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Liquid extraction surface analysis in-line coupled with capillary electrophoresis for direct analysis of a solid surface sample

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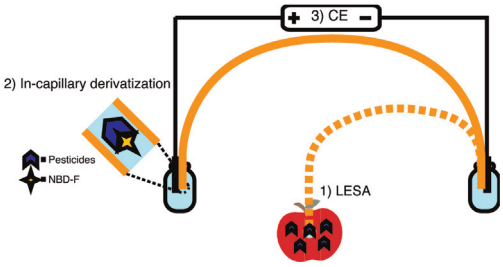
HIGHLIGHTS

- LESA is a direct surface sampling technique without additional sample pretreatment.
- LESA was coupled with CE to expand sample types applicable to CE to solid surfaces.
- LESA–CE was used for non-infiltrative organophosphorus pesticides on apples.

GRAPHICAL ABSTRACT



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ABSTRACT

A surface-sampling technique of liquid extraction surface analysis (LESA) was in-line coupled with capillary electrophoresis (CE) to expand the specimen types for CE to solid surfaces. The new direct surface analysis method of LESA–CE was applied to the determination of organophosphorus pesticides, including glufosinate-ammonium, aminomethylphosphonic acid, and glyphosate on the external surface of a fruit such as apple. Without any sample pretreatment, the analytes sprayed on the surface of a half apple were directly extracted into a liquid microjunction formed by dispensing the extractant from the inlet tip of a separation capillary. After extraction, the analytes were derivatized in-capillary with a fluorophore 4-fluoro-7-nitro-2,1,3-benzoxadiazole and analyzed with CE-laser induced fluorescence (LIF). The limits of detection for glufosinate-ammonium, aminomethylphosphonic acid, and glyphosate were 2.5, 1, and 10 ppb, respectively, which are at least 20 times lower than the tolerance limits established by the U.S. Environmental Protection Agency. Thus, we demonstrated that LESA–CE is a quite sensitive and convenient method to determine analytes on a solid surface avoiding the dilution from sample pretreatment procedures including homogenization of a bulk sample.

1. Introduction

Capillary electrophoresis (CE) is well suited for the analysis of analytes in aqueous solutions. For water-insoluble analytes, nonaqueous CE [1–4] and micellar electrokinetic chromatography (MEKC) [5,6] can be used. In addition, headspace extraction has recently been in-line coupled to CE [7,8] for the analysis of gaseous analytes evaporated from a liquid sample. However, it is not yet easy to analyze a solid sample with CE, since labor-intensive sample pretreatment processes are required. For example, a solid sample should be grounded, homogenized, centrifuged, extracted

Abbreviation: LESA, liquid extraction surface analysis; EPA, environmental protection agency; OPPs, organophosphorus pesticides; AMPA, aminomethylphosphonic acid; ACN, acetonitrile; NBD-F, 4-fluoro-7-nitro-2,1,3-benzoxadiazole; LIF, laser induced fluorescence; MEKC, micellar electrokinetic chromatography; SPE, solid phase extraction.

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into an organic solvent, and then reconstituted into an aqueous solution suitable for CE.

Here, we propose to perform liquid extraction surface analysis (LESA) using a homemade CE setup to analyze a solid surface sample directly. LESA is a surface sampling technique that extracts chemicals on the surfaces of various solid samples without sample pretreatment. Since the development of a commercial LESA device using a chip-based robotic nanoelectrospray platform [9], LESA-electrospray ionization/mass spectrometry (ESI/MS) has been utilized in the analysis of food surfaces as well as biological tissues [10–14]. For better speciation and quantification, HPLC has been hyphenated to LESA–MS [15]. LESA can be in-line coupled with CE simply by using a separation capillary of a homemade CE setup instead of a pipet tip on the robotic arm of a commercial LESA device. Moreover, the capillary has an advantage over the pipet tip in reducing the sampling surface area.

As a representative application of LESA–CE to a solid surface sample, non-infiltrative pesticides on apple skin were analyzed. When non-infiltrative pesticides are applied to fruits such as apples, they remain on the fruit skin without being translocated to the fruit pulp. Glufosinate-ammonium and glyphosate are widely used non-infiltrative organophosphorus pesticides (OPPs) for the last thirty years worldwide. The U.S. Environmental Protection Agency (EPA) limits the allowable amount of glufosinate-ammonium and glyphosate in an apple to 50 [16] and 200 ppb [17], respectively. These two OPPs and aminomethylphosphonic acid (AMPA) which is a metabolite of glyphosate on the apple skin were directly extracted into the separation capillary and then the extracts were derivatized by a fluorophore in-capillary and detected by laser induced fluorescence (LIF) [18]. One simple way of sampling the OPPs would be rinsing the apple with an extraction solvent, but its off-line nature limits future development. Here we present the developed in-line LESA–CE/LIF as a simple and sensitive method for the analytes on the apple skin without a homogenizing step of a bulk apple which is required for conventional analysis methods. One important achievement of LESA–CE was the expansion of specimen types for CE to a solid surface.

2. Experimental

2.1. Reagents

Glufosinate-ammonium, AMPA, glyphosate, ethanol, sodium dodecyl sulfate (SDS), sodium tetraborate, and HCl were purchased from Sigma (St. Louis, MO, USA). Acetonitrile (ACN) was from Burdick and Jackson (Radnor, PA, USA). 4-Fluoro-7-nitro-2,1,3-benzoxadiazole (NBD-F) was from TCI (Tokyo, Japan). NaOH was from Dae Jung Chemicals (Siheung, Korea). For each analyte, 40 ppm standard stock solution was prepared in ethanol and stored at 4 °C. Pesticide mixtures were prepared by diluting the stock solutions with ethanol. Derivatization reagents of NBD-F were prepared in ACN. 100 mM sodium tetraborate and 100 mM SDS were used as stock buffer solutions. A run buffer of 10 mM sodium tetraborate containing 10 mM SDS and 10 vol% ACN was prepared by mixing appropriate volumes of the stock solutions and ACN, and then by titrating to pH 9.90 with 1.0 M NaOH. The run buffer solution was filtered through a 0.45 μm syringe filter (Sigma). An extraction solvent of 10 mM sodium tetraborate was prepared by diluting the 100 mM sodium tetraborate with deionized water. Before use, the pH of the extraction solvent was adjusted to 8.75 with 1.0 M HCl for compatibility with the in-capillary derivatization of analytes dissolved in the solvent [18]. Deionized water was prepared with a Nanopure II purification system (Barnstead, Dubuque, IA, USA).

2.2. Apparatus

Experiments were performed with a homemade CE set up [19,20] comprised of a high voltage power supply (CZE1000R; Spellman, Hauppauge, NY, USA) and an LIF detection system. Analytes were excited at 488 nm with a 10 mW argon-ion laser (Omnichrome, Chino, CA, USA). Fluorescent light was collected at a right angle through a 10× microscope objective (Edmund Industrial Optics, Barrington, NJ, USA), passed through a 488 nm notch filter (NT67-108; Edmund Industrial Optics) and a 520 nm band pass filter (Melles Griot, Irvine, CA, USA), and detected with an integrated photomultiplier tube system (PMT; HC 120-01, Hamamatsu, Bridgewater, NJ, USA). The power supply and PMT were interfaced to a computer using an MIO-16-XE DAQ board (National Instruments, Austin, TX, USA). The LabView 7.0.1 program (National Instruments) was used for data acquisition and analysis. A fused silica capillary of an internal diameter of 75 μm and 60 cm in length (50 cm to the detector) from Polymicro Technologies (Phoenix, AZ, USA) was used. Before a run, the capillary was rinsed with 0.1 M NaOH, water, and then a run buffer each for at least 10 min with a syringe.

2.3. Sample preparation

Apples grown with a conventional farming system were purchased from a local store. Pesticide-free apples were obtained from a local shop for organic agricultural products without pesticides. Both unwashed and washed apples were analyzed. Apple halves were weighted individually. A mixture of three pesticides in 5 mL of ethanol was sprayed against the surface of an apple half and air-dried for 15 min. A random slice of apple skin was fixed to a Teflon plate of 50 mm diameter which was placed on a micrometer-controlled vertical translation stage with an adhesive tape.

2.4. LESA

Fig. 1 shows the scheme for LESA–CE/LIF using a homemade CE set up. The inlet end of a capillary filled with a run buffer was immersed in an extraction solvent vial and the outlet end in a destination vial containing the run buffer. The extraction solvent was injected by gravity, raising the extraction solvent vial by 7.5 cm above the destination vial for 315 s. The volume of injection estimated with the Poiseuille equation was 350 nL. The inlet of the capillary containing the extraction solvent was transferred to a capillary holder aligned to a target spot on the sample surface. The distance between the sample surface and the capillary was adjusted to 0.5 mm with the micrometer on the vertical translation

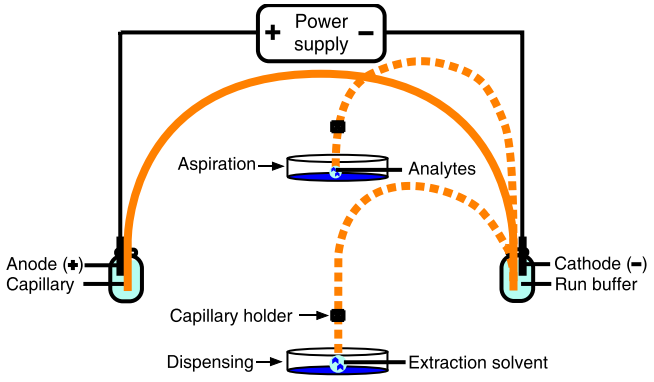

Fig. 1. Scheme for LESA–CE. Dashed lines represent the extraction cycle of dispensing and aspiration steps. LESA: extraction solvent of 10 mM sodium tetraborate buffer of pH 8.75; injection of 350 nL extraction solvent; dispensing of 330 nL; aspiration of 340 nL; repeat of dispensing/aspiration cycles.