Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible

This is an author's version published in: **http://oatao.univ-toulouse.fr/24105**

A revised experimental protocol for implementing the actinometry method with the Reinecke's salt

Robbie Radjagobalou[a,b], Jean-François Blanco[a], Victoria Dias da Silva Freitas[a], Caroline Supplis[c],
Fabrice Gros[c], Odile Dechy-Cabaret[b], Karine Loubière[a,*]

[a] Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France
[b] Laboratoire de Chimie de Coordination, CNRS, Toulouse, France
[c] Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut Pascal, Clermont Ferrand, France

ABSTRACT

The present short note aims at proposing a revised experimental protocol to implement the actinometry method with Reinecke's salt. It consists in substituting, for the dosing of the thiocyanate anions produced, perchloric acid ($HClO_4$) by nitric acid (HNO_3), the latter being carefully chosen regarding the chemical equilibria occurring in the aqueous medium and the moderate risks of HNO_3. This substitution has been rigorously validated by carrying out the experiments in a dedicated torus batch photoreactor enabling simple treatment of experimental results from a one-dimensional model.

1. Introduction

Chemical actinometers are widely used in different application fields to determine the photon flux entering a reactive medium; the knowledge of this latter being of prime importance to study any photochemical reactors [1,2]. They involve a wavelength-dependent photoreaction characterized by a known quantum yield in a given spectral range [2]. For the visible domain, the Reinecke's salt is the popular actinometer, involving the following chemical equation:

$$[Cr(NH_3)_2(NCS)_4]^- + H_2O \xrightarrow{h\nu} [Cr(NH_3)_2(NCS)_3H_2O] + NCS^- \qquad (1)$$
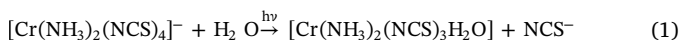
The use of the Reinecke's salt presents however some drawbacks: (i) the experiments should be performed in a dark room, (ii) the reaction medium is sensitive to the temperature and (iii) toxic reactant is used (perchloric acid). Consequently, alternative actinometers for the visible light have been proposed to determine the incident photon flux in the visible spectrum, mostly with irradiated volumes in the range of milliliter [3–7]. Unfortunately, these latter actinometers are either not commercially available (*i. e.* synthetically obtained), or expensive. Therefore, the Reinecke's salt remains an affordable actinometer, in particular for an implementation at pilot- or industrial -scale photoreactors.

The associated quantum yield is relatively stable ($\phi = 0.29 \pm 0.02$) in the range of 400–700 nm when the pH of the solution is between 3 and 5 [2]. Wegner and Adamson pioneered the experimental protocol of the Reinecke's salt as an actinometer [8], which was later revised by Cornet et al. [9]. This lab protocol is based on the use of the perchloric acid at a concentration moderately high ($0.5 \, mol.L^{-1}$). Nevertheless, this acid is nowadays classified as a highly toxic chemical product [10] as various studies have pointed out the impact of perchlorate ions ClO_4^- on animal and human metabolisms and on the environment [11,12]. Moreover, during the aging of the perchloric acid, ClO_4^- decomposes into Cl_2O_7 (dichlorine heptoxide) which is a precursor of an explosive mixture (ClO_2 (chlorine dioxide) and O_2 (dioxygen)) [13,14].

The present research note aims at proposing a revised experimental protocol to implement the actinometry method with the Reinecke's salt. For that, perchloric acid will be substituted by nitric acid, the latter being carefully chosen according to a study of chemical equilibria occurring in the aqueous medium. This substitution will be rigorously validated by carrying out experiments in a dedicated torus batch photoreactor enabling simple treatment of experimental results from one-dimensional models [15]

2. Description of the revised protocol

2.1. Photodissociation of the Reinecke's salt

According to Eq. (1), the rate of this photodissociation is equal to the rate of the production of the thiocyanate anion, NCS^-. Therefore, the dosing of the NCS^- ions, which are produced during a given

---

irradiation time τ, enables to monitor the kinetic of the photoreaction. The absorption of the actinometer covers a wide range in the visible spectrum of light, with a maximum at 525 nm. It is important to note that the absorption of the by-product, $[Cr(NH_3)_2(NCS)_3(H_2O)]$, is of the same order of magnitude than the one of the actinometer, thus implying that its absorption should be taken account in the modelling [16]. Furthermore, as described by Szychlinski et al. [17], under acidic condition, the by-product could react with water according to Eq. (2);
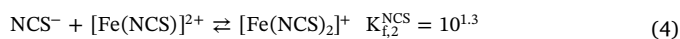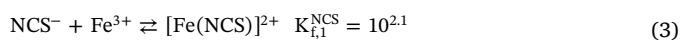
$$[Cr(NH_3)_2(NCS)_3H_2O] + H_2O \rightarrow [Cr(NH_3)_2(NCS)_2(H_2O)_2]^+ + NCS^- \tag{2}$$
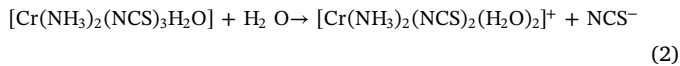
Therefore, in some conditions more than one NCS^- ion ligand could be substituted by molecules of water, and thus inducing a bias in the determination of the consumed molar quantity of the Reinecke's salt during a given irradiation time and an overestimation of the amount of NCS^- produced. To limit this second reaction, Rochatte et al. [16] recommended to work at low conversions χ, namely below a maximal value, noted χ_{max}, equal to 30%.

The molar quantity of thiocyanate ions produced during the photoreaction (Eq. (1)) is classically evaluated by spectrophotometry. Iron (III) thiocyanate complexes can be formed when the NCS^- ions are in the presence of Fe^{3+} ions [18]. These complexes are known to absorb intensively in the visible spectral domain of light [19].

2.2. Monitoring of the absorbance of the iron (III) thiocyanate complexes

All the values of formation constants for the iron complexes for the jth equilibrium are given at 25 °C and noted $K_{f,j}^i$, where i refers to the ligand.

In the aqueous medium for the spectrophotometric analysis, Fe^{3+} ions should be in excess against NCS^- ions [20]:
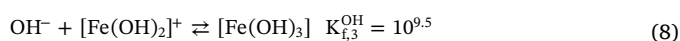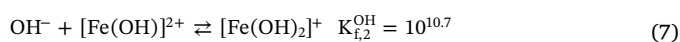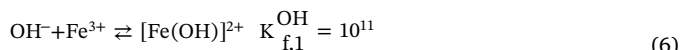
$$NCS^- + Fe^{3+} \rightleftarrows [Fe(NCS)]^{2+} \quad K_{f,1}^{NCS} = 10^{2.1} \tag{3}$$

$$NCS^- + [Fe(NCS)]^{2+} \rightleftarrows [Fe(NCS)_2]^+ \quad K_{f,2}^{NCS} = 10^{1.3} \tag{4}$$

When $C_{Fe^{3+}} \geq 10 \times C_{NCS^-}$, the equilibrium exposed in Eq. (3) is preponderant when compared to the one in Eq. (4). In this case, the reaction of interest during the spectrophotometric analysis is the one described by Eq. (3). The maximum of absorbance of the solution is observed at 450 nm when $C_{Fe^{3+}} \geq 10 \times C_{NCS^-}$ (the sample for the reference solution being always a non-irradiated Reinecke's salt solution). The concentration of the thiocyanate ions is determined according to

$$C_{NCS^-} = \frac{\theta.A_{450}}{l.\varepsilon_C} \tag{5}$$

Where, l (m) is the width of the glass cell for the spectrophotometry, A_{450} (-) is the absorbance of the solution measured at 450 nm, θ (-) the dilution factor applied for the sample and ε_C (L. mol^{-1}. cm^{-1}) the decadic molar absorption coefficient of $[Fe(NCS)]^{2+}$ measured at 450 nm, 25 °C and at the dilution rate θ.

Various iron (III) hydroxide complexes (Eqs. (6)–(8)) could be formed depending on the value of the pH [21]:

$$OH^- + Fe^{3+} \rightleftarrows [Fe(OH)]^{2+} \quad K_{f,1}^{OH} = 10^{11} \tag{6}$$

$$OH^- + [Fe(OH)]^{2+} \rightleftarrows [Fe(OH)_2]^+ \quad K_{f,2}^{OH} = 10^{10.7} \tag{7}$$

$$OH^- + [Fe(OH)_2]^+ \rightleftarrows [Fe(OH)_3] \quad K_{f,3}^{OH} = 10^{9.5} \tag{8}$$

Furthermore, in an acidic medium, the most likely iron (III) hydroxide complex to be formed is $[Fe(OH)]^{2+}$. Therefore, from the expression of the constant of formation of $[Fe(OH)]^{2+}$;

$$(C_{[Fe(OH)]^{2+}})_{eq} = \frac{K_{f,1}^{OH} . K_e. (C_{Fe^{3+}})_{eq}}{10^{-pH}} \tag{9}$$
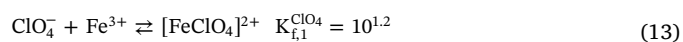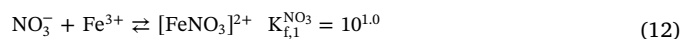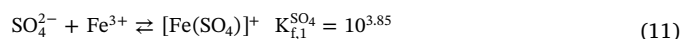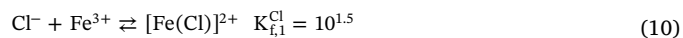
Where, K_e (-) is the equilibrium constant of the autoprotolysis of water

and equal to 10^{-14} and $(C_{Fe^{3+}})_{eq}$ and $(C_{[Fe(OH)]^{2+}})_{eq}$ the concentrations of Fe^{3+} and of $[Fe(OH)]^{2+}$ in the medium at the equilibrium.

As a consequence, the monitoring of the acidity becomes essential in order to correctly drive the selectivity of formation of hydroxide complexes [22]. In order to limit the formation of $[Fe(OH)]^{2+}$, a mineral acid must be added to the ferric solution, which consists in dissolving the iron (III) nitrate nonahydrate $Fe(NO_3)_3.9H_2O$ in water.

Several options of mineral acids can be proposed in analytical chemistry such as hydrochloric acid, sulfuric acid or nitric acid, knowing that the original protocol of Wegner and Adamson used perchloric acid [3].

Using independently the four acids previously mentioned involves the complexation reactions described below [20].

$$Cl^- + Fe^{3+} \rightleftarrows [Fe(Cl)]^{2+} \quad K_{f,1}^{Cl} = 10^{1.5} \tag{10}$$

$$SO_4^{2-} + Fe^{3+} \rightleftarrows [Fe(SO_4)]^+ \quad K_{f,1}^{SO_4} = 10^{3.85} \tag{11}$$

$$NO_3^- + Fe^{3+} \rightleftarrows [FeNO_3]^{2+} \quad K_{f,1}^{NO_3} = 10^{1.0} \tag{12}$$

$$ClO_4^- + Fe^{3+} \rightleftarrows [FeClO_4]^{2+} \quad K_{f,1}^{ClO_4} = 10^{1.2} \tag{13}$$

From Eq. (3) and Eq. (11), the SO_4^{2-} ions form a complex with Fe^{3+} more stable than $[Fe(NCS)]^{2+}$ since $K_{f,1}^{SO_4} > K_{f,1}^{NCS}$. Thus, the sulfuric acid should be excluded.

The occurrence of $[Fe(NCS)]^{2+}$ is predominant when using the perchloric ($HClO_4$), the nitric (HNO_3) and the hydrochloric (HCl) acids as $K_{f,1}^{NO_3}$, $K_{f,1}^{ClO_4}$ and $K_{f,1}^{Cl}$ are inferior to $K_{f,1}^{NCS}$. Consequently, $HClO_4$, HNO_3 and HCl favor the formation of $[Fe(NCS)]^{2+}$ complex.

Note that the assay of NCS^- by Fe^{3+} is not affected by redox reactions when comparing the redox potentials of the present ionic species.

In addition, when the condition of a large excess of Fe^{3+} is not fulfilled, the use of HCl should be avoided since $K_{f,1}^{Cl} > K_{f,2}^{NCS}$. And taking into account the toxicity of perchloric acid and perchlorate ion, the nitric acid is therefore the most suitable acid that can be selected to prepare the ferric solution.

2.3. Experimental protocol

In the following experiments, the Reinecke's salt was purchased from Sigma Aldrich (CAS: 13573-17-6; lot: MKB54395 V (100 g); purity: $\geq 93.0\%$; 336.43 g.mol^{-1}). The procedure proposed by Cornet et al. [9] was carried out in this study. The first step consisted in permuting NH_4^+ by K^+ ions. Hence, the Reinecke's salt was solubilized at 20 °C in a solution of potassium hydroxide such as the initial concentration of the potassium hydroxide and of the Reinecke's salt were fixed respectively at 0.1 mol.L^{-1} and at 0.015 mol.L^{-1} for all the experiments. The obtained pH after mixing was approximately equal to 13 which made possible the ammoniac stripping by mechanical agitation ($pKa[NH_3/NH_4^+] = 9.2$). Then, a solution of concentrated sulfuric acid (98%) was added gently in order to reduce the pH between 4 and 5. Note that the whole procedure was carried out in a dark room.

The spectrophotometric measurements were also inspired from Cornet et al. [9]. Absorption spectra were measured by a Shimadzu UV-160A and the samples were analyzed in plastic cells of 10 mm at room temperature of 25 °C in the dark. By means of the revised procedure, the ferric solution was composed of 0.1 mol.L^{-1} of iron (III) nitrate nonahydrate $Fe(NO_3)_3.9H_2O$ and 0.5 mol.L^{-1} of nitric acid HNO_3 (63% weight fraction). At last, the solution from the reaction medium (or the reference solution) for the spectrometric analysis was prepared as following: to 0.5 mL of an irradiated solution (or 0.5 mL of a non-irradiated solution), was added successively, in this order, 1.5 mL of the ferric solution and 10 mL of deionized water.

Note that the reference solution should be kept during all the experiment time in the dark so as to prepare the blank at each measurement, as the Reinecke's salt could react slowly with water according to

a thermal pathway [17]. The applied dilution factor θ and the final pH were then equal to 24 and 1.2 for all the samples, respectively. Under this dilution, at 450 nm, ε_C was determined and found equal to 3400 ($\pm$ 100) L. mol^{-1}. cm^{-1}, which is the same value as already reported in [4]. Finally, the concentration of NCS^- was determined by using Eq. (5).

The dilution factor fixed at 24 was chosen so as to allow measuring absorbances with cells having an optical path of 10 mm in the detection range of the Shimadzu apparatus. Finally, as $\frac{C_{Fe^{3+}}}{C_{NCS^-}} > 10$ with $C_{Fe^{3+}}$ = 0.0125 mol.L^{-1}, the maximal concentration of NCS^- to be analyzed was equal to 1.88×10^{-4} mol.L^{-1} (for χ_{max} = 30%) in the solution.

Two precautions were taken:

(i) It was verified that the absorbance of the Reinecke's salt and the by-product $[Cr(NH_3)_2(NCS)_2(H_2O)_2]^+$ were negligible at 450 nm. According to [16], the molar absorption coefficient at 450 nm of the Reinecke's salt and of the by-product were equal to 30.4 L.mol^{-1}. cm^{-1} and to 29.5 L.mol^{-1}. cm^{-1}, respectively. Then, considering (a) the maximal conversion ($\chi = \chi_{max}$ = 30%), (b) an initial concentration of the Reinecke's salt equal to 0.015 mol.L^{-1} and (c) a dilution factor θ of 24, the absorbance of iron (III) complexes, of the Reinecke's salt and of the by-product were respectively equal to 0.638, 0.013 and 0.006 at 450 nm (for an optical length of 10 mm).
(ii) The determination of NCS^- via the protocol was feasible only if $[Fe(NCS)]^{2+}$ was predominant. Let's assume $\chi = \chi_{max}$, i. e. a maximal conversion in NCS^- ; as $C_{Fe^{3+}} >> C_{OH^-}$ and $C_{Fe^{3+}} >> C_{NCS^-}$, the final concentrations of $[Fe(NCS)]^{2+}$ and of $[Fe(OH)]^{2+}$ were equal to the initial concentration of NCS^- (= 1.88×10^{-4} mol.L^{-1}) and of OH^- (= 1.58×10^{-13} mol.L^{-1}), respectively. Thus $(C_{[Fe(NCS)]^{2+}})_{final} >> (C_{[Fe(OH)]^{2+}})_{final}$, the conditions to form predominantly the iron (III) thiocyanate complex were fulfilled.

3. Validation of the revised experimental protocol

To validate this revised protocol, specific experiments were carried out in a benchmark batch flat torus photoreactor which offered the advantage to be perfectly characterized [15,16]. This photoreactor was irradiated by a quasi-collimated blue light LED panel (λ = 457 nm) of a 12.5×12.5 cm^2 surface (the emission spectrum of this LED panel is reported in Rochatte et al. [16]). Furthermore, due to its specific design, the photoreactor could be described according to a one-dimensional Cartesian geometry enabling thus to define rigorously the specific surface of illumination as the inverse of the optical path δ (a_{light} = 40 m^{-1} with δ = 0.025 m). The dark volume fraction was also determined and equal to 0.103 (which corresponds to the part of the volume not directly irradiated at the boundary, enabling then to easily correct the actual specific illuminated surface in case of conserved geometry). In addition, the reactor could be assumed as perfectly stirred [10].

The experimental concentration of NCS^- obtained using perchloric acid for the preparation of the ferric solution was compared with those where nitric acid was replaced by perchloric acid. The spectrophotometric analysis was conducted by regularly taking samples (at every 180 s for low photon flux density, 120 or 90 s for higher densities).

Fig. 1 illustrates this comparison for different conditions of emitted photon fluxes. A good agreement was obtained whatever the acid used for each emission light. It showed that the use of the nitric acid permitted to calculate similar conversions in NCS^- when the perchloric acid was used and for all the light emission modes.

To validate completely the new experimental protocol, the next step consisted in determining the received photon flux densities q_0 from the experimental results (Fig. 1), whatever the acid used. For that, a simple mathematical model was elaborated based on the coupling of the mass balance with the photon transport equation (Eq. (14)).

Considering that (a) the reactor behaved as a perfectly mixed reactor (i. e. the concentration is uniform in the entire volume), (b) the light was monochromatic, emitted perpendicularly to the flow direction as a mono-directional and collimated light source, uniformly distributed along the reactor walls, and (c) the optical surface of the reactor was flat and non-reflective, Rochatte et al. [16] demonstrated that the analytical expression of the production of NCS^- during the irradiation time, noted τ (s), was given by

$$\frac{dC_{NCS^-}}{d\tau} = (1 - f_d). \varphi. a_{light}. q_0. \frac{\bar{\kappa}_R. C_R}{\bar{\kappa}_R. C_R + \bar{\kappa}_P. C_P}. (1 - e^{-(\bar{\kappa}_R.C_R + \bar{\kappa}_P.C_P).\delta})$$

(14)

Where q_0 (mol. $m^{-2}.s^{-1}$) was the incident photon flux density, C_R (mol. m^{-3}) the concentration of the Reinecke's salt, C_P (mol. m^{-3}) the concentration of the by-product, δ (m) the optical path, a_{light} (m^{-1}) the irradiated specific surface, φ (-) the quantum yield, and f_d (-) the dark volume fraction. The mean molar naperian absorption coefficient of the Reinecke's salt, $\bar{\kappa}_R$ (m^2. mol^{-1}), and the mean molar naperian absorption coefficient of the by-product, $\bar{\kappa}_P$ (m^2. mol^{-1}) were calculated according to

$$\bar{\kappa} = \frac{\int_{\lambda_{min}}^{\lambda_{max}} \kappa_\lambda. f_\lambda^{LED}.d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} .f_\lambda^{LED}.d\lambda}$$

(15)

Where f_λ^{LED} (-) is the density function of the blue light LED panel and κ_λ (m^2. mol^{-1}) is the naperian absorption coefficient at each wavelength λ (m). The values of f_λ^{LED}, and of κ_λ of Reinecke's salt and of the by-product are reported in [10]. Eq. (15) allowed to calculate a mean value of the absorption coefficient by taking into account the emission spectrum of the light source. This method of calculation was verified to be well adapted for the batch flat torus photoreactor irradiated by the blue light LED panel [16].

Note that the flat torus photoreactor was built in such manner that the assumptions underlying the establishment of Eq. (14) were fulfilled.

The resolution of the latter equations was done using the software Matlab®. The identification of q_0 in Eq. (14) was made by minimizing the difference between the variations of the thiocyanate ion concentrations with the irradiation time predicted by Eq. (14) and the experimental ones.

From the modelling (Eq. (14)), the incident photon flux density q_0 related to each experimental protocol could be calculated (see Table 1). Both experimental protocols then led to almost similar incident photon flux densities where the maximal relative standard deviation was equal to 5%.

At last, the incident photon flux density was also determined via a physical method using a LI-COR® quantum sensor (LI-190Sa) connected to a LI-189 display (see Table 1). The latter measured the flux densities in the Photosynthetically Active Radiation domain ([400 nm; 700 nm]) directly in μmol.$m^{-2}.s^{-1}$ and was calibrated at the factory with an uncertainty of 5%. The region of interest (i.e. the area where the liquid circulated into the reactor) was fractioned into 16 surfaces of measurement (which represented 15% of the total illuminated surface). Taking into account the deviation between these measurement points, and the latter uncertainty, the relative standard deviation on the values of q_0 from LI-COR® was estimated to 15%. Table 1 shows that these values were consistent with those obtained with the actinometry methods.

4. Conclusion

In this short note, the classical experimental protocol to determine the incident photon flux density by actinometry with the Reinecke'salt was revised. As the use of the acid perchloric could cause serious damages to the environment and injuries to experimenters, the proposed method consisted in substituting the perchloric acid by a less hazardous
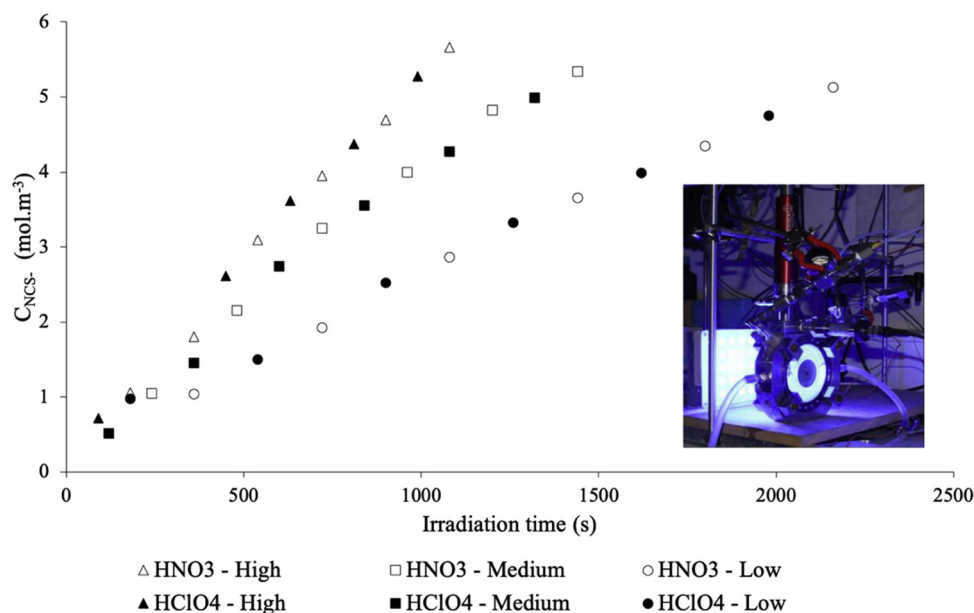
Fig. 1. Photography of the flat torus photoreactor and variation of the concentration in NCS$^-$ as a function of the irradiation time, depending whether perchloric acid or nitric acid was used (see [16] for more details about the design of the flat torus reactor with the blue LED).

Table 1
Incident photon flux densities q_0 related each experimental protocol resulting from the modelling (Eq. (14), with a relative standard deviation estimated to 5%) and measured by a LI-COR® quantum sensor (a relative standard deviation estimated to 15%).

Level of light power	q_0 ($\mu mol. m^{-2}.s^{-1}$)		
	Actinometry method using HNO_3	Actinometry method using $HClO_4$	LI-COR®
Low	260 ± 10	270 ± 10	260 ± 40
Medium	460 ± 20	450 ± 20	470 ± 70
High	610 ± 30	650 ± 30	670 ± 100

acid. The choice of the acid resulted from a study of the chemical equilibria and at last, the acid nitric was selected. Finally, the new protocol was rigorously validated in a benchmark batch photoreactor.

In the future, a way to improve the proposed protocol would be to use cells with 1 mm of optical pathlength for the measurement of absorbance making possible the decrease of the dilution factor and, consequently, the increase of the occurrence of the formation of iron (III) thiocyanate complexes.

References

[1] A.M. Braun, M.-T. Maurette, E. Oliveros, Technologie photochimique. Presses polytechniques romandes, (1986).
[2] H.J. Kuhn, S.E. Braslavsky, R. Schmidt, Chemical actinometry, Int. Union Pure Appl. Chem. (2004) 1–47.
[3] H.G. Heller, J.R. Langan, Photochromic heterocyclic fulgides. Part 3. The use of (E)-a-(2.5-dimethyl-3-furylethylidene)(isopropylidene)succinic anhydride as a simple convenient chemical actinometer, J. Am. Chem. Soc. (1981) 341–343.
[4] H.D. Brauer, R. Schmidt, G. Gauglitz, S. Hubig, Chemical actinometry in the visible (475–610 nm) by meso-diphenylhelianthrene, Photochem. Photobiol. 37 (6) (1983) 595–598.
[5] A.R. Santos, R. Ballardini, P. Belser, M.T. Gandolfi, V.M. Iyer, L. Moggi, Photochemical investigation of a photochromic diarylethene compound that can be used as a wide range actinometer, Photochem. Photobiol. Sci. 8 (12) (2009) 1734–1742.
[6] S.P. Pitre, C.D. McTiernan, W. Vine, R. Dipucchio, M. Grenier, J.C. Scaiano, Visible-light actinometry and intermittent illumination as convenient tools to study Ru(bpy)₃Cl₂ mediated photoredox transformations, Sci. Rep. 5 (July) (2015) 1–10.
[7] A. Roibu, S. Fransen, M.E. Leblebici, G. Meir, T. Van Gerven, S. Kuhn, An accessible visible-light actinometer for the determination of photon flux and optical path-length in flow photo microreactors, Sci. Rep. 8 (1) (2018) 1–10.
[8] E.E. Wegner, A.W. Adamson, Photochemistry of complex ions. III. Absolute quantum yields for the photolysis of some aqueous chromium(III) complexes. Chemical actinometry in the long wavelength visible region, J. Am. Chem. Soc. 88 (3) (1966) 394–404.
[9] J.-F. Cornet, A. Marty, J.B. Gros, Revised technique for the determination of mean incident light fluxes on photobioreactors, Biotechnol. Prog. 13 (4) (1997) 408–415.
[10] Sigma-Aldrich, Safety Data Sheet of Perchloric Acid. Sigma-Aldrich, 2018.
[11] W.E. Motzer, Perchlorate: problems, detection, and solutions, Environ. Forensics 2 (2001) 301–311.
[12] B.C. Blount, J.L. Pirkle, J.D. Osterloh, L. Valentin-blasini, K.L. Caldwell, Urinary perchlorate and thyroid hormone levels in adolescent and adult men and women living in the United States, Environ. Health Perspect. 114 (12) (2006) 1865–1871.
[13] G.F. Smith, Further Applications in the Use of Perchloric Acid, GF Smith chemical Co, Columbus, Ohio, 1942.
[14] J. Leuleu, J. Triolet, Réactions Chimiques Dangereuses, 2ème éditi., (2003).
[15] G. Dahi, A. Eskandari, J. Dauchet, F. Gros, M. Roudet, J.-F. Cornet, A novel experimental bench dedicated to the accurate radiative analysis of photoreactors: the case study of CdS catalyzed hydrogen production from sacrificial donors, Chem. Eng. Process. Process Intensif. 98 (2015) 174–186.
[16] V. Rochatte, G. Dahi, A. Eskandari, J. Dauchet, F. Gros, M. Roudet, J.-F. Cornet, Radiative transfer approach using Monte Carlo Method for actinometry in complex geometry and its application to Reinecke salt photodissociation within innovative pilot-scale photo(bio)reactors, Chem. Eng. J. 308 (2017) 940–953.
[17] J. Szychlinski, P. Bilski, K. Martuszewski, J. Blazejowski, Complementary study on the use of the potassium Reinecke's salt as a chemical actinometer, Analyst 114 (6) (1989) 739–741.
[18] S.Z. Lewin, R.S. Wagner, The nature of iron (III) thiocyanate in solution, J. Chem. Educ. (1953) 445–449.
[19] M. Lister, D. Rivington, Some measurements on the iron(III) - Thiocyanate system in aqueous solution, Can. J. Chem. 33 (111) (1955) 1572–1590.
[20] G. Charlot, L'analyse qualitative et les réactions en solution, Masson Cie, 1963 p. 226.
[21] D. Monier, W. Haerdi, Y. Rusconi, Elements de Chimie analytique, analyse qualitative minérale (Eléments de radiochimie), Librairie de l'Université Géorg., Genève, 1963, p. 277.
[22] D.M. Zall, D. Fisher, M.Q. Garner, Photometric determination of chlorides in water, Anal. Chem. 28 (11) (1956) 1665–1668.