



Use of dielectric barrier discharge ionization to minimize matrix effects and expand coverage in pesticide residue analysis by liquid chromatography-mass spectrometry

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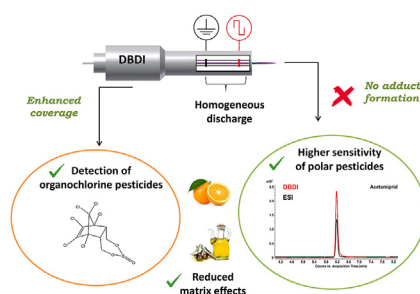
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HIGHLIGHTS

- Thorough evaluation of analytical performance of DBDI source for LC-MS.
- Optimized homogeneous regime helium DBD plasma enhances signal significantly.
- Enhanced ionization coverage compared with electrospray and APCI.
- Minimized matrix effects due to the absence of sodium adduct formation.
- Sensitivity matching (or even exceeding) commercial electrospray ionization.

GRAPHICAL ABSTRACT



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ABSTRACT

Although electrospray ionization (ESI) remains the gold standard ionization source for LC-MS, it exhibits two main limitations: the occurrence of matrix effects and the limited ionization coverage towards nonpolar compounds. Dielectric barrier discharge ionization (DBDI) has gained attraction in recent years as a versatile ionization method in different applications and formats. Here, we report a thorough evaluation of DBDI as ionization interface for LC-MS, which reveals attractive advantages over ESI and atmospheric pressure chemical ionization (APCI) provided its singular ionization mechanism versatility. A suite of 80 pesticides across a wide range of physicochemical properties were selected and the results were compared with both ESI and APCI sources. Using a helium plasma operated in homogeneous regime with square-wave AC waveform and relatively low voltages (2.5 kV), not only DBDI was able to ionize compounds only amenable so far by GC-MS (eg. organochlorine species), but also offered a competitive performance in terms of sensitivity when contrasted with the commercial electrospray ionization source under equivalent conditions. Unlike ESI, DBDI mechanism occurs in the gas-phase, so the method is less affected by liquid-phase surface phenomena that yield ion suppression in ESI. Data collected in the positive ion mode revealed negligible matrix effect values (<10% suppression) for most of the studied compounds in different complex matrix extracts such as wastewater, orange or olive oil. This is also

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consistent with the absence of adduct formation whereas with ESI source, Na adduct formation is quite common with these species. In general, both sensitivity and average limits of quantitation for DBDI were similar to those obtained by ESI and better than APCI. Results showed that analyte coverage with DBDI is enhanced with respect to ESI and APCI sources being able to effectively analyze organochlorine compounds.

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1. Introduction

The combination of liquid chromatography with mass spectrometry (LC-MS) by means of atmospheric pressure ionization interfaces (mainly electrospray) is mainstream for a plethora of applications within trace quantitative organic analysis. Perhaps, the main issues associated to this approach are the occurrence of matrix effects and the restricted ionization coverage towards nonpolar species offered by electrospray ionization, which limits the versatility of the technique [1]. Matrix effects represent a major concern in small-molecule trace analysis as they severely compromise not only quantitative performance but also method reproducibility [2,3]. A matrix effect is considered to be an (unexpected) suppression or enhancement of the analyte response due to co-eluting matrix constituents [4,5]. Matrix effects strongly depend on the nature of the analytes and on the properties of coeluting compounds [6]. The fundamental basics involved in this effect are diverse, although most explanations are linked to liquid-phase and differential surface activity of coeluting molecules [7].

Several approaches have been attempted to prevent matrix effects. The most obvious one is additional sample workup [8], leading to the selective removal of potential coeluting interferences. As an alternative, sample or extract dilution [9] is applied if the expected fit-for-purpose concentrations meet the overall sensitivity of the method. Different strategies related to the use of isotopically labelled (internal) standards have been also proposed to diminish the effects of ionization suppression [10,11], although their efficiency and widespread use are limited by the lack of standards, their cost and also by isotope effects which lead to retention time shifts so that ionization suppression or enhancement is not accurately compensated [12]. Alternative ionization sources have been also proposed to overcome the problems associated to electrospray ionization signal suppression or enhancement [13,14]. In the past, the use of atmospheric pressure chemical ionization and electron impact ionization methods has been proposed to minimize matrix effects [15], based on the fact that ionization mechanism occurs after solvent elimination. Thus, no surface-related effects are expected with these alternative ionization methods.

One of the fastest growing topics in mass spectrometry is the development of ambient ionization methods, so that both sampling and ionization steps are undertaken without the restrictions of electrospray ionization. Amongst these methods, plasma-based ambient ionization methods [16,17] are based on reactant species capable of effectively ionizing analytes of interest. These species are generated using noble gases or with the surrounding environment, after the application of DC or AC voltages. Dielectric barrier discharge ionization (DBDI) has gained attraction in recent years as a versatile ionization method available in different formats (viz. ambient ionization probes [18,19], GC-MS [20], LC-MS [21,22] or CE-MS [23] interfaces). Since its first description it has become very popular for applications in analytical science because of its outstanding features, including flexibility and simplicity of setup, low energy consumption, good portability, and high chemical activity.

Many applications have been addressed by DBDI including ambient mass spectrometry imaging [24], environmental analysis,

biological, pharmaceutical analysis and food safety [25–29]. DBDI uses low-temperature plasmas at atmospheric pressure to generate ions. The DBD is typically formed between two electrodes, with at least one dielectric layer which separates the electrode from the plasma. DBDI was also proven to be an interesting ionization technique for liquid chromatography mass spectrometry coupling (LC-MS) [21]. The DBDI probe can be implemented into a commercial API (atmospheric pressure ionization) source so that the LC eluent was nebulized and vaporized in the same manner as for APCI. These features lead to enhanced analyte coverage compared to commercially available LC-MS sources as was reported [21,30] to measure non-polar non-ESI-amenable compounds such as polycyclic aromatic hydrocarbons (PAHs) and organochlorine compounds. Follow-up fundamental studies on the AC waveform applied [31,32] have led to significant progress and further improve the performance of DBDI plasmajet towards soft ionization of small molecules, with respect to first reports [21,30,32].

Here, we report a thorough evaluation of DBDI as ionization interface for LC-MS, which reveals attractive advantages over ESI and APCI, due to its singular ionization mechanisms versatility. A dramatic increase of sensitivity was achieved compared to first reports [21,30,33] by using a helium plasma operated in homogeneous regime, due to the use of relative low voltages (2.5 kV) and square-wave AC waveforms. A suite of 80 pesticides across a wide range of physicochemical properties were selected and the results were compared with both electrospray and APCI sources. Matrix effects, analyte coverage, sensitivity and salt adduct formation were evaluated with the three different approaches.

2. Experimental section

2.1. Chemical and reagents

Pesticide analytical standards were purchased from Fluka, Pestanal[®] quality (Madrid, Spain) and Sigma-Aldrich (Steinheim, Germany). Individual stock solutions of the studied compounds (ca. 500 $\mu\text{g mL}^{-1}$ each) were prepared in methanol, acetonitrile and mixtures of acetone-acetonitrile (25:75) and stored at -20°C . HPLC-grade methanol (MeOH), acetone, acetonitrile (ACN), formic acid (HCOOH), ammonium formate, magnesium sulfate anhydrous (MgSO_4), sodium acetate (AcNa) and sodium chloride were also purchased from Sigma-Aldrich (Steinheim, Germany). Primary-secondary amine (PSA) and EMR lipid removal sorbents were obtained from Agilent Technologies (Santa Clara, CA, USA). A Milli-Q Plus ultra-pure water system from Millipore (Milford, MA, USA) was used throughout the study. Working solutions were prepared by appropriate dilution of the stock solutions with MeOH and water to match the initial mobile phase composition of the LC gradients used.

2.2. Pesticide selected and matrices tested

80 representative multiclass analytes covering the main classes of pesticides (herbicides, fungicides, insecticides, acaricides), pesticide breakdown products and reagents in their production (such as pentachlorobenzene) were selected to evaluate the

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