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Chemometric optimization of a low-temperature plasma source design for ambient desorption/ionization mass spectrometry

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ABSTRACT

Low-temperature plasmas (LTPs) are attractive sources for atomic and molecular mass spectrometry (MS). In the past, the LTP probe, which was first described by Harper et al., was used successfully for direct molecular mass spectrometric analysis with minimal sample pretreatment in a variety of applications. Unfortunately, the desorption/ionization source itself is commercially not available and custom-built LTP set-ups with varying geometry and operational configurations were utilized in the past.

In the present study, a rapid chemometrics approach based on systematic experiments and multivariate data analysis was used to optimize the LTP probe geometry and positioning relative to the atmospheric-pressure inlet of a mass spectrometer. Several parameters were studied including the probe geometry, electrode configuration, quartz tube dimensions, probe positioning and operating conditions. It was found that the plasma-to-MS-inlet distance, the plasma-to-sample-plate distance, and the angle between the latter are very important. Additional effects on the analytical performance were found for the outer electrode width, the positioning of the electrodes, the inner diameter of the quartz tube, the quartz wall thickness, and the gas flow. All experiments were performed using additional heating of the sample to enhance thermal desorption and maximize the signal ($T = 150\text{ }^{\circ}\text{C}$). After software-assisted optimization, attractive detection limits were achieved (e.g., $1.8 \times 10^{-7}\text{ mol/L}$ for 4-acetamidothiophenol). Moreover, relative standard deviation (RSD) improved from values of up to 30% before optimization to $<15\%$ RSD after the procedure was completed. This chemometrics approach for method optimization is not limited to LTP-MS and considered to be attractive for other plasma-based instrumentation as well.

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1. Introduction

Low-temperature plasma probe mass spectrometry (LTP-MS) is an ambient desorption/ionization (ADI) method that features a dielectric-barrier discharge (DBD) as the plasma source. The discharge is formed in a flowing gas and generates reagent ions such as protonated water clusters, O_2^+ and O_2^- species, N_2^+ , and $\text{NO}_2^-/\text{NO}_3^-$ species [1,2], which are then used for sample desorption/ionization in ambient air. The original set-up, which is frequently used today, was first introduced by Harper et al. [1] in 2008. Since then, LTP-MS was used, sometimes with modifications to original dimensions and operating conditions, for different applications. These include the direct analysis of food, food additives [3,4], agrochemicals [5,6], drugs [7,8], and explosives [9]. Huang et al. [4] as well as Soparawalla et al. [6] used a miniaturized mass spectrometer with LTP ion source to demonstrate in situ analysis capabilities and portability. Further applications include the monitoring of chemical reactions [10], imaging [11], and detection of indoor volatile organic compounds [12].

Until now, only few studies have concentrated on the fundamental desorption and ionization processes in LTP-MS. Shelley et al. [13] studied ionization matrix effects in LTP in comparison to flowing atmospheric pressure afterglow (FAPA) and direct analysis in real time (DART). Chan et al. [14,15] used spectroscopic plasma diagnostics to elucidate the reaction mechanisms that are responsible for afterglow formation and reagent-ion formation in LTP-MS. For the first time, a mechanism was suggested where metastable helium atoms (He^m) and helium dimer ions (He_2^+) play an important role for the generation of excited nitrogen species and, in turn, protonated water clusters.

Optimization of dielectric-barrier discharges was reported in the past. Lu et al. [16], for example, optimized the frequency of the applied voltage and added nitrogen to the helium flow for efficient plasma reactivity. UV emission power density and the presence of reactive species, namely excited NO, N_2 , were used as indicators for plasma reactivity. Meiners et al. [17] investigated the influence of different dielectric materials and corresponding geometries on the DBD efficiency in air by measuring the plasma power, electron density and emission of excited N_2 species. In a recent study, Abdul-Majeed et al. [18] combined DBD in argon with optical emission spectroscopy for mercury analysis. Their focus was to optimize reagent addition, argon gas flow, and

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applied power for best sensitivity of a Hg emission line (253.7 nm) by means of experimental design. However, a chemometric optimization of the LTP probe when coupled to an Exactive high-resolution mass spectrometer was not reported.

In this study, a chemometrics approach using multivariate data analysis was applied to LTP-MS for probe and performance optimization using the software MODDE 9.0 (MKS Umetrics AB, Sweden). [19]. It features controlled experiments and statistical analysis for method optimization. An optimization tool allows to screen for relevant parameters and to optimize them simultaneously for best response. In addition, the approach considers interactions between the parameters, which would not be included, for example, in a time-consuming one-factor-at-a-time-optimization or in standard Plackett–Burman experimental designs. Experimental data are evaluated using regression analysis and a model is constructed which helps to explore an experimental area and selects appropriate parameter combinations in order to perform a limited number of experiments. Three approaches with different parameter combinations are chosen for the optimization process due to complexity of the whole LTP-MS system. In the first experiment, the influence of source geometry is explored. Second, the configuration of the electrodes is optimized. Third, quartz barrier dimensions and operating conditions of the LTP source are considered.

In many published LTP-MS studies, additional heating of the sample is required to enhance thermal desorption and maximize the signal. Because of this and as a starting point of the optimization, additional heating was used as well and fixed at the highest attainable value (150 °C). Two model compounds (4-acetaminophenol, 4-acetamidothiophenol) with high volatility were selected as response factors in optimization experiments.

2. Materials and methods

2.1. Reagents

4-Acetamidothiophenol and 4-acetamidophenol were purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany) and used without further purification. All solvents were ordered from Sigma-Aldrich Chemie GmbH and Fluka Chemie GmbH (Buchs, Switzerland).

2.2. LTP probe

Configuration of the LTP probe before optimization is based on a design described previously [1]. An inner stainless steel pin electrode (1 mm diameter) and an outer copper ring electrode (20 mm wide, 10 mm distance to capillary exit) were used to generate a dielectric barrier discharge in a quartz glass tube (6 mm outer diameter, 2 mm inner diameter). A high-voltage alternating current (AC) of 10 kV_{pp} at 31 kHz was applied to the inner pin electrode (power supply model Minimax3, Information Unlimited, Amherst, MA, USA) to generate the plasma. Helium (high purity grade 4.6, Westfalen AG, Muenster, Germany) was used as discharge gas and fed into the capillary by the use of a T-piece (Swagelok Company, Solon, OH, USA).

2.3. LTP-MS analysis

For optimization experiments, a 4-acetamidophenol solution was prepared in acetonitrile (ACN) at a concentration of 1×10^{-4} mol/L. Triplicate analysis was performed with 5 μ L aliquots pipetted on a heated sample well plate ($T = 150$ °C). The temperature was set to the highest value that was attainable when using a heating foil. In previous studies additional heating of the sample was found beneficial for thermal desorption (with 150 °C as the optimal value for the analytes studied). Similarly, experiments with the second model compound were carried out with a 1×10^{-4} mol/L solution of 4-acetamidothiophenol in ACN. A high-resolution mass spectrometer (model Exactive HCD, Thermo Scientific, Bremen, Germany) was used for mass spectrometric detection.

Operating parameters are listed in the supporting information (cf. Table S-1). Ionized species produced transient mass spectrometric signals, which were recorded and further processed with Thermo Excalibur software 2.1 (Thermo Scientific) and Origin Pro 8.0 (OriginLab, Northampton, MA, USA).

2.4. Calibration with LTP-MS

External calibration was performed before DOE optimization with dilutions of 4-acetamidothiophenol at concentrations of 1×10^{-4} , 7.5×10^{-5} , 5×10^{-5} , 3.5×10^{-5} , 1×10^{-5} , 5×10^{-6} , and 1×10^{-6} mol/L, which were analyzed in triplicate. After optimization steps, lower concentrated standards of 5×10^{-5} , 1×10^{-5} , 5×10^{-6} , 1×10^{-6} , 5×10^{-7} , 1×10^{-7} , and 5×10^{-8} mol/L were analyzed in the same way. Limits of detection (LODs) were calculated from calibration curves and their residual standard deviations.

2.5. Optimization of LTP parameters

Parameters of the LTP ion source were optimized in three approaches with the design of experiments (DOE) (Fig. 1).

First, the distance between mass spectrometer inlet and LTP probe ($x = 2$ –10 mm), the distance between mass spectrometer inlet and sample plate ($y = 0$ –5 mm), the distance between the LTP probe and sample plate ($z = 2$ –10 mm), and the angle between the LTP quartz tube and sample plate ($\alpha = 40^\circ$ – 80°) were optimized (cf. Fig. 1A). Second, the relative position of the electrodes to the capillary exit (5–30 mm), the width of the outer ring electrode (5–30 mm), and the diameter of the inner pin electrode (0.5–1.5 mm) were investigated (cf. Fig. 1B). Subsequently, an optimization of the distance between the outer and the inner electrode (–15–30 mm) followed (cf. Fig. 1C). Third, the thickness (1–3 mm) and inner diameter (1–3 mm) of the capillary (cf. Fig. 1D) as well as the operating parameters helium flow rate (200–400 mL/min) and applied voltage (7–10 kV) were optimized. The frequency of the power supply could not be changed and was fixed at 31 kHz.

2.6. Design of experiments

For experimental design and data analysis, the software MODDE 9.0 (MKS Umetrics AB, Sweden) was used. First, a screening part with primal experiments was performed to identify important parameters that have an influence on the response. After the identification of those parameters, an optimization process was conducted with the goal to achieve the highest response. This experimental optimization process covered geometry parameters, electrode configuration, capillary dimensions, and operating conditions of LTP-MS. A schematic diagram of the experiments is depicted in Fig. 2.

The overall experimental process comprises several sub-steps. At the beginning, factors, i.e. different parameters that are subject to change, and a response that is monitored are defined in an experimental region. In this project, the peak area of the model compound 4-acetamidophenol was chosen as the response value for screening and optimization (due to its high relative ionization efficiency in LTP). An experimental matrix is constructed with selected factors at different combinations of minimum, maximum, and center values for each factor. Then, resulting factor combinations are analyzed in a random order in LTP-MS. Lastly, obtained results for the peak area of the model compound are used to construct and evaluate an appropriate model with multiple linear regressions.

For the screening part, an interaction model with a full factorial parameter design was generated in this study. Typically, a polynomial function with linear or interaction terms is applied in screening experiments. In optimization experiments, a central composite face-centered design was chosen for the experimental region and the data were fitted with a quadratic model. In this model, the polynomial function includes

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