〈FIA Award for Science〉

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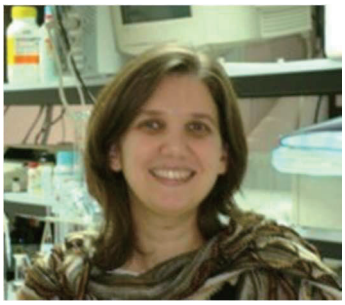

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Development of flow-based systems for automatic sample treatment and for antioxidant assessment

Sample treatment is definitely the bottleneck of analytical procedures. Thus, automation of this step is a relevant feature, with significant impact on analysis throughput. To address this issue, the bead injection (BI) technique implemented in lab-on-valve (LOV) flow systems provides several advantages [1], namely the automatic assemble of solid-phase extraction column and its discard after use, providing a fresh portion of sorbent for each sample. Applications were developed under this scope for evaluation of UV filters in environmental samples [2], riboflavin in food and biological tissues [3], and cotinine in saliva [4].

The main fundamental contribution in this topic was the proposal of a methodology that allowed for the first time the use of non-spherical sorbents in bead injection protocols [5]. Several strategies were tested and the best results were attained with a resuspension step, where a flush of carrier is applied to the beads' reservoir before their aspiration for further solid-phase column assembly. This operation mode expanded BI-LOV application to conventional C18 silica sorbents and molecularly imprinted polymers [3].

Other contributions to this topic addressed the implementation of solid phase extraction in multisyringe flow injection systems (MSFIA) [6-9], among other applications developed using this technique [10-15]. Using automatic solid-phase extraction, screening methods were developed for determination of total phenolics [16] or nitrophenols [17]. The method for evaluation of total phenolics was upgraded by online coupling to HPLC for individual quantification of ten priority phenolic pollutants [18, 19]. Collaboration with other research groups, namely from University of Balearic Islands in Spain, provided flow systems for sample treatment before liquid chromatographic analysis [20, 21] and for bioaccessibility assessment [22-24].

Concerning the evaluation of antioxidant capacity, the features offered by flow injection analysis and derived techniques were exploited to decrease analysis time and to provide measurements not attainable by conventional batch analysis. For instance, analytical methods should foster reaction conditions as close as possible to *in vivo* conditions regarding temperature and pH. The determination of scavenging capacity against hypochlorous acid using chemiluminescence detection is generally performed at alkaline pH. Using a multichannel multisyringe flow injection system, the analysis was performed after 3 s of reaction with a sudden shift of pH just before detection [25]. IC50 values were different from those obtained in batch methods performed under alkaline pH, providing better correlation to the biological action of target drugs.

For implementation of end-point measurements in antioxidant assessment, different strategies were devised. For the DPPH assay using the coloured radical 2,2-diphenyl-1-picrylhydrazyl, a mathematical model was applied to the bleaching profile obtained in the first 4 min of reaction after flow stop in order to estimate the total amount of antioxidant present in the sample [26, 27]. A different approach, designated as "kinetic matching", was first proposed for the evaluation of copper(II) reducing capacity (CUPRAC assay) [28]. Based on the flow injection principle that quantification can be performed before reaction end-point is reached as long as kinetic control is maintained through reproducible transport of solutions inside the fluid conduits, accurate quantification is attained as long as a "kinetic matching" standard is available. The kinetic matching standard must have a kinetic reaction profile similar to that found in the sample and antioxidant capacity is expressed in terms of kinetic matching standard or Trolox amount [29-31]. This concept was recently extended to miniaturized LOV analysis, fostering the application of 1 μL of sample [32].

Flow systems were also developed for evaluation of total antioxidant capacity [33-35], for determination of flavonoids as bioactive compounds [36], and for assessment of scavenging capacity against biologically relevant species, namely peroxyl radicals [37], nitric oxide [38] and hydrogen peroxide [39, 40]. Review articles were published upon this topic [41-43], including a critical overview about MSFIA systems [43].

The contribution described above expanded the application of flow injection techniques to several types of samples (biological, food and environmental), addressing current analytical challenges. In fact, in 2015, the Portuguese National prize of innovation and technology transfer "*INOVPORTUGAL*" was attributed to WINOVE project, where a business model using a LOV analyser for field evaluation of oenological parameters was proposed.

References

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