

Introduction

For almost half a century, flow methods of analytical measurements have had an established position in chemical analysis. Their roots can be traced back to the beginning of column-chromatographic methods and to a continuous monitoring of various physico-chemical parameters in industrial installations. The flow of the monitored medium through a suitable detector enabling the continuous recording of changes of the measured physico-chemical quantity provided the possibility of eliminating the collection of fractions in chromatographic separation or a sampling step in process monitoring, which in both cases was an evident step towards mechanisation of these operations for analytical purposes. These two streams of applications of flow measurements, the detection in column chromatography and capillary electrophoresis, and also process and environmental monitoring, evolve continuously and they are nowadays a part of analytical instrumentation of great importance.

An additional impact on the development of flow analysis in analytical laboratories was made by its new laboratory applications not connected with chromatographic detection, which appeared at the end of the fifties. Their principle was a replacement of all manipulations with a liquid sample to be analysed that was involved in the conventional manual procedure into manipulations with a segment of fluid (analysed sample) in a suitably designed flow system that ended with a flow-through detector. The main advantage of this concept is that it is the simplest way of mechanising practically all operations that need to be made with the sample in the whole analytical procedure. Then, instead of measuring the sample volume, using several pieces of glassware, transferring a sample between them (which is the main source of incidental contamination), waiting for a reaction to occur and waiting for a steady detector response, in a flow system after optimisation of the geometry of the system and a detector and also hydrodynamic conditions, the only operations to be done for each individual sample are its delivery to the flow analyser and reading or recording of transient or steady signals. So, the basic advantages of flow-analytical measurements compared to manual procedures are better reproducibility (precision) of determinations, a larger throughput and reduction of the sources of

contamination. The result of determination in the flow system is not only a function of the chemistry applied, but also depends on the dynamics of the occurring process and the conditions of its observation in the time domain. These factors, together with involved on-line operations of preconcentration or separation of the analyte from the matrix, affect the selectivity of flow determinations. The flow conditions of measurement compared to static measurement may additionally enhance the analytical signal due to convection, or provide additional kinetic discrimination of interferences. Through the appropriate configuration of a flow system, a multicomponent determination can also be realised (without employing a chromatographic retention). This can also be gained sometimes by differences in the kinetics of reactions employed for a given determination.

The first successes of laboratory flow measurements have been connected with a technique of segmentation of a flowing stream with air segments, which allows one to restrict dispersion of the sample segment (reduce dilution during the flow). Such a measurement and appropriate instrumentation have been very readily accepted by overloaded clinical chemistry laboratories for routine diagnostic purposes, and later also by environmental, agricultural, and even industrial ones.

The next milestone in the evolution of flow measurements occurred in the middle of the seventies, when it was demonstrated that measurement of the flow system can be simplified and made an even more efficient instrument for chemical-analytical determinations. The main credit for this invention has to be given to Ruzicka and Hansen of the Technical University of Denmark, although at the same time, or in the same cases even earlier, in several research groups all over the world similar studies were carried out. They convincingly demonstrated the elimination of stream segmentation, and conducting measurements with waiting for steady-state analytical signal may not only worsen the flow measurement, but can simplify it and make it more efficient.

The proposed methodology and the coined name *flow injection analysis* have been very quickly accepted by the analytical community. In the first few years of its development the interest in this technique has grown exponentially, as expressed by the number of publications in scientific journals. At the beginning of the nineties its alterations named *sequential flow analysis* and *batch injections analysis* have been invented, which are discussed in a separate chapter. The number of papers published on flow injection techniques in the nineties is almost ten thousand; numerous companies provide instruments and

accessories, and many developed flow injection methods appear as standard procedures in various regulations.

It would certainly be too boastful to state that flow injection methodologies have nowadays dominated chemical analysis, because chromatographic methods without doubt are most often employed in the majority of routine analytical laboratories, discrete analysers are used most frequently in clinical chemistry for diagnostic purposes, or atomic spectroscopy dominates inorganic analysis. Moreover, even in chromatographic techniques or atomic spectrometry methods the addition of flow injection sample pretreatment may significantly improve the value of numerous procedures. The biggest role of flow injection methods in contemporary analysis seems to be mechanisation of various methods with common detection methods still performed manually in numerous analytical laboratories.

Regarding the broad existing original literature this book does not pretend to be a complete review of the state-of-the-art in this field. It has been written as a result of following more or less scrupulously current publications and as a result of the author's own experiences in the design of instrumentation and development of analytical procedures almost since this methodology was invented. It has been prepared to guide through the evolution of this methodology and to illustrate its impact on chemical analysis in the twenty-five years since its invention.

This book is not only a result of my own experiences but also a result of creative contacts and collaboration with numerous partners and friends in the analytical community. My collaboration with Jarda Ruzicka and Elo H. Hansen in their laboratory at Lyngby in 1981 has significantly affected my interest in flow analysis. The long years of joint research with Mark E. Meyerhoff at the University of Michigan and Peter W. Alexander at the University of New South Wales in Sydney, and then later at the University of Tasmania, have been extremely fruitful, interesting and valuable for me. I also address my special thanks to all my students and co-workers in the Department of Chemistry, University of Warsaw, for their contributions to my knowledge and experience.

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