



Fabrication of polymer microsphere particle standards containing trace explosives using an oil/water emulsion solvent extraction piezoelectric printing process

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ABSTRACT

We present a methodology for fabricating polymer microspheres using inkjet printing of a biodegradable polymer containing either high explosives or high explosive simulant. Poly(DL-lactide/glycolide) 85:15 (PLGA) microsphere production is based on an oil/water emulsion solvent extraction process. The inkjet printing process allows for precise control of the microsphere diameter and the chemical composition. The microspheres can be used as calibrants or verification standards for explosives trace detection instruments. Gas chromatography/mass spectrometry analysis demonstrated that the composition of the microspheres was consistent with predicted concentrations based on the amount of analyte incorporated into the polymer solution and the inkjet operating parameters. We have demonstrated that the microspheres can be fabricated with a mass fraction of 70% of an analyte compound.

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1. Introduction

Current national priorities in homeland security have led to the widespread deployment of explosives trace detection systems throughout the United States. In a typical implementation of such a detection system, an ion mobility spectrometer (IMS) is used to identify micrometer sized explosive particles on people and their belongings [1]. Samples are typically collected by physical swiping of a suspect surface with a hand wand or small piece of cloth (called a trap). After sampling, the trap is inserted into the IMS instrument where the particles of interest on the trap are thermally vaporized and analyzed. This method is effective for screening objects like a briefcase or a laptop computer, but it is not optimal for screening people or their clothing and is also slow and limited in sample throughput. To address these issues, another approach currently being deployed is the walk-through portal detection system. In this system, a person enters a chamber similar to a metal detector, and is interrogated with multiple air jets that dislodge particles from the person and/or their clothing. An air shower stream carries the

dislodged particles to a collector, which in turn admits this material to a detector (generally an IMS) [2].

In order to characterize and validate the performance of these systems, well-characterized test materials are required. Explosives residues are typically found as small particulates with size distributions ranging from sub-micrometer to several 100 μm in diameter [3]. In order to make realistic standards to serve as effective test materials for trace detection instruments, particulate test standards should have several desirable properties: appropriate size and aerodynamic behavior; known chemical composition; known surface adhesive properties; a distinguishable IMS detector response. Particle size is particularly important because particle release from surfaces by air jets and aerodynamic transport are particle diameter-dependant [4,5]. Some additional considerations include useful lifetime of the standard in the local ambient environment, contamination control at the test site that results from standard testing, and the safety (non-toxicity) of the materials in the event of accidental human exposure.

One novel and promising method for generation of these trace particle standards is the production of uniform polymer microspheres containing the explosive compound (or simulant) of interest by inkjet printing. The use of polymer microspheres is advantageous because they are monodisperse, the sphere diameters can be tailored for specific tests, and the microspheres may contain high levels of test compound.

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In this paper, we present a methodology for fabricating uniform polymer microspheres by using inkjet printing of a biodegradable polymer containing the compound of interest. This approach was originally developed for drug delivery applications using inkjet printing of a polymer solution containing poly(DL-lactide/glycolide) (PLGA) and paclitaxol [6,7]. Here we use a similar approach for preparing PLGA spheres containing high explosives or a simulant. Uniform microspheres have been made by piezoelectric fluid flow disruption over 35 years ago [8]. Production is based on an oil/water emulsion solvent extraction process that produces polymer microspheres [9]. Others have presented methods for making drug delivery microspheres, using a co-flow polymer/water system [10]. One reason to incorporate drugs into polymer microspheres (PLGA and polylactide, PLA) is that the polymer slowly degrades or dissolves by hydrolysis in the body to provide a slow release drug delivery platform [11–13].

We have demonstrated the incorporation of two high explosives, 1,3,5,7-tetranitroperhydro-1,3,5,7-tetrazocine (HMX) and 2,4,6 trinitrotoluene (TNT), and one simulant, 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT, CAS number 128-37-0), into PLGA microspheres. We are using the simulant BHT because it is a food additive, considered safe for human consumption and gives a good IMS response in the negative ion mode where explosives are detected. A safe simulant is desirable to prevent contamination of the security check points and to prevent potential health risk from accidental human exposure. The above analytes contained in the PLGA microspheres have been correctly identified for the respective compound by a table-top IMS.

2. Experimental

2.1. Materials

The polymer solution was made by dissolving either 0.3 g or 0.6 g of poly(DL-lactide/glycolide) 85:15 (PLGA, Polysciences Inc., Warrington, PA)¹ into 10 mL dichloroethane (DCE) (Sigma–Aldrich, St. Louis, MO). Low and high concentration solutions of BHT (Sigma–Aldrich, St. Louis, MO) were made by dissolving either 0.07 g or 5 g BHT into 10 mL DCE. HMX was first dissolved in acetone (J.T. Baker) and then the acetone solution was added to the DCE to make a 2.73×10^{-4} g/mL HMX solution in DCE–acetone. For a low concentration solution of TNT, 0.025 g of TNT was dissolved in 10 mL DCE. A final solution of polymer and analyte was made by mixing a known volume of analyte solution into the PLGA–DCE solution. Approximately 200 μ L of rhodamine B (Eastman Kodak Co., Rochester, NY) was also added to the final polymer–analyte solution as a fluorescent dye marker.

2.2. Microsphere fabrication

Microspheres were prepared by an oil/water emulsion process using a piezoelectric inkjet printer (sphere jet) to deliver precisely controlled microdrops of the polymer solution. The sphere jet is a drop-on-demand piezoelectric inkjet printer (MicroFab Technologies Inc., Plano, TX) with a 50- μ m orifice diameter jet, operated in a pressure assisted mode to prepare PLGA microspheres containing analytes of varying concentrations. A magnified image of the inkjet printer producing a stream of monodisperse droplets

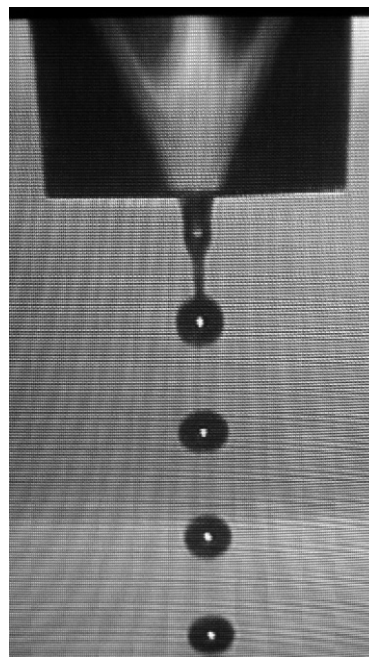


Fig. 1. Inkjet printer operating in a continuous mode producing uniform droplets.

is shown in Fig. 1. The waveform and frequency were controlled using the instrument's software (JetLab2) and pressure regulation was maintained using a pressure regulator (Druck DPI 530, Druck Inc., Fairfield, CT). Operating parameters were varied to allow for controlled production of microspheres, but typical parameters include a frequency of 10 kHz, rise time 1 μ s, dwell time 30 ms, and dwell voltage of 30 V. A video camera with strobe illumination (Advanced Illuminations, Signatech, Rochester, VT) was used to monitor the shape and relative size of the jetted droplets. The pressure-controller driven stream of the polymer solution flowed through the inkjet tip forming microspheres as a result of uniformly disrupting (or chopping) the stream by the capillary piezoelectric tip. The jetting process takes place under water where the microspheres are captured and cured in a 500-mL beaker (containing filtered, deionized water) continuously stirred for several minutes to several hours. Any DCE that remained after sphere formation was allowed to evaporate. Using vacuum filtration, a small volume (approximately 25 mL) of the microsphere suspension was filtered through a 25- μ m diameter polycarbonate filter with a 1.0- μ m pore size and the remaining solution was filtered through a 47- μ m polycarbonate filter with a 1.0- μ m pore size. Optical microscopy was used to image the microspheres collected on the 25 mm filter and the microspheres collected on the 47 mm filter were dried and carefully removed from the filter using a spatula and stored in 5 mL closed vials.

Three different jetting experimental configurations were examined as a way to reduce the variability of the microsphere size distribution. The first configuration is considered a "pure-shear" mode because the piezoelectric nozzle is directly submerged in the 500 mL beaker filled with rotationally stirred water. The droplets are immediately sheared from the nozzle by the rotating body of water. The limitation of this method is that it makes it difficult to focus the camera on the nozzle and droplets because of the curved walls of the beaker. Configurations 2 and 3 were designed to overcome this visualization issue by using a co-flow tube with flat glass walls (see Fig. 2a and b). Results of these three arrangements will be discussed later.

¹ Commercial equipment, instruments, and materials, or software are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement of these items by the NIST, nor does it imply that they are the best available for the purpose.

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