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Ultrasonic nebulization extraction/low pressure photoionization mass spectrometry for direct analysis of chemicals in matrices

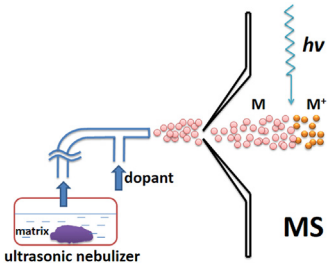
Chengyuan Liu [a], Yanan Zhu [a], Zhongyue Zhou [a, b], Jiuzhong Yang [a, b], Fei Qi [a, b], Yang Pan [a, *]

[a] National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, People's Republic of China
[b] Power Machinery and Engineering of Ministry of Education, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

HIGHLIGHTS

- A strategy combining ultrasonic nebulization extraction and low-pressure photoionization (UNE-LPPI) was developed.
- Good linearities for phenanthrene and pyrene in soil powder in the range of 10–400 ng mg^{-1} were obtained.
- The components in tablets and plant tissues can be extracted and ionized effectively by UNE-LPPI.
- UNE-LPPI generally forms the molecular ions, providing a complementary ionization method to APPI.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel ultrasonic nebulization extraction/low-pressure photoionization (UNE-LPPI) system has been designed and employed for the rapid mass spectrometric analysis of chemicals in matrices. An ultrasonic nebulizer was used to extract the chemicals in solid sample and nebulize the solvent in the nebulization cell. Aerosols formed by ultrasonic were evaporated by passing through a transferring tube, and desolvated chemicals were ionized by the emitted light (10.6 eV) from a Krypton discharge lamp at low pressure (~68 Pa). First, a series of semi/non-volatile compounds with different polarities, such as polycyclic aromatic hydrocarbons (PAHs), amino acids, dipeptides, drugs, nucleic acids, alkaloids, and steroids were used to test the system. Then, the quantification capability of UNE-LPPI was checked with: 1) pure chemicals, such as 9,10-phenanthrenequinone and 1,4-naphthoquinone dissolved in solvent; 2) soil powder spiked with different amounts of phenanthrene and pyrene. For pure chemicals, the correlation coefficient (R^2) for the standard curve of 9,10-phenanthrenequinone in the range of 3 ng–20 μg mL^{-1} was 0.9922, and the measured limits of detection (LOD) was 1 ng ml^{-1}. In the case of soil powder, linear relationships for phenanthrene and pyrene from 10 to 400 ng mg^{-1} were obtained with correlation coefficients of 0.9889 and 0.9893, respectively. At last, the feasibility of UNE-LPPI for the detection of chemicals in real matrices such as tablets and biological tissues (tea, *Citrus aurantium* peel and sage (*Salvia officinalis*) leaf) were successfully demonstrated.

* Corresponding author.
E-mail address: panyang@ustc.edu.cn (Y. Pan).

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1. Introduction

Direct mass spectrometric analysis of samples has gained great interests in recent years, as it requires little or no pretreatment or separation, and allows rapid chemical analysis in real time [1–3]. Two-step ionization technique is one of such analytical strategies, where the overall process in the formation of ions includes two main separate steps: 1) generating and sampling neutral particles/droplets from condensed samples; 2) ionizing the neutral species. In the first step, sampling is usually fulfilled by heated carrier gas, laser desorption, laser-induced shockwaves, and thermal desorption, etc. In the second step, a variety of post-ionization methods are carried out, especially ambient ionization sources using charged particles or photons. Up to now, more than 20 types of two-step ionization methods have been reported [2,3].

Ultrasound/ultrasonic, the sound waves with frequencies higher than the upper audible limit of human hearing, has been widely used in analytical chemistry. For instance, ultrasound from piezoelectric device can assist sample extraction from soil, food, medicals, and plants [4–8]. Moreover, ultrasonic nebulization (UN) can be applied for sampling in inductively coupled plasma mass spectrometry (ICP–MS) [9–11], electrospray ionization mass spectrometry (ESI–MS) [12], and extractive electrospray ionization mass spectrometry (EESI–MS) [13], by virtue of its ability to produce small and uniform droplets with diameter smaller than 5 μm from liquid samples [12]. In addition to conventional ultrasonic-based methods, a new technique called ultrasonic nebulization extraction (UNE) has also been developed in recent years [14–16]. Chemicals in solid sample can be extracted rapidly, and aerosols can be generated at the same time due to the so-called “ultrasonic fountain”.

Currently, there is increasing interests of using photoionization in mass spectrometry, owing to its favorable characteristics of soft ionization, no polarity discrimination, and reduced ion suppression compared with electrospray ionization [17–20]. Low pressure photoionization (LPPI) occurs in sub-atmospheric pressure (generally less than 1 Torr). Compared to atmospheric pressure photoionization (APPI), LPPI can minimize ion–molecule reactions which can lead to competition for charge and ion suppression effects [21,22]. LPPI is generally used for the ionization of gaseous compounds and volatile liquid [21–32]. Over the years, several attempts have been made to introduce semi-volatile compounds into vacuum, using heated capillary or membranes inlet [25,28,30,33].

Here we report a novel technique which combines UNE and LPPI (UNE–LPPI) for the rapid analysis of various chemicals in complex matrices. Some semi/non-volatile chemicals with different polarities in real samples (tablets and biological tissues) were successfully analyzed by UNE–LPPI, and the direct quantification performance for components in soil powder was well established. We show that UNE–LPPI exhibits several advantages: 1) it needs no tedious pretreatment and chromatographic separation. Components in various matrices could be efficiently extracted and vaporized for post-LPPI; 2) it's a direct method for fast semi-quantification analysis of chemicals in complex matrices. Compared with UNE–LPPI, other existing APPI-related analytical techniques such as desorption atmospheric pressure photoionization (DAPPI) [34] and infrared laser ablation atmospheric pressure photoionization mass spectrometry (LAAPPI–MS) [35] are not applicable for quantitative analysis due to their “surface analysis” characteristic; 3) The spectra obtained by UNE–LPPI generally show molecular ions rather than protonated molecular ions due to less ion–molecule reactions under relatively low pressure condition, providing a complementary ionization method to APPI.

2. Experimental

2.1. Chemicals and sample preparation

9,10-Diphenylanthracene, theophylline, thymine, carbazole, danthron, phenanthrene, verapamil hydrochloride, quinine, acetaminophen, norgestrel, estradiol, 1,4-naphthoquinone, pyrene, 9,10-phenanthrenequinone, 9,10-dicyanoanthracene, 5-nitro-2-furoic acid, and uracil were purchased from Sigma–Aldrich (St. Louis, MO). Cyclo(gly–gly) and cyclo(gly–val) were obtained from TCI (Japan). All chemical standards are of >99% purity and used without further purification. HPLC grade methanol and acetonitrile were obtained from Merck (Darmstadt, Germany). Toluene (>99%) and acetone (>99%) used as dopants were bought from Sinopharm chemical reagent company (Shanghai, China). Nitrogen (purity 99.9%) used as carrier gas was purchased from Nanjing Special Gas Factory Co, Ltd. (China).

For quantitative analysis in positive ion mode, 30 μg per milliliter (μg mL^{-1} or ppm) of 9,10-phenanthrenequinone stock solution was prepared in methanol/water (v:v = 1:3), and the following concentrations were prepared: 20, 5, 3, 0.3, 0.03 and 0.003 μg mL^{-1}. In the case of negative ion mode, 40 ppm 1,4-naphthoquinone stock solution was prepared in methanol/water (v:v = 1:4), and the following concentrations were prepared: 20, 10, 3, 0.3, 0.03 and 0.003 μg mL^{-1}. All these solutions were prepared from respective stock solution using corresponding aqueous solvents.

The soil sample was collected from the campus of University of Science and Technology of China. Fine powder of soil was obtained by pulverizing the soil sample with a grinding rod and sieving it through an 80-mesh sieve. Contaminated soil was made by mixing 40 mg freeze dried fine powder of soil with a series of stock solution of phenanthrene and pyrene dissolved in methanol. After the solvent volatilized completely, the soil powder was put into 4 mL methanol/water (v:v = 1:1) solvent in the nebulization cell and was treated by UNE for 10 min after closing the glass valve (see Fig. 1). The soil powder containing 10, 30, 50, 100, 250 and 400 ng mg^{-1} analytes were analyzed in sequence.

The Saridon tablets (250 mg of acetaminophen, 150 mg of propyphenazone, and 50 mg of caffeine for each tablet) were purchased from Shandong Xinhua Pharmaceutical Company Limited (Shandong, China). The tablet was crushed, and 0.05 mg powder was directly put into 4 mL deionized water in the nebulization cell. Owing to the good solubility of the tablet in water, UNE was carried out for only 20 s before nebulization. Tea, *Citrus aurantium* peel, and sage (*Salvia officinalis*) leaf were obtained from a local supermarket. In the experiments, a piece of tea (10.2 mg), *C. aurantium* peel (9.7 mg), and sage leaf (10.8 mg) were put into the nebulization cell separately, treated by UNE for 10 min with 4 mL methanol/water (v:v = 1:1) solvent, and then mass-analyzed after nebulization.

2.2. Ultrasonic nebulization system

The ultrasonic nebulization system was built according to the setup described by Montaser [36]. This system comprises of an ultrasonic nebulizer (Model 402AI, Yuwell Medical Equipment & Supply Corp., Suzhou, China), a glass nebulization cell, and a transfer tube (Fig. 1). The working frequency for the transducer of the ultrasonic nebulizer is 1.7 MHz ± 10%. The glass nebulization cell consists of a cylindrical upper part (I.D. 16 mm, height 35 mm) and lower part (I.D. 8 mm, height 10 mm). The bottom of the cell was covered by a thin polyethylene membrane transparent to ultrasonic waves, which was fixed by an O-ring. A glass valve was set at the outlet of the cell, and would be closed when UNE treatment was carried out.

When the ultrasonic nebulizer was switched on, sample solution in the nebulization cell would be transformed into aerosol by ultrasonic waves propagated from the transducer. The aerosol then