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Automatic flow kinetic-catalytic methods

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ABSTRACT

Kinetic-catalytic analytical methods are simple and highly sensitive strategies for chemical analysis, that rely on simple instrumentation. For that reason, they have been implemented to the quantification of a large number of chemical species such as transition metals, non-metallic anions and organic compounds. Flow techniques are presented as an efficient tool to overcome the main limitations of the kinetic-catalytic methods. Solving problems related with sample handling, the reproducible data acquisition, reproducible temperature control and the implementation of different kinetic determination methods (initial rate, fixed time and fixed measure).

Herein we review the recent applications of novel approaches to perform fully automated kinetic-catalytic methods based on computer controlled flow techniques. We also describe new devices and materials such as chip-based flow injection analyzers and the use of nanoparticles to improve the performance of this class of analytical methodologies.

Contents

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1. Introduction

Kinetic reactions have been used for analytical purposes since the late nineteenth century [1]. The kinetic-catalytic analytical methods were developed in parallel with instrumental methods. Since the '80s, they achieved a huge development and are currently considered well established methods for chemical analysis [2–4]. The first catalytic method automated with flow techniques was presented also in this period [5]. In 1993 Chrough [6] presented the automation of a kinetic method as one of the trends to be developed in the following years. For the last twenty years, important improvements have been introduced in parallel to the technological developments. In year 2000, over 1000 papers were already published on the development of kinetic analytical methods. However, less than 10% of them were dedicated to the automation and the development of tools for this purpose [7,8]. Nowadays, kinetic methods, and particularly kinetic-catalytic methods, are still an active area in constant development. Within the last 10 years, many scientific articles have been published related with automation and the development of new materials to kinetic-catalytic method of analysis [4,9–11].

Kinetic-catalytic methods (KC) are based on the catalytic effect of a substance on a reaction capable to produce an analytical signal [3]. The quantification is based on the possibility to establish a ratio of proportionality between the analytical signal of the catalyzed reaction and the concentration of catalyst. Transition metals, inorganic anions and some organic molecules have been determined in a wide variety of samples due to their catalytic effect in the oxidation of a substance (usually an organic molecule) producing colored, fluorescent or chemiluminescent species [3,9]. KC methods typically present very low detection limits, since the action of the catalyst is required at a very low concentration level in order to produce a detectable analytical signal. The obtained high sensitivity increased the applicability of these type of reactions to the analysis at trace levels because of its comparability in terms of sensitivity with other techniques much more expensive such as atomic absorption spectrometry (AAS), or inductively coupled plasma with atomic emission spectroscopy (ICP-AES) or mass spectrometry (ICP-MS) [9].

KC methods require a strict control of the experimental parameters and conditions. KC methods are highly dependent of the time required for the mixing, reaction and data acquisition steps. The precise control of temperature is also required, due to an exponential effect on the reaction kinetics. Furthermore, temperature oscillations affect other physical solution parameters such as viscosity, or gas solubility. Therefore, the control of these parameters during the mixing and reaction steps will be crucial for the satisfactory implementation of the KC method. However, the accurate control of these parameters may be difficult to accomplish when operating in batch mode, with open systems more susceptible to the introduction of experimental errors [6].

In order to overcome these limitations, initial attempts for the automation of KC methods were developed using stopped-flow analyzers [12]. It was followed by the implementation of KC methods using flow techniques (FTs), offering important benefits for the smart automation of this kind of analytical methods [13–15]. The high automation capacity of FTs, allows highly reproducible experimental conditions due to the high precision on the control of the different instruments and devices. The significant reduction of sample and reagent volumes, the use of closed systems, and the high analysis throughput increased the popularity of the automation of KC methods using FTs. A large number of the published papers on KC automation using FTs are based on the use of the flow injection analysis (FIA) [9,10]. The sequential injection analysis (SIA) has been also implemented for this purpose [16]. More recently multipumping flow systems (MPFS) [17] and multisyringe flow injection analysis (MSFIA) [18–24] has been exploited as tools for the automation of KC methods. Additionally, novel flow devices have been developed for the miniaturization of KC analytical systems, such as chips with integrated flow conduits presented by Abouhiat et al. [19] and Phansi et al. [22]. These chips are monolithic devices integrating mixing and reaction coils, thermostatic chambers and the detection cell in a reduced space. (Fig. 1). The integration of KC methods on a chip also enabled the implementation of initial rate determination methods under controlled temperature. Table 1 shows the recent milestones on the automation KC methods using FTs.

Apart from the advances made towards device integration and miniaturization, the use of metallic nanoparticles (NPs) has also been recently exploited as a useful strategy to advance KC methods of analysis. NPs such as Ag-NPs, Au-NPs, and Pt-NPs, have an enhancing effect on the chemiluminescence (CL) of luminol-based CL systems [29]. This effect has been explored for the KC analysis of organic molecules with groups -OH, -NH_2 and -SH, such as amino acids, polyphenols or uric acid, among others, due to their inhibiting effect on the luminol-oxidant-NP system [29].

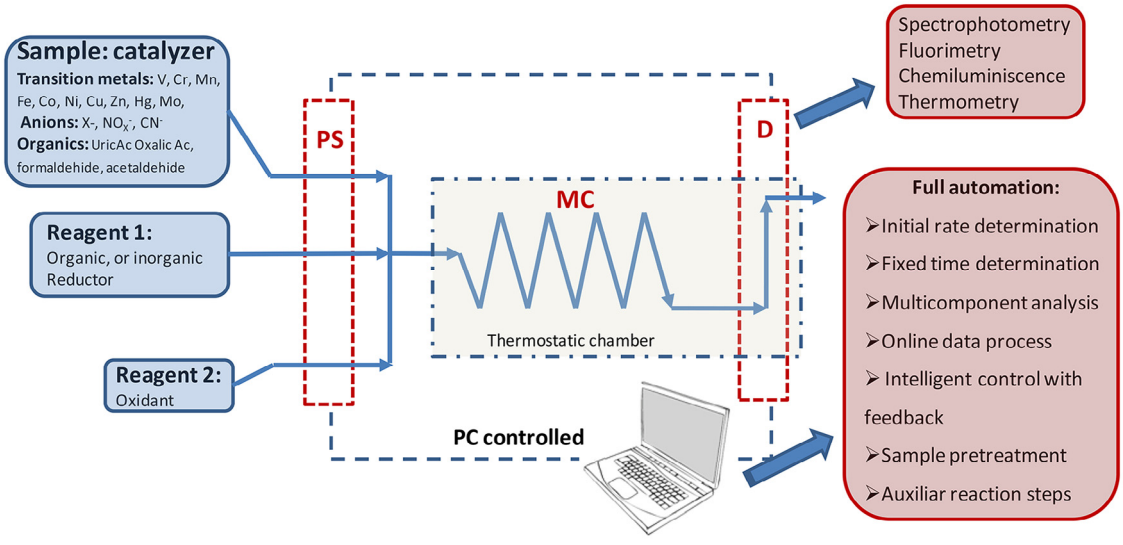

Fig. 1. Schematic diagram of a kinetic-catalytic system fully automated using flow techniques. PS, propulsion system; MC, mixing and reaction coils; D, integrated detection cell with light source and detector.