of new approaches or the improvement of existing methodologies. However, there is still a lack of studies reporting the fabrication of devices capable of performing *in situ* analysis, in addition to the development of portable AIMS devices hyphenated to miniaturized mass spectrometers. Thus, studies are still needed, especially using consolidated techniques for biological samples, for their application in environmental matrices as a way of new approaches for rapid analysis of such complex matrices.



**Figure 4.** A) Schematic representation of the LAESI ionization mechanism, and B) Schematic representation of the Nano-DESI ionization mechanism

## CONCLUSIONS

In this review, some of the main AIMS techniques that have been applied for the profile analysis and quantification of emerging contaminants in environmental matrices were discussed. Thus, it was possible to observe that the DESI, DART, PSI, and EESI techniques have wide application in environmental matrices, contributing to fast, sensitive, and high analytical performance analyses. Furthermore, when compared to existing conventional techniques, they show analytical capacity equal or superior in different analysis.

The techniques derived from the concepts established since the creation of DESI in 2004, bring with them advantages over conventional ionization techniques. The application of methodologies based on systems by AIMS shows analysis with a shorter analysis time than conventional techniques, lower consumption of organic solvents (highlighted in the concept of green chemistry). Advances in the development and optimization of systems by AIMS must meet the complexity of environmental matrices. Despite being techniques widely applied to biological matrices, imaging techniques such as DESI, Nano-DESI, and LAESI, which are few used in this scientific field, represent a new alternative for chemical monitoring of previously challenging matrices.

In general, the development of methodologies based on AIMS with a focus on environmental analysis still needs a more critical view, considering the development of *in situ* analysis systems, for quick and reliable analysis not only in large urban centers but also in remote locations, where the risk of contamination and lack of monitoring is greater.

### Conflicts of interest

The authors declare no conflicts of interest.

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