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Review

Recent advances and future prospects of mesofluidic Lab-on-a-Valve platforms in analytical sciences – A critical review

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ABSTRACT

Miniaturization and automation in analytical sciences have evolved tremendously over the past decade within the framework of green analytical chemistry. This manuscript outlines the unrivalled merits of advanced flow methodology capitalizing on mesofluidic platforms for the simplification and acceleration of the overall analytical process. Introduced back in 2000, the Lab-on-a-Valve concept (LOV), allied to sequential injection analysis, has emerged as an appealing downscaled analytical tool for pressure-driven sampling at the low μL level. Not the least, for advanced on-chip sample processing involving renewable micro-solid phase extraction (so-called bead injection analysis), non-chromatographic speciation or chemical vapor generation using programmable flow, for optical and electrochemical detection on-chip including optosensing approaches, or as a front end to modern detection equipment or column separation systems.

It is the intention of this work to offer the authors' own critical vision as to where the field of LOV is being directed on the basis of the survey of the current state-of-the art of mesofluidic systems and identify what are the major cutting-edge challenges to be yet undertaken and what opportunities are offered by LOV for real-world applications that might not be at present tackled by lab-on-a-chip microfluidic approaches.

Contents

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Manuel Miró received his M.Sc. (1998) and Ph.D. (2002) in Chemistry at the University of the Balearic Islands, Spain. He has conducted post-doctoral research in several universities including the Technical University of Berlin, Technical University of Denmark and University of Natural Resources and Applied Life Sciences in Austria. He is currently Associate Professor in Analytical Chemistry at the University of the Balearic Islands and member of the IUPAC Chemistry and Environment Division. In 2007 he was appointed Review Editor of Analytica Chimica Acta. His publication record shows over 110 refereed articles including 7 book chapters, with an H-index of 26 and over 1600 citations. His research interests are focused on the development of on-line sample processing strategies for isolation and/or preconcentration of trace levels of environmental pollutants exploiting the various generations of flow injection, including Lab-on-a-Valve mesofluidic platforms, in hyphenation with modern analytical instrumentation.

Elo Harald Hansen retired at the end of 2006 from the Technical University of Denmark (DTU), where he was Professor in Analytical Chemistry at the Department of Chemistry. He graduated with a M.Sc. in 1964 at DTU and obtained his Ph.D. from the same university in 1967. In 1986 he was conferred with the Doctor of Science degree. From 1967 to 1969 he was Postdoctorate Fellow of the National Research Council of Canada in Ottawa. He is together with Professor Jaromir Ruzicka one of the inventors of Flow Injection Analysis, and has published more than 200 scientific papers in international periodicals. He has given lectures all over the world, and has received numerous national and international rewards for his research accomplishments.

1. Introduction

As an extension of their invention of flow injection analysis (FIA) [1] and its rapid acceptance, use and developments, Ruzicka and Hansen in 1984 published a paper [2] where a novel approach for constructing miniaturized flow systems for analyses was described. It was *partly* based on the fact that the eventual readout in any flow system dedicated to wet chemical assays is the result of two kinetic processes that occur simultaneously, namely the physical process of zone dispersion and the superimposed chemical processes resulting from reaction between analyte and reagent species. While we in regard to miniaturisation can do preciously little about the chemistries, we can indeed manipulate the physical parameters, that is, the dimensions of the FIA manifolds. And *partly* inspired by the concepts of integrated electronic circuitry, and by designs of gas chromatographs on silicon chips as originated at Stanford University [3], which fostered the idea of miniaturization being based on integration of all components of a flow-through manifold into one unit, approximately of the size of a credit card, afforded the so-called μFIA platforms. This would imply that instead of the individual manifold components (injection unit, mixing coils, separation (dialysis or gas diffusion) units and flow-through detectors) being joined by means of flexible tubing and nuts, the whole system of channels ought to be fabricated into a planar surface of a plate, the plate being sufficiently thick to be mechanically stable and to accommodate optical flow cells, electrodes of electrochemical sensors, packed reactors, separation microcolumns, as well as inlets and outlets by means of which the integrated conduits could be connected with external sources of liquids. The idea was to be realized in practice by imprinting or engraving the channels in the planar surface, which then should be sealed by another (thinner) plate, so that the cross-section of the channels was either semicircular or square. The resulting conduits should even be able to be stacked on top of each other to form a multilayered structure. A specifically attractive feature of this concept would be that one or several detectors might be placed in the flow path exactly where desired, whereas in flow-injection manifolds a compromise between the ideal and what was possible in practice was dictated by the physical size and geometry of the available flow-through detector.

As it turned out the realization of and construction of the integrated μFIA conduits became in practice, however, a much more complex task than might appear from the straightforward idea outlined above. Two groups of problems, conceptual and technological, were revealed as the practical work progressed, and it was actually the interplay of these two groups of problems that was most difficult to solve, because material properties often impose constraints on intended designs. In order to appreciate and understand the solutions to these problems, and set them into context, it is of interest to look at the approaches taken by Ruzicka and Hansen.

When downscaling, it is necessary to address the concepts of similarity. The traditional FIA systems were built around a flow channel of certain dimensions and geometrical form (usually coiled tubing) and it would therefore seem to be an easy matter to miniaturize it by simply scaling down existing manifolds. The difficulty was that such an approach will not yield channels which would behave exactly like macrochannels, because a simple reduction of all dimensions does not produce channels which are physically similar. This may be better understood by briefly reviewing the concept and principles of similarity as applied to fluid mechanics [4]. The use of this concept for scaling and modelling of the behaviour of fluids is based on three types of similarities. The simplest, geometric similarity, is similarity of shape, and operates with a scaling factor which is the ratio of any length in one system to the corresponding length in the other system. Yet, when the channel for FIA were to be miniaturized, perfect geometrical similarity will be impossible to obtain, because the roughness of the walls and other imperfections of the channels cannot be reduced proportionately when the overall dimensions are scaled down. Furthermore, an excessive reduction of the cross-sectional area of the channels is undesirable, because solid particles present in some biological, environmental and industrial sample materials could block a very narrow channel. Finally, since the idea was to imprint or to engrave a channel into a planar surface, rather than to wind a miniaturized coil, the concept of geometric similarity could not be applied.

Kinematic similarity is similarity of motion and implies geometric similarity together with similar time intervals. Its scaling factors are velocities and accelerations. This would be a useful tool, if FIA systems of geometric similarity were available, because kinematic similarity would allow pumping rates to be adjusted. Dynamic similarity is a similarity of forces, which could also comprise a scaling factor; this type of similarity includes geometric and kinematic similarities, thus being a valuable tool for comparison of scaled models. Outside the field of fluid mechanics, is the chemical similarity where the fixed ratios of reactants at corresponding points in the flowing streams serve as a scaling factor. Thus, in order for two systems to behave similarly, certain ratios of like magnitudes must be fixed.

Whatever quantities are chosen, the ratio of their magnitudes (i.e., the scaling factor) is dimensionless. Several scaling factors may be needed to describe a complex system like FIA, but once