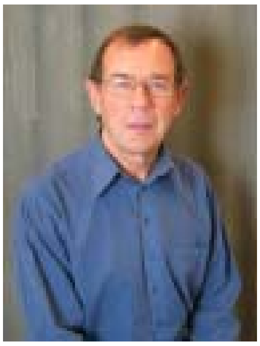

Progress towards establishing flow injection analysis routine methods - a personal reflection

Bo Karlberg

Department of Analytical Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden *bo.karlberg@anchem.su.se*

Almost 30 years ago I gave my first lecture on the topic “Flow Injection Analysis, FIA”. It was quite late in the evening and it was by no means a carefully prepared and scheduled lecture. The place was Arlanda (Stockholm’s international airport) and, more precisely, in the customs office. I had arrived on a plane from Copenhagen and I was probably looking rather guilty since I was politely asked to unpack all of the items that I was carrying in various pieces of hand luggage. The Lego plate with its attached pieces of plexiglass mixers and polyethylene coils generated some curiosity since the arrangement seemed to be rather peculiar – was it a new kind of toy? However, the real interest was focused on the plastic syringes. Their presence had to be explained, especially since no white powder and/or injectable liquid could be found anywhere in my hand luggage.

“Well, what you see here are items enabling me to practise a new and revolutionary technique called Flow Injection Analysis. It involves manually injecting a liquid sample using a syringe. You have to imagine that there is some kind of pump here that delivers an aqueous reagent solution. This is the septum injector, glued to this Lego block. You fill the syringe with the aqueous sample and inject like this. The sample and the reagent solutions then get mixed here in this reaction coil mounted onto this second Lego block. Finally, you have to imagine that a flow-through detector is placed right here”. Essentially, that was the whole FIA lecture. But FIA should not be explained – it ought to be demonstrated.

I left the airport legally carrying the very first FIA system to be brought into Sweden. The system - the classical Lego-based FIA system - had been produced and assembled in Copenhagen for me by Jarda Ruzicka and Elo Hansen.

Since then FIA and related flow-based techniques have become well-established and are used daily in a huge number of research laboratories around the world. Japanese researchers were early adopters of the FIA technique. An impressing fact is that the Japanese Association for Flow Injection Analysis, JAFIA, recently celebrated its 20th anniversary. I had the privilege to be involved in the development of the first commercial analyzer (Bifok) and our company was immediately approached by several Japanese companies who were interested in future cooperation. Further comment on the subsequent commercial development of FIA is beyond the scope of this paper, which briefly considers methods based on FIA and related flow techniques used for routine, non-research purposes, focusing on methods authorised by standardisation bodies, especially the International Standardisation Organisation (ISO).

It is a well-known fact that the creation of a new international standard method is a time-consuming process. It normally takes several years before a standard method can be authorised and implemented after the first draft has been proposed. Proficiency tests must be performed and the method must be examined by a group of experts. Meetings, discussions, method amendments and votes are just some of the numerous, tedious steps involved in the process.

For reasons that are not readily apparent the ISO jointly describes a number of “flow methods”, i.e. methods based both on air-segmented flow analysis and flow injection analysis, in contrast to the general rule forbidding the choice of two options for a single standard method. Obviously, an exception has been made in this case. Initially, one discussion topic was the fact that a batch method for a given wet chemistry procedure very exactly defines the volume proportions between the sample and the reagent(s). Consequently, such batch methods can be quite easily “transferred” to air-segmented flow schemes since the proportions can often be easily maintained by choosing appropriate flow rates for the sample and the reagent(s). Conceptually, there was no obstacle in this respect. The same proportions can also be achieved in an FIA system, but it is not a straightforward process. The dispersion coefficient, D, cannot always be predicted. Instead, in most cases, it must be determined specifically for the system to be used. If the system then is found to yield a D-value that deviates from the target D-value, the hardware must be modified, e.g. a larger sample volume must be introduced, or the flow rate changed. However, we know that the sample dilution is fully controllable and adjustable. This "controlled dispersion" feature was proposed at an early stage to be one of the cornerstones of the FIA technique. Unfortunately, this terminology has caused confusion and delays in the standardisation process. It would have been more satisfactory to refer to "adjustable sample dilution" in this context.

Currently issued FIA ISO methods are listed in the Table below. The nitrate, ammonium and phosphate methods are by far the most important and widely used.

FIA was successfully hyphenated with atomic absorption spectroscopy (AAS) at an early stage. Since its commercial introduction by Perkin-Elmer the FIA-AAS technique has gained general acceptance and has substantially enhanced performance, especially for the hydride generation procedure.

Can we expect further standard methods based on FIA? Probably yes. The question is now rather: when can we expect the first standard methods based on sequential injection analysis, SIA? The response times offered by FIA and SIA are short, but the response time for a new international standard based on either of these techniques is, unfortunately, likely to be very, very long.

ISO number	Title
13395:1996	Water quality -- Determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection
11732:1997	Water quality -- Determination of ammonium nitrogen by flow analysis (CFA and FIA) and spectrometric detection
14402:1999	Water quality -- Determination of phenol index by flow analysis (FIA and CFA)
15682:2000	Water quality -- Determination of chloride by flow analysis (CFA and FIA) and photometric or potentiometric detection
16264:2002	Water quality -- Determination of soluble silicates by flow analysis (FIA and CFA) and photometric detection
14403:2002	Water quality -- Determination of total cyanide and free cyanide by continuous flow analysis
15681-1:2003	Water quality -- Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) -- Part 1: Method by flow injection analysis (FIA)
15681-2:2003	Water quality -- Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) -- Part 2: Method by continuous flow analysis (CFA)
14673-3:2004	Milk and milk products -- Determination of nitrate and nitrite contents -- Part 3: Method using cadmium reduction and flow injection analysis with in-line dialysis (Routine method)
ISO/DIS 23913	Water quality -- Determination of chromium(VI) and the sum of chromium(III) and chromium(VI) -- Method using flow analysis (FIA and CFA) and spectrometric detection