



## Review

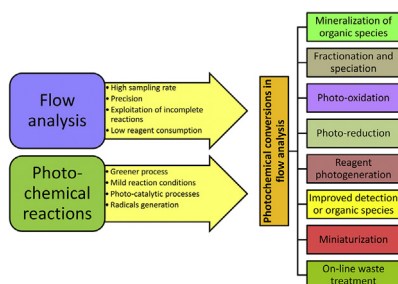
## A critical review on photochemical conversions in flow analysis

Diogo L. Rocha <sup>a</sup>, Marcos Y. Kamogawa <sup>b</sup>, Fábio R.P. Rocha <sup>c,\*</sup><sup>a</sup> Center of Natural and Human Sciences, Federal University of ABC, Avenida dos Estados, 5001, 09210-170, Santo André, SP, Brazil<sup>b</sup> Luiz de Queiroz College of Agriculture, University of São Paulo, PO Box 9, 13418-970, Piracicaba, SP, Brazil<sup>c</sup> Center for Nuclear Energy in Agriculture, University of São Paulo, PO Box 96, 13400-970, Piracicaba, SP, Brazil

## HIGHLIGHTS

- Critical review of coupling photochemical processes to flow analysis.
- Discussion of flow approaches and design of flow-through photoreactors.
- General overview of the applications with tables highlighting the main aspects.
- Quantitative and partial analyte conversions, fractionation and speciation analysis.
- Discussion on miniaturization, reagentless procedures, and in-line waste treatment.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 7 May 2015

Received in revised form

10 September 2015

Accepted 11 September 2015

Available online 25 September 2015

## Keywords:

Flow analysis

Photochemical reactions

Sample treatment

Photo-assisted digestion

Reagent photogeneration

Speciation

## ABSTRACT

Photochemical conversions are cost-effective and environmental friendly processes that require mild experimental conditions and avoid generation of highly acidic wastes. Treated samples are then compatible with most of the analytical techniques. These characteristics become more relevant when the photoconversions are accomplished to flow analysis, thus allowing exploitation of incomplete reactions, the effective use of the photogenerated unstable radicals and in-line sample treatment. Decreasing of reagent consumption and waste generation, sample processing in a closed environment, and improvement of efficiency of the photochemical processes are other inherent advantages. These aspects are critically reviewed in this article, which emphasizes applications to fractionation and speciation analysis, photo-induced luminescence, miniaturization, and in-line waste treatment. Design of flow-through photochemical cells, use of auxiliary reagents in homogeneous and heterogeneous media, and configurations of flow manifolds are also discussed.

© 2015 Elsevier B.V. All rights reserved.

## Contents

1. Introduction	12
2. Photochemical reactions pathways	12
3. Operational aspects and system designs	14
4. Applications	17
4.1. Quantitative conversions	17
4.2. Fractionation and speciation analysis	20

\* Corresponding author.

E-mail address: [fprocha@cena.usp.br](mailto:fprocha@cena.usp.br) (F.R.P. Rocha).

4.3. Reagent photogeneration .....	23
4.4. Enhanced detectability .....	23
4.5. Kinetic-based applications .....	24
4.6. Incomplete conversions .....	26
4.7. On-line waste treatment .....	27
4.8. Miniaturization .....	27
5. Conclusions and trends .....	28
Acknowledgements .....	28
Abbreviations .....	28
References .....	29

## 1. Introduction

Sample preparation is one of the most important steps in analytical procedures [1]. Chemical and physical transformations of the sample aim at enhanced analyte detectability and elimination of matrix effects. Sample treatments vary from simple dilutions to time-consuming quantitative decompositions. Additionally, this step is highly susceptible to analyte losses and contamination, especially when carried out in open vessels during long time intervals. Ultraviolet (UV) irradiation allows sample decomposition under mild conditions, being an alternative to avoid the previously mentioned drawbacks and paving the way for greener sample preparation [2].

UV radiation comprises wavelengths within 100 and 400 nm [3,4] and it is classified as UV-A (400–315 nm), UV-B (315–280 nm) and UV-C (280–100 nm). In the UV-C spectral region, radiation presents enough energy to break chemical bonds. For example, the radiation at 250 nm is equivalent to *ca.* 544 kJ mol<sup>-1</sup>, which is enough to break chemical bonds such as C – C (*ca.* 450 kJ mol<sup>-1</sup>) [2,3]. Irradiation in the 200–100 nm range requires experiments under vacuum because of the strong radiation absorption by molecular species in the atmosphere, such as oxygen [3]. Therefore, applications involving UV vacuum [5] are not usual. UV radiation at wavelengths higher than 200 nm and, more scarcely, visible radiation are then used for sample treatment. Some limitations are due to the available radiation sources, as the most common ones emit a limited number of lines (*e.g.* low pressure Hg vapor lamp) or present low conversion efficiency of electric power into radiation (*e.g.* deuterium lamp).

UV irradiation promotes either oxidation or reduction of chemical species [3,6]. Photo-oxidation is most common for sample treatment either for organic matter elimination or analyte conversion to its inorganic form. The first analytical use of UV radiation was proposed in 1961 [7] for organic matter decomposition before determination of total dissolved carbon (TDC) in seawaters. Iron (III) was used to generate oxidizing radicals and quantitative decomposition was attained in 3 h. Since then, studies on photo-conversion processes revealed that different species (*e.g.* H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) can generate oxidizing radicals; improvements in sample irradiation (*e.g.* new designs of flow-through reactors, high power sources and combination of UV irradiation and temperature) have led to better efficiency, and novel applications have been proposed in different fields.

Photoconversion relies on the generation of radicals due to the homolytic breakdown of chemical bonds. Sample components (*e.g.* organic matter) yield radicals that promote chain reactions forming reactive species [3]. The process is favored in the presence of dissolved O<sub>2</sub> because singlet oxygen is formed after UV irradiation and the energy is afterwards transferred to organic molecules. Risks related to heating are minimized because the process is often

carried out close to room temperature. In special situations, however, temperature may reach *ca.* 90 °C due to the heat emanated from the light source. As hours or even days may be required for quantitative organic matter decomposition, some chemicals are often added to accelerate the photochemical processes. For photo-oxidation, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, H<sub>2</sub>O<sub>2</sub>, Fenton reagent and O<sub>3</sub> are the most usual radical generators in homogenous systems [2,3]. Heterogeneous systems exploit semiconductors such as TiO<sub>2</sub>, which may restrict the detection approach as a suspension of small solid particles is often obtained at the end of the process. A more recent strategy for UV-assisted process involves quantum dots (QDs) [8], which are semiconductors of small particle size (1–12 nm). QDs show a wide applicability as fluorescence probes as well as emitters or catalysts in chemiluminometric reactions, as previously reviewed [9]. In addition, generation of reactive species from irradiation of the nanomaterials (usually with visible light) has been also exploited in indirect applications involving CL in flow systems [10].

Aiming at photoreduction, organic species with carbonyl or amino groups [6,11] are generally added to the medium. In spite of its potentiality, this process has been scarcely exploited for analytical purposes. Applications have been mainly focused on the reduction of species of Hg [12] and Se [13] prior to determinations by cold vapor or hydride generation atomic absorption spectrometry (CV-AAS or HG-AAS), respectively. Another representative application refers to nitrate determination after conversion to nitrite [11,14]. Recently, photoreduction of phosphomolybdic acid in ethanolic medium was demonstrated [15].

Flow analysis is characterized by highly reproducible sample processing conditions and timing, allowing exploitation of analytically useful reactions without attaining chemical equilibrium [16]. Analysis time is then minimized and kinetic aspects can be exploited. Additionally, flow systems can be built-up in a variety of configurations, allowing implementation of different tasks, including photochemical processes [17,18]. Analyte losses (by volatilization or during sample manipulation), risks of contamination, and to the analyst are minimized by flow-based sample preparation [3].

Fig. 1 shows the general characteristics and main potentialities of flow-based systems involving in-line photochemical processes. Advantages of the approach have been exploited in several procedures, especially for total determinations, fractionation and speciation analysis, and enhancement of detectability of organic analytes. Kinetic-based applications, reagent photogeneration, and in-line waste treatment have also been proposed in a lesser extent. These applications are discussed in section 4.

## 2. Photochemical reactions pathways

Generation of radicals prevails in photochemical processes in flow systems as means to enhance the reaction rate in comparison

Download English Version:

<https://daneshyari.com/en/article/1163246>

Download Persian Version:

<https://daneshyari.com/article/1163246>

[Daneshyari.com](https://daneshyari.com)