Automatic Water and Wastewater Quality Monitoring Systems

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Abstract. Water and wastewater quality monitoring programs have to be established in order to fulfill current legal requirements as well as environmental and social concerns. This entails a large number of samples to be analyzed in a short period of time. Flow analysis techniques allow the automation of the analytical methodologies providing great advantages, i.e. improved reproducibility, low reagents consumption and waste generation, as well as high analysis frequency. Sequential Injection Analysis (SIA) is an excellent tool for developing automatic analyzers with multiparametric capabilities. In this chapter, four multiparametric SIA systems which are able to determine key parameters in water and wastewater such as BOD, COD, TOC, TSS, global N, total P, nitrate, nitrite, ammonium, orthophosphate, anionic detergents, sulfate, pH and conductivity are presented and discussed in detail.

Keywords: Sequential Injection Analysis, automation, water and wastewater analysis, multiparametric monitoring.

1   Introduction

Water pollution is an environmental issue, since it affects plants and organisms living in it, damaging not only individual species and populations, but also natural biological communities. Concerns for environmental conservation and improvement of the environmental health have increased during the last decades, and this has led to an increase in environmental monitoring programs. Drinking water is subject to strict quality controls in order to guarantee human health. Thus, the European Council Directive 98/83/EC [1], the World Health Organization (WHO) [2] and the United States Environmental Protection Agency (USEPA) [3] stipulate reference limit values for the most relevant physicochemical parameters in water for human consumption. Regarding wastewater quality monitoring, the European Council Directive 91/271/EEC [4] stipulates that all EU Members States have to appropriately equip

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wastewater treatment plants in all cities with a certain number of equivalent-inhabitants, in order to monitor the required parameters. Usually wastewater quality is characterized both by global pollution parameters, such as biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) or total suspended solids (TSS), and by nitrogen and phosphorous compounds. The characterization of wastewater at the inlet and outlet of the treatment plants is an effective way to control the process efficiency and to guarantee the final quality of treated water. Also in some industrial processes, the quality control of the water involved is of great relevance to guarantee the good performance and the safety of the equipment. All these entailed an increasing demand for control analyses and the large number of samples with which analysts can be confronted imposes various challenges to analytical chemists such as the need to develop new methods exhibiting as much selectivity, sensitivity, sample and reagent economy, throughput, cost-effectiveness, simplicity and environmental friendliness as possible.

Since the beginnings of automation of analytical methods, various different flow techniques have been developed and used for analytical and monitoring applications. They have gained importance for clinical, industrial and environmental purposes as they allow highly reproducible fast determinations. Automation and miniaturization of fluidic-based analysis are essential to make them fast and efficient for routine and research tasks [5]. The development of automatic methods of analysis arose in the 1950s, when clinical tests started to be increasingly used for diagnostic purposes in medicine that led to a spectacular increase in the demand for laboratory tests which, for obvious economic reasons, could not be met simply by hiring more laboratory staff. The solution to this problem was provided by segmented flow analysis (SFA) [6], which afforded not only substantially increased throughput, but also substantial savings in samples and reagents. SFA laid the foundations for modern flow techniques. Although originally flow techniques were performed for off-site measurements, their outstanding feature is the capability for both in-situ and real-time monitoring [7,8] of chemical parameters in waters, with some such flow analyzers being included in the United States Environmental Protection Agency (USEPA) directions [9,10].

Earliest automatic methods used devices suited to particular applications. This restricted their scope to very specific uses such as the control of manufacturing processes or to those cases where the number of samples to be analyzed was large enough to justify the initial effort and investment required. Ever since, SFA was developed by Skeggs in 1957 [6], flow techniques have been in continuous evolution towards new developments such as those of Flow Injection Analysis (FIA) [11] by J. Ruzicka and E.H. Hansen in 1975; Sequential Injection Analysis (SIA) [12], by J. Ruzicka and G.D. Marshall in 1990; Multicommutated Flow Analysis (MCFIA) [13], by B.F. Reis et al. in 1994; Multisyringe Flow Injection Analysis (MSFIA) [14], by V. Cerdà et al. in 1999, Multi-Pumping Flow Systems (MPFS) [15], by R. Lapa et al. in 2002 and Lab-On-Valve (LOV) [16] by J. Ruzicka in 2000, and have aroused special interest in relation to many other automatic methodologies of analysis. Moreover, substantial advantages can be derived from their combination.

FIA is undoubtedly the most widely accepted flow technique. Its widespread success can be ascribed to its ease of implementation and, especially, to its computer-less working capability. By contrast, all subsequent flow techniques require computer control. This initially hindered further development of the latter owing to unavailability of suitable commercial software and general lack of experience in coupling personal computers to instruments. However most of the advantages of current flow techniques are in part consequence of the incorporation of computers; in fact, computers flexibility allows the implementation of the same analytical method (hardware), with little or no alteration, on different types of samples simply by software modification.

Nevertheless, no other flow technique can match SIA in multiparametric determination capabilities. Unlike FIA, SIA can be turned into a true multiparametric analysis system simply by using a switching valve with an appropriate number of channels to hold the different analytical reagents, delivery of which can be precisely programmed via the associated computer. In this respect, SIA is much closer than FIA to the original SFA systems that afforded the determination of up to twenty parameters per sample -except that SIA operates in a much simpler and, especially, more economical manner.

All in all, flow techniques have gone through two generations. On the one side, flow systems were initially operated exclusively by hand (e.g. in SFA and FIA). On the other side, computers facilitated the development of the so-called second generation of flow techniques such as SIA, MCFIA, MSFIA or LOV, based on multicommutation operation. Multicommutated flow techniques have shown great potential in comparison with previous flow techniques in minimizing reagents consumption and waste production, providing more environmentally friendly methodologies, since liquids are only propelled to the system when required and returned to their reservoirs when not. All of them have common components such as impulsion pumps, which act as liquid drivers and a series of plastic tubes or manifold intended to carry liquid streams to the detector.

Wastewater sample pretreatment plays a major role in their analysis. Suspended matter in wastewater samples may include different kind of solids: floating, sedimentable and colloidal solids. Suspended solids effects are related to their size and origin, but from a physical point of view, their interference with the light penetration (turbidity) is the most notable effect. So, when a spectrophotometric detection is performed, it is mandatory to carry out a sample pretreatment in order to eliminate the suspended matter. Most widely used procedures are centrifugation, filtration and flocculation [17]. Usually, the choice depends on the type of analyte to determine, e.g., if the analyte is easily oxidized, flocculation is preferred. However, if the pretreatment is intended to be carried out on line, filtration is the best option. Also, there are devices which allow the liquid to flow through them while retaining the suspended matter. These devices have to be placed on the input line of the sample. For example, a sampling system (particle size exclusion sampling – PSES) was developed by Wurl et al. in 2000 to prevent an obstruction of the manifold by big sediment particles (d > 0.8 mm) when analyzing river water samples [18]. This PSES device consists of sixteen induction tubes, with an internal diameter (i.d) of 0.3 mm

smaller than the i.d. of the manifold, in order to serve as a filter. If an induction coil is obstructed the further induction tubes are available to sample the water. There are other devices which consist of a piece of PVC with hundreds of perforations leading to a central duct connected to the system. These devices require a frequent cleaning, in order to avoid the blocking of the conduits of entrance and to ensure a constant sample flow rate. In the case of volatile analytes, it is possible to use a diffusion gas cell. In such methodologies, the donor stream could be raw wastewater since the target analyte passes through the membrane to the acceptor stream without requiring any kind of pretreatment.

Several methods based on SIA have been developed for the determination of key environmental parameters with different detection systems [19]. In this chapter, several automatic monitoring systems based on SIA for water and wastewater quality determination are presented and discussed in detail.

2   Sequential Injection Analysis (SIA)

Sequential injection analysis was developed by J. Ruzicka and G. Marshall as an alternative to FIA. SIA has over time proved that its scope departs markedly from that of the former technique.

Fig. 1 shows a schematic depiction of a typical SIA system. A two-way piston pump is connected to the central port of a multiposition valve via a holding coil (HC) which is made to address the peripheral ports of the unit, for sequential aspiration of the sample and reagents, via the central communication channel (CC) in the selection valve.
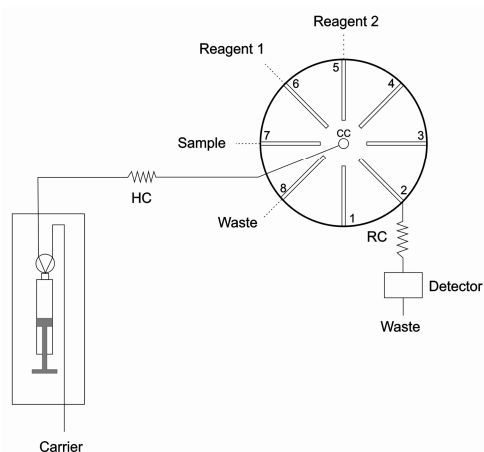

Fig. 1. Schematic depiction of a typical SIA system. HC: Holding Coil; RC: Reaction Coil; CC: Central Conduit.

One of the side ports of the valve is connected to the detector. Side ports can also be used for other purposes such as discharging waste or connection to other devices (e.g. a microwave oven, photo-oxidation system, another multi-position valve or mixing chamber). In a SIA system using a single reagent, the central port of the switching valve is connected to the sample channel and the pump is set to aspirate a preset volume of sample at a fairly low flow-rate in order to avoid the formation of bubbles. Then, the central port is connected to the appropriate side port in order to aspirate a preset volume of reagent. Next, the valve is actuated in order to connect its central port with the channel leading to the detector and an appropriate volume of carrier is dispensed to drive the sample and reagent to the detector. All this occurs under a laminar flow; as a result, the detector profile is no longer rectangular, but rather exhibits the typical asymmetric shape of FIA peaks. As can be seen in Fig. 2, dispersion in a SIA system leads to the sample and reagent plugs overlapping and forming the reaction product to be detected. A typical SIA manifold includes two types of coil, namely: a holding coil (HC) inserted in the channel connecting the
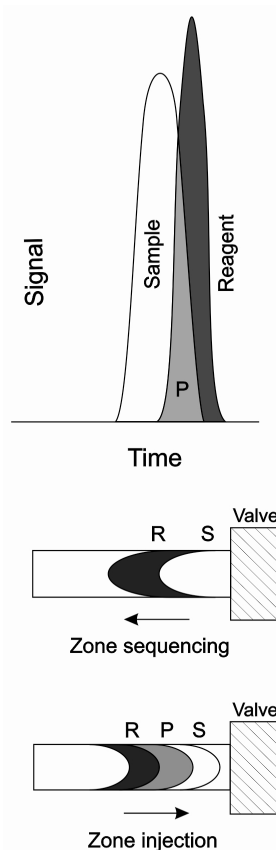

Fig. 2. Overlapping sample and reagent plugs in a SIA system. R: Reagent; P: Product; S: Sample.

piston pump to the central port of the switching valve that is used to prevent the sample and reagents from reaching the piston pump -cleaning of which otherwise would be labor-intensive and time-consuming- and a reaction coil (RC) in the channel leading to the detector that is intended to ensure adequate overlap between sample and reagent plugs in order to allow a quantitative amount of reaction product to form.

One of the essential features of SIA is its computerized control. The power of computers has grown so dramatically that nowadays they allow an automatic method to be set for adaptation to quite different needs; such a high flexibility simplifies the development of effective solutions at substantially reduced costs. The computer controls the connection of the central port to its side ports, starts and stops the pump in order to aspirate or dispense liquids, selects their volume and adjusts the flow-rate. Thus, residence times need no longer to be controlled via the length of the manifold tubes and flow-rates of the peristaltic pump; rather, by the computer being controlled and adjusted in each step of the process at will in a highly reproducible manner, making SIA a highly flexible analytical tool.

A major advantage of SIA over FIA is its ease of implementation, whereas in FIA using a different method very frequently entails altering the configuration of the manifold, switching to another method in SIA seldom requires more than using a different computer file containing the operational settings to be used with each procedure. Data acquisition and processing are also possible thanks to its computerized control. Nevertheless, this was one of the greatest initial hindrances to SIA development, which resulted in the development of barely a few tens of methods during its first year of existence due to the scarcity of commercially available software and the lack of experience in interfacing computers to analytical instruments. Only during the past decade, with the inception of commercial software, SIA has gained ground in the field of routine analyses. The incorporation of computers into SIA systems has also facilitated the implementation of stopped-flow methods. It is shown that sample handling in the sequential injection mode, which employs forward, reversed and stopped flow, can be programmed to accommodate a wide variety of assays. It suffices to calculate the volume of carrier to be delivered and stops the system when a peak is obtained at the detector in order to readily implement various analytical methodologies including classical kinetic, spectrophotometric, polarographic, voltammetric and anodic stripping methods. In addition, computers have increased the flexibility of analytical systems by allowing a number of operations mimicking those performed manually to be programmed by easy on-line implementation. Thus, samples can be aspirated and supplied with a reagent; their mixture driven to a photoreactor; and an aliquot withdrawn, sent to a solid-phase pre-concentration unit and eluted from it with a view to sequentially detecting the analytes by using several detectors that can be arranged serially at the same port or radially at different ports -or even in a serial/radial mixed configuration.

Moreover, as stated previously, no other flow technique can match SIA in multiparametric determination capabilities. Currently available switching valves can have more than twenty side ports. Also, the number can be increased by connecting a side port in a valve to the central port of several others. Such a high degree of expandability is exclusive of SIA.

   Another advantage derived from the way a SIA system operates is the dramatically reduced consumption of sample and reagents. In a FIA system, sample and reagent consumptions are virtually independent of the analysis frequency as the peristaltic pump continuously propels the sample and reagents at a constant flow-rate throughout. In SIA, however, the piston pump only works during the time strictly needed to aspirate the amount of sample and reagents needed for a given determination. As an example, a SIA monitor for determining ammonium ion in wastewater needs ten times less reagents than does a comparable FIA monitor [20]; this is of high economic and practical significance, especially with equipment that is intended to operate unattended over long periods (e.g. automatic analyzers for field measurements).

   Also, the fact of using piston pumps makes SIA a more robust technique. Since, its predecessors (FIA and SFA) use peristaltic pumps as liquid drivers and these operate with tubing made of materials which are relatively easily damaged by some fluids (viz. acids, bases and, especially, solvents); by contrast, piston pumps use glass or polytetrafluoroethylene (PTFE) tubing, which are highly inert and ensure a long life time. Furthermore, in SIA, the propulsion system holds mostly the carrier solution, that is to say, the sample, reagents and solvents seldom reach it.

   One difficulty of SIA operation arises from the way plugs are stacked; this hinders mixing of the sample and reagents (especially with more than two, which require using a sandwich technique that consists on inserting sample plugs between two reagents zones, improving the mixture of them). When many reagents are required a feasible solution could be using a mixing chamber [21] in one of the side ports to homogenize the different sample/reagent mixtures with the aid of a magnetic stirrer.

   SIA is versatile, capable of accommodating a wide variety of assays without the need for system reconfiguration, and compatible with a wide range of detectors. Nowadays, the only disadvantages of SIA in front of FIA are the lower injection frequency due to the sequential working mode and the lower mixing capacity between solutions also due to the sequential operational mode. Nonetheless, the benefits of minimizing reagents consumption and so waste generation, and the multiparametric capabilities of SIA make it a powerful tool for developing automated multiparametric environmental analyzers for field measurements.

3   SIA System for Simultaneous Determination of Nitrate and Nitrite

An automated sequential injection system for monitoring nitrate and nitrite in water samples was developed using the Griess reagent [22]. A sandwich arrangement allowed the simultaneous determination of the two parameters. Thus, nitrite was determined in one end of the sample zone by diazotization-coupling reactions and spectrophotometric detection of the azo dye formed. In the other end, nitrate was similarly determined after its on-line reduction to nitrite using a copperized cadmium column.

The system included a liquid driver, a selection valve and a spectrophotometer. The liquid driver consisted of an autoburette equipped with a 5-mL syringe and connected to a personal computer via an RS-232C serial interface. The software package AutoAnalysis (Sciware Systems, Spain) [23] was used for instrumental control, data acquisition and processing. A six-port selection valve, computer-controlled through a PC-9225 board, was used as liquid distributor. The manifold was constructed with PTFE tubing. The activation of the reduction column was carried out in three steps: first, the cadmium granules were washed with HCl and subsequently coated with copper by dipping them into a 1% $CuSO_4$ solution for ca. 1 min. Finally, the copperized cadmium granules were washed with deionized water, and packed into a methacrylate tube (40 mm length and 1.5 mm i.d.), plugged with glass wool. The reduction column was inserted between RC1 and RC2. Fig. 3 shows a schematic depiction of the SIA system for nitrate and nitrite determination.
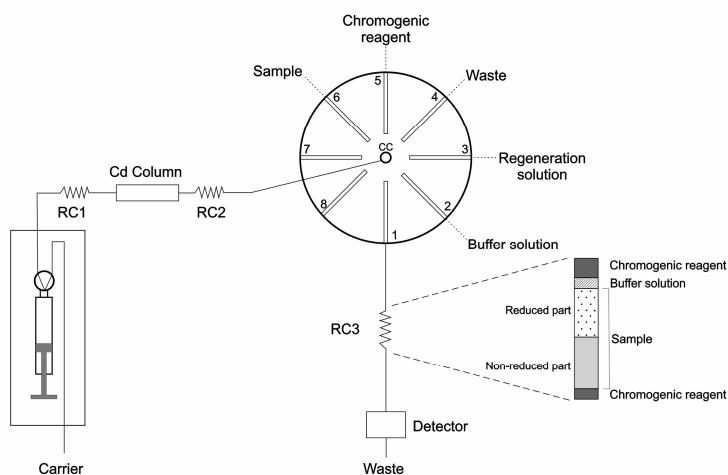

Fig. 3. Schematic depiction of the SIA system for nitrate and nitrite determination. RC: Reaction Coil.

Once the instrumental blank was set, the measuring cycle was started. The basic steps of the cycle comprised the aspiration of chromogenic reagent (Griess reagent, 50 µl) through port 5 of the selection valve, and its storage into the reaction coil RC3. Then, the sequential aspiration of buffer solution (port 2, NH_4Cl + $Na_2B_4O_7$.10 H_2O + EDTA, 40µl) and sample (port 6, 1800 µl) was carried out. Next via RC2, part of the sample passed through the reduction column where nitrate was converted into nitrite. Afterwards, the flow is reversed and the whole volume aspirated in the previous step (1840 µl) is dispensed to RC3. The buffer and sample zones were thus stacked between the valve and the chromogenic reagent introduced in the reactor previously. Next step is the aspiration of chromogenic reagent (port 5, 80 µl). Finally, the injection of the content of RC3 towards the detector takes place and absorbance measurements are registered at 540 and corrected at 420 nm.

Thereby, the sandwich arrangement, with the sample placed between two Griess reagent zones, led to the formation of the azo dye in both sub-zones of the injected sample and hence a readout with two peaks per injection was obtained, the first corresponding to nitrite alone (non-reductive conditions) and the second to nitrite plus nitrate (reductive conditions). The accuracy with which both peaks could be resolved depended on the parameters governing the mutual dispersion of reagent and sample, namely: sample and reagent volumes, zone sequencing, flow rates and length of the tubing.

Since the reduction column seemed to be the most problematic part of the entire system, its long-term stability was examined in detail. The lifetime of the reductor depended on the kind of samples analyzed. When the system was applied to the analysis of natural waters there was no need to replace the column for several months. In contrast, severe problems arose when applying the method to the analysis of wastewaters, probably due to contamination of the column. To solve this drawback a reactivating solution (port 3, 2 mL) passing through the column provided new copper to regenerate the external coating of the cadmium granules and EDTA to avoid the precipitation of $Cd(OH)_2$ or other hydroxides on the reduction column [24]. The column was finally washed with water, leaving the system ready for further analysis. Two different slopes of calibration curves for nitrite and nitrate, both under reductive conditions, were obtained. This fact indicates incomplete reduction of nitrate to nitrite, probably due to short contact times of the sample with the cadmium granules. The reduction efficiency was ca. 50%.

The main interference was that of phosphate, which caused an adverse effect even at low levels, showing a maximum tolerated concentration of 1 mg L^{-1}. The magnitude of the interference was found to be proportional to the concentration of phosphate in the sample and to the time of contact between this ion and the column. However, the column activity was restored with the regeneration process described above.

Most relevant figures of merit are shown in Table 1.

Table 1. Most relevant figures of merit of some SIA monitoring systems for the determination of key environmental parameters in water samples

SIA	Parameter	LOD	Linear working range	Repeatability (RSD, n=10)	Ref.
2 param.	Nitrate	0.006 mg N L^{-1}	0.028-1.400 mg N L^{-1}	1.3 %	[22]
	Nitrite**	0.001 mg N L^{-1}	0.007-0.560 mg N L^{-1}	0.8 %	
3 param.	Nitrate	0.021 mg N L^{-1}	0.14-1.82 mg N L^{-1}	2 %	[25]
	Nitrite**	0.002 mg N L^{-1}	0.01-0.42 mg N L^{-1}	0.5 %	
	Sulfate	3 mg SO_4^{2-} L^{-1}	75-300 mg SO_4^{2-} L^{-1}	1.3 %	
8 param.*	Hydrazine	0.01 mg N_2H_4 L^{-1}	0.03-2 mg N_2H_4 L^{-1}	1.2 %	[33]
	Ammonium	0.13 mg NH_4^+ L^{-1}	0.4-8 mg NH_4^+ L^{-1}	1.6 %	
	Iron	0.04 mg Fe L^{-1}	0.13-1 mg Fe L^{-1}	1.7 %	
	Silicate	0.03 mg SiO_2 L^{-1}	0.1-1.5 mg SiO_2 L^{-1}	2.5 %	
	Phosphate	0.05 mg PO_4^{3-} L^{-1}	0.2-1.5 mg PO_4^{3-} L^{-1}	2.2 %	

*Plus: pH, specific and acid conductivity. ** Non-reductive conditions.

4   Multiparametric Monitoring System for Sulfate, Nitrite and Nitrate Determination

A multiparametric flow analysis method for the automatic determination of nitrite, nitrate and sulfate ions in wastewater and drinking water samples based on SIA was developed [25]. Again, SIA allowed the integration of different techniques in a single manifold for monitoring of multiple environmental parameters. However, there are scarce applications to determine nitrite, nitrate and sulfate in drinking water and wastewater within the same system; mainly, due to the difficulty to keep the manifold free of precipitate after the sulfate determination by the turbidimetric method.

This analyzer exploited spectrophotometric detection after a previous chemical transformation of the analytes of interest. For the determination of nitrite, the colorimetric modified Griess reagent (sulphanilamide, N-(1-naphthyl) ethylene diamine and HCl) was used, which consists in the formation of colored azo reddish purple complex. Nitrate ion was reduced to nitrite in the presence of cadmium (Cd). Commercial cadmium grains coated with copper sulfate ($CuSO_4$) were used to fill a methacrylate column (55 mm length and 4 mm i.d.). The concentration of nitrate was calculated by the difference of TN determination and nitrite measurement. The turbidimetric method was carried out to determine sulfate. The sulfate ion precipitates in acetic acid with barium chloride ($BaCl_2$), forming barium sulfate crystals ($BaSO_4$) of uniform size. To prevent the coating of $BaSO_4$ on tubing walls a colloidal emulsifier such as arabic gum (gum acacia) was added during the sulfate analysis.

The system included a piston pump type, a selection valve and a spectrophotometer, all of them connected to a personal computer (Fig. 4). The piston pump type consisted on an autoburette equipped with a 10-mL syringe which was
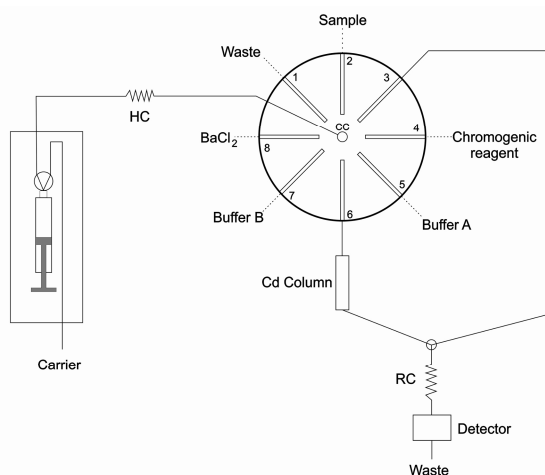

Fig. 4. Schematic depiction of the three-parametric SIA analyzer. HC: Holding Coil; RC: Reaction Coil; CC: Central Conduit.

used as liquid driver. Spectrophotometric measurements were made at 540 nm. An eight-port selection valve was used as a liquid distributor. The reduction column was inserted in the detector line between the eight-port selection valve and the reaction coil, using a three-way connector. Instrument control is performed using the software package AutoAnalysis (Sciware Systems).

Management of the sample and reagents through the selection valve was as follows: port 2 was used for sample aspiration, port 4 for the chromogenic solution, buffer solution A (NH_4Cl, $Na_2B_4O_7 \cdot 10\ H_2O$ and EDTA) and buffer solution B ($MgCl_2 \cdot 6H_2O$, $CH_3COONa \cdot 3H_2O$, KNO_3, CH_3COOH and 5% (m/v) arabic gum dissolved in water) flowed through port 5 and port 7, respectively, and the $BaCl_2$ solution was aspirated through port 8. Port 1 was employed as waste and for loading cleaning solution. The reduction column was connected to port 6. Port 3 was connected to the reaction coil and the detector.

The measuring cycle was carried out using a sandwich technique. For NO_2^- determination, the sample (2 mL) and the chromogenic solution (0.5 mL) were loaded and sent to the reaction coil and then to the detector through port 3. For NO_3^- determination, sample (2 mL), chromogenic reagent (0.5 mL) and buffer solution A (0.08 mL) were loaded from their containers and then impelled through the reduction column located in port 6; after the reduction of NO_3^- to NO_2^-, they were passed through the reaction coil and the detector. For SO_4^{2-} determination, sample (1 mL), $BaCl_2$ solution (0.5 mL) and buffer solution B (0.2 mL) were loaded through their respective ports and then sent to the reaction coil and after that to the detector. After each SO_4^{2-} determination, a washing process with the cleaning solution (EDTA in NaOH) was performed to remove the precipitate that potentially could have been added to the tubing, leaving the system ready for further assays. The column activation and regeneration were accomplished as in the previous described system for nitrate and nitrite determination proposed by Cerdà et al. [22].

Thus, the accomplished repeatability (as relative standard deviation, RSD) of 1.9% for nitrate, was lower than those acquired in different works which vary in a range of 2.3–3.7% [26-28]. However, the repetitive running of the regeneration solution not only decreased the sampling rate but also shortened the lifetime of the column due to the breakdown of the cadmium granules into smaller particles.

As described previously, the most important interference for the analytical determination of nitrate was the effect of PO_4^{3-} on the reduction column. In this approach, a concentration up to 300 mg PO_4^{3-} L^{-1} was studied without signal variations in the determination of 1.12 mg N L^{-1} of nitrate. This could be due to the higher flow rate used, causing a short contact time between the ion and the column, despite the high concentration of the phosphate ion. The determination of sulfate could be affected by the presence of cations such as Ca^{+2}, Mg^{+2} and K^+, which are commonly found in water samples. The study of interferences in the analytical determination of 200 mg L^{-1} of sulfate showed that concentrations of 500 mg L^{-1} Ca^{+2} and 40 mg L^{-1} K^+ had an interfering effect in the precipitation of $BaSO_4$, whereas 800 mg L^{-1} Mg^{+2} did not interfere.

Table 1 summarizes the major figures of merit presented by each parameter of this system. The detection limits established in the standard methods (0.1 mg N L^{-1},

0.18 mg N L^{-1}, and 1 mg L^{-1} for nitrate, nitrite and sulfate, respectively) [17] were almost completely surpassed by the ones achieved in this work, with the exception of the sulfate detection limit.

The multiparametric method was applied to tap water, groundwater and wastewater (from inlet and outlet of a treatment plant). Recovery tests were performed and results showed recoveries of 95-109%, 102-109% and 95-103% for sulfate, nitrite and nitrate, respectively. This proved a good accuracy in the working range for monitoring of these three ions by the proposed system, making it suitable for drinking water and wastewater samples.

Although regeneration process of the column and washing steps were mandatory in order to avoid the decreasing efficiency of nitrate reduction to nitrite and to prevent the adhesion of $BaSO_4$ to the tubes walls, respectively, these minor drawbacks did not affect the system performance. Moreover, the cleaning cycles were carried out in a fully automated approach. Besides, the developed system did overcome the typical interference of phosphate ion in the determination of sulfate reported at bibliography.

5   A Wastewater Quality Monitoring System

A simple portable wastewater quality monitoring system based on spectrophotometric detection was developed by Thomas et al. [20] for the measurement of BOD, COD, TOC, TSS, global N and total P. Other parameters such as nitrate, nitrite, ammonium, orthophosphate or anionic detergents can be also directly measured with this system.
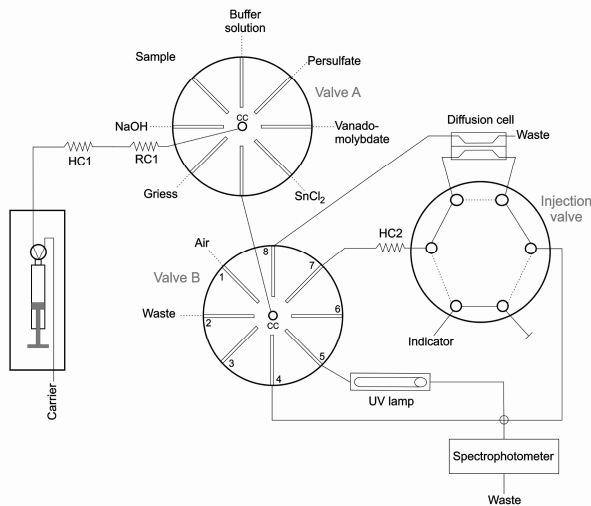

Fig. 5. Schematic depiction of the SIA wastewater quality monitoring system. RC: Reaction Coil; HC: Holding Coil; CC: Central Conduit; S: Syringe.

The proposed multiparametric monitoring analyzer was a SIA system coupled with two simple spectrophotometric detectors especially designed for the system. The SIA system consisted of a 5-mL automatic burette, a two valve multiposition module, an injection valve, a diffusion cell and a photo-oxidation reactor. Parameters were measured either by directly exploiting the UV-spectrum of the sample or by a chemical reaction with a reagent. All the operations and data acquisition were PC-controlled. Fig. 5 shows the scheme of the SIA multiparametric monitoring system.

For the analysis of BOD, COD, TOC, TSS, nitrate and detergents, a direct exploitation of the UV spectrum was used. In practice, the acquisition of spectra was carried out between 200 and 350 nm with the UV detector. The general procedure included a saturation test, a test of restitution quadratic error (between measured and restituted spectra) for the autovalidation of the procedure, and calculation of the parameters. Results for the different parameters were displayed simultaneously 30 seconds after the beginning of the spectrum acquisition.

For TN and organic phosphorus determination, UV photo-digestion was required. The digestion with UV radiation was chosen as the most convenient option for the automatic monitoring system in order to avoid potential problems caused by high temperatures and gas bubble formation usually associated with other methods such as microwave digestion. The photo-oxidation reactor consisted of a 15-W mercury lamp (λ = 254 nm) placed inside an aluminum cylinder, a PTFE tube (150 length and 1.5 mm i.d.) coiled around it and a cooling fan, which was used to keep its temperature low. The TN determination procedure can be briefly described as follows: first, the sample is sandwiched between two reagents and buffer zones, as follows: buffer (100 µL sodium tetraborate, pH 9) - oxidant reagent (30 µL potassium persulfate) - sample (50 µL) - oxidant (30 µL potassium persulfate) - buffer (100 µL sodium tetraborate, pH 9) then the mixture is propelled to the UV reactor, after 3-5 min, the mineralized mixture is pushed through the UV detector where organic and inorganic nitrogen compounds are oxidized into nitrate which is afterwards measured using the previous described UV multiwavelength procedure.

In order to determine either inorganic orthophosphates or total phosphorus (also as orthophosphates after mineralization) a reagent has to be added. The vanadomolybdate method was chosen for its good reproducibility and reagent stability to determine orthophosphates. The absorbance was read at 430 nm. For total phosphorous determination the SIA manifold was basically the same as used for orthophosphate determination, but with UV digestion. Potassium persulfate was used as oxidant and the flow was stopped for a certain time (150 s) to oxidize organic phosphorus compounds into orthophosphate. Finally, the mixture was transported to the detector for orthophosphate determination by means of the vanadomolybdo-phosphate method.

Nitrite determination was carried out using a standard colorimetric method based on a modified Griess reaction. The Griess reagent used was a mixture of sulfanilamide (SAM), N-(1-Naphthyl)ethylenediamine dihydrochloride (NED) and HCl. Absorbance was read at 530 nm [29,30]. The difference between the TN and the sum of the concentrations of nitrates and nitrites before photooxidation is the Kjeldahl nitrogen (TKN). The organic nitrogen can also be calculated.

Finally, ammonium was analyzed by a colorimetric method after conversion to ammonia with 0.01 mol L^{-1} NaOH and its diffusion through a hydrophobic membrane into the acceptor shell containing an acid-base indicator solution (bromothymol blue). The change in the absorbance, at 640 nm, of the acid-base indicator solution used as acceptor stream was measured and referred to the ammonium content in the sample.

In order to validate the proposed monitoring analyzer, results of the different parameters were compared with those of reference methods. The comparison was carried out for each parameter by calculating the correlation coefficient and by testing the validity of the following hypotheses: value of slope and intercept of the regression line (respectively 1 and 0), and validity of the linearity. For global parameter estimation (TSS, BOD, COD, and TOC) and for nitrate determination, the proposed system was tested with 85 treated wastewaters samples from several treatment plants. The correlation coefficient values (r^2), respectively 0.87, 0.73, 0.91 and 0.92, showed that the correlation coefficient were quite good for all the global parameters but for BOD, probably because the measurement principle of the reference method is very different. Moreover, this parameter was the only one with a negative test of validity (slope different from 1). For the other parameters (ammonium, nitrite, organic nitrogen, orthophosphate and organic phosphorus), SIA procedures were optimized and tested with a series of standard solutions and of real samples [29-32]. In conclusion, for almost all the parameters tested, the correlation coefficient values were close to or greater than 0.9 and the validity test was always positive, showing that the proposed monitoring system could be an excellent alternative to current reference methods for wastewater quality monitoring. Furthermore, being a much simpler, economic, handy multiparametric analyzer.

6 SIA System for Monitoring the Water Quality in the Energy Cogeneration System of a Municipal Waste Incinerator

Leading-edge urban solid waste ashing plants use burning heat energy to obtain electrical power. Water fed to their boilers for conversion into steam should be highly pure in order to minimize corrosion, scaling and similar phenomena, which can lead to malfunctioning and a reduced useful life. This highlights the need of a proper management and control of the water supply. A multiparametric monitor based on sequential injection analysis for the sequential determination of up to eight parameters, namely: pH, specific and acid conductivity, hydrazine, ammonium, phosphate, silicate and total iron, was developed by Bauzá et al. [33].

Acid conductivity was determined by passing the sample through a cation-exchange resin in order to retain ammonium ion and release protons. This parameter was deemed the most accurate indicator of dissolved solids in boiler water. Chemical parameters were determined spectrophotometrically: hydrazine by reaction with p-dimethylaminobenzaldehyde, ammonium by the modified Berthelot reaction, iron with o-phenanthroline, and phosphate and silica by formation of a molybdoheteropoly blue dye in the presence of ascorbic acid as reductant.

The system consisted of a multisyringe burette equipped with four 10-mL syringes, a selector module consisting of two 10-way selection valves, an autosampler, a conductimeter equipped with a temperature probe, a homemade conductivity cell made of poly(methyl)methacrylate (PMMA) and gold-coated bronze tubular and wall-jet electrodes, a column (53 mm length and 4 mm i.d.) used to measure acid conductivity also made from PMMA, a pH-meter equipped with a cell which closely mimicked a batch system involving immersion of the electrode in solution, a glass–Ag/AgCl microelectrode (3mm diameter), a Hewlett–Packard HP 8452A diode array spectrophotometer equipped with a 18μl flow-cell (10 mm light path) and a personal computer to govern the system and acquire data by using three communication channels (viz. two RS232 serial ports for the pH-meter and the multisyringe, and an HP-IB parallel port for the spectrophotometer). Instrumental control and data acquisition was carried out by software AutoAnalysis (Sciware Systems). The manifold was constructed with PTFE tubing. Fig. 6 shows the scheme of the SIA monitor.

The procedure for conductivity and acid conductivity involved using valve B and syringe 4 to drive the sample (7 mL) toward the measuring cell. Conductivity measurements were made under continuous-flow conditions since they avoided baseline drifts. Acid conductivity was determined similarly except that the sample (5 mL) was passed through the cation-exchange resin. The resin was found to be able to process up to 60 samples without the need for regeneration. However, the column was regenerated (7 mL of 1mol L^{-1} HCl and 100 mL of distilled water) after each working day in order to ensure optimum conditions operation of the system. Hydrazine was determined by reaction with p-dimethylaminobenzaldehyde (DAB), using valve A and syringe 2 in the multisyringe to aspirate the reagent (0.8 mL) and the sample (0.2 mL). A wait of 30 s allowed a yellow quinone to form, then the colored compound was propelled to the detector for absorbance measurement at 455 nm (with correction at 650 nm). Iron was determined by reaction with o-phenanthroline. Valve B and syringe 3 were used to aspirate hydroxylamine (0.1 mL), sample (0.3 mL) and o-phenanthroline (0.05 mL). The mixture was driven to the spectrophotometer for measurement of the absorbance difference (A_{510}–A_{650}).

Ammonium determination was based on the modified Berthelot reaction. In the first step, ammonium reacted with hypochlorite to form chloramine, which then reacted with phenol to obtain indophenol blue. This reaction was quite slow and required the presence of a catalyst (sodium nitroprusside) in addition to heating and stopping the flow for 1 min in a water bath at 45 ºC in a knotted reaction coil (KRC). By the use of valve A and syringe 2, the hypochlorite (0.2 mL), the sample (0.35 mL) and the salicylate (0.35 mL) were aspirated. Absorbance measurements of the reaction product were made at 640nm (spectral oscillations caused by changes in refractive index were corrected by subtracting the absorbance at 800 nm).

Silicate and phosphate determinations were based on kinetic differences in the formation rates of their molybdoheteropoly blue derivatives. The procedure started by using valve A and syringe 1 to aspirate the molybdate for silicate determination (0.35 mL) and sample (1 mL) via a thermostated coil (1 min at 45 ºC). Meanwhile, the determination of phosphate by using syringe 2 to aspirate antimonyl tartrate–oxalic
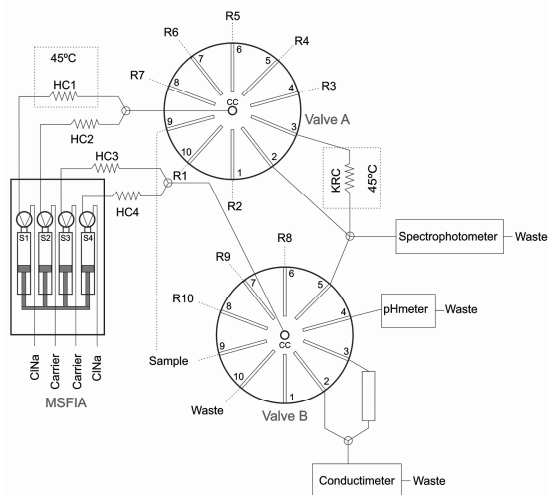
Fig. 6. Schematic depiction of the SIA system for monitoring water in the energy cogeneration system of a municipal waste incinerator. R1: Salicylate; R2: Hypochlorite; R3: Tartrate; R4: Oxalic Acid; R5: Ascorbic Acid; R6: Molybdate; R7: DAB; R8: Hydrochloric Acid; R9: Hydroxylamine; R10: o-phenantroline; HC: Holding Coil; KRC: Knotted Reaction Coil; S: Syringe.

acid buffer (0.25 mL), ascorbic acid (0.30 mL), ammonium molybdate (0.20 mL) and sample (0.75 mL) was performed. Finally, a reaction mixture volume of 4 mL was propelled to the detector for measurement of the absorbance difference (A_{650}–A_{774}). This procedure was followed to determine silicate, which involved aspirating ascorbic acid (0.7 mL), and oxalic acid (0.35 mL), adding to the mixture of the thermostated coil and driving to the detector for spectrophotometric measurement (A_{810}–A_{550}).

The pH was simultaneously determined with silicate and phosphate, using valve B and syringe 4, the sample (3.0 mL) was propelled to the pH electrode for measurement ensuring that it would not be diluted on its way to the measuring electrode and that the cell holding the sample would be properly rinsed with it.

Potential interferences to determine hydrazine were examined (i.e. iron, silicate, phosphate and ammonium). Silicate and phosphate concentrations up to 10 mg L^{-1} resulted in no signal change. Silicate levels in the studied sample type are usually in the µg L^{-1} region and phosphate is usually present in samples from the reboiler, at concentrations close to 1 mg L^{-1}. Iron and ammonium exhibited no interfering effect at concentrations 100 times higher than that of hydrazine. Any interference from iron would have been rather unexpected; in fact, this metal is rarely encountered among these analyses unless the system is corroded. Potential interferences for iron determination were studied at concentrations up to 50 mg L^{-1} for ammonium, and 10 mg L^{-1} for silicate, phosphate and hydrazine, none was found to have an appreciable effect on the analytical signal. In the case of ammonium determination, silicate exhibited no interfering effect at concentrations 50 times higher than that of

ammonium. Phosphate and iron at concentrations up to 20 times higher than that of the analyte were found not to interfere, and so was hydrazine at equal concentrations to ammonium—which is usually the case in water from energy cogeneration plants. In the simultaneous determination of phosphate and silicate, the addition of tartaric acid was found to prevent the formation of molybdosilicate in the time span of the experiment—and hence the interference of silicate with the determination of phosphate. For the determination of silicate, the molybdophosphate was ligand-exchanged with oxalate in order to obtain phosphate and molybdo-oxalate. Because molybdosilicate is an inert species not amenable to ligand exchange with oxalate, it remained in solution for further reduction and detection. Thus, reactions required careful optimization of the working conditions in order to avoid mutual interferences.

Main figures of merit are shown in Table 1. The determinations integrated in the described monitor departed slightly from individual and separate SIA determinations due to the compromises adopted in order to be able to perform several determinations at once. Overall, the sensitivity was adequate for determining the five chemical parameters in water from a water–steam cycle at a cogeneration waste incinerator plant. Also, the precision was acceptable. The proposed monitor affords a triplicate determination of eight target parameters within 30 min.

7   Conclusions

Water and wastewater characterization is of great environmental and public health interest, thus the need of water and wastewater quality monitoring systems is highlighted. Automation provides a fast response to a large volume of samples. Particularly, SIA has proved to be an outstanding tool for developing automatic monitoring analyzers. Moreover, SIA expansibility and flexibility provide to this flow technique multiparametric capabilities unaffordable by other automation techniques. Also, SIA outfits each system with accurate control of reagents and sample volumes, of their flow rate, as well as of injection throughputs, resulting in low consumption of sample and reagents, a minimal waste generation, optimum sensitivity, good reproducibility and repeatability. Furthermore, sample handling in the sequential injection mode, which employs forward, reversed and stopped flow, can be programmed to accommodate a wide variety of assays allowing a number of operations mimicking those performed manually to be programmed by easy on-line implementation.

The four analyzers described above share some benefits such as simplicity, portability, savings, and effectiveness. It is worth pointing out that one of the proposed analyzers is able to determine up to 11 parameters within the same system by the use of low cost devices and without any system reconfiguration. Another great advantage of these automatic analyzers is the higher analysis frequency in comparison with manual routine analysis, e.g. the eight-parametric SIA system affords a triplicate determination of eight target parameters within 30 min. Therefore, these monitoring systems could be used to monitor key parameters in certain fields where the continuous assessment of these is required, e.g. wastewater treatment plants, drinking water treatment plant or industrial processes.

References

[1] Council Directive 98/83/EC on the quality of water intended for human consumption, pp. 32–54 (1998)

[2] World Health Organization (WHO) Guidelines for Drinking-Water Quality, Incorporating 1st and 2nd Addenda, 3rd edn. Recommendations, vol. 1. (2004)

[3] United States Environmental Protection Agency (USEPA) 40 CFR ch. 1(7-1-09 Edition) (2009)

[4] Council Directive 91/271/EEC concerning urban waste water treatment, pp. 40–52 (1991)

[5] Trojanowicz, M.: Advances in flow analysis. Wyley-VHC, Weinheim, Germany (2008)

[6] Skeggs, L.: An automatic method for colorimetric analysis. American Journal of Clinical Pathology 28, 311–322 (1957)

[7] Trojanowicz, M., Benson, R.L., Worsfold, P.J.: Recent developments in water quality monitoring by flow injection analysis. Trends Analytical Chemistry 10, 11–17 (1991)

[8] Alexander, P.W., Di Benedetto, L.T., Dimitrakopoulos, T., Hibbert, D.B., Ngila, J.C., Sequeira, M., Shiels, D.: Field-portable flow-injection analyzers for monitoring of air and water pollution. Talanta 43, 915–925 (1996)

[9] USEPA, ESS Method 140.4: Chloride - Automated Flow Injection Analysis (1993)

[10] USEPA, ESS Method 220.3: Ammonia Nitrogen and Nitrate + Nitrite Nitrogen, Automated Flow Injection Analysis Method (1991)

[11] Ruzicka, J., Hansen, E.H.: Flow injection analyses. I. New concept of fast continuous flow analysis. Analytica Chimica Acta 78, 145–157 (1975)

[12] Ruzicka, J., Marshall, G.D.: Sequential injection: a new concept for chemical sensors, process analysis and laboratory assays. Analytica Chimica Acta 237, 329–343 (1990)

[13] Reis, B.F., Giné, M.F., Zagatto, E.A.G., Lima, J.L.F.C., Lapa, R.A.: Multicommutation in flow analysis. Part 1. Binary sampling: concepts, instrumentation and spectrophotometric determination of iron in plant digests. Analytica Chimica Acta 293, 129–138 (1994)

[14] Cerdà, V., Estela, J.M., Forteza, R., Cladera, A., Becerra, E., Altimira, P., Sitjar, P.: Flow techniques in water analysis. Talanta 50, 695–705 (1999)

[15] Lapa, R.A.S., Lima, J.L.F.C., Reis, B.F., Santos, J.L.M., Zagatto, E.A.G.: Multi-pumping in flow analysis: concepts, instrumentation, potentialities. Analytica Chimica Acta 466, 125–132 (2002)

[16] Ruzicka, J.: Lab-on-valve: universal microflow analyzer based on sequential and bead injection. Analyst 125, 1053–1060 (2000)

[17] Standard Methods for the Examination of Water & Wastewater, 22nd edn. American Public Health Association (APHA), American Water Works Association (AWWA) & Water Environment Federation, WEF (2012)

[18] Wurl, O., Elsholz, O., Baasner, J.: Monitoring of total Hg in the river Elbe: FIA-device for on-line digestion. Fresenius Journal of Analytical Chemistry 366, 191–195 (2000)

[19] Cerdà, V., Cerdà, A., Cladera, A., Oms, M.T., Mas, F., Gómez, E., Bauzá, F., Miró, M., Forteza, R., Estela, J.M.: Monitoring of environmental parameters by sequential injection analysis. Trends Analytical Chemistry 20, 407–418 (2001)

[20] Thomas, O., Theraulaz, F., Cerdà, V., Constant, D., Quevauviller, P.: Wastewater quality monitoring. Trends Analytical Chemistry 16, 419–424 (1997)

[21] Pinto, P.C.A.G., Saraiva, M.L.M.F.S., Lima, J.L.F.C.: A flow sampling strategy for the analysis of oil samples without pre-treatment in a sequential injection analysis system. Analytica Chimica Acta 555, 377–383 (2006)

[22] Cerdà, A., Oms, M.T., Forteza, R., Cerdà, V.: Sequential injection sandwich technique for the simultaneous determination of nitrate and nitrite. Analytica Chimica Acta 371, 63–71 (1998)

[23] Sciware Systems, S.L., `http://www.sciware-sl.com`

[24] Otsuki, A.: A reactivation solution for a copperized cadmium column in the automatic determination of nitrate in natural waters. Analytica Chimica Acta 99, 375–377 (1978)

[25] Ayala, A., Leal, L.O., Ferrer, L., Cerdà, V.: Multiparametric automated system for sulfate, nitrite and nitrate monitoring in drinking water and wastewater based on sequential injection analysis. Microchemical Journal 100, 55–60 (2012)

[26] Ensafi, A., Rezaei, B., Nouroozi, S.: Simultaneous spectrophotometric determination of nitrite and nitrate by flow injection analysis. Analytical Sciences 20, 1749–1753 (2004)

[27] Mesquita, R.B.R., Ferreira, M.T.S.O.B., Segundo, R.L.A., Teixeira, C.F.C.P., Bordalo, A.A., Rangel, A.O.S.S.: Development of a sequential injection system for the determination of nitrite and nitrate in waters with different salinity: application to estuaries in NW Portugal. Analytical Methods 1, 195–202 (2009)

[28] Haghighi, A., Farrokhi-Kurd, S.: Sequential flow injection analysis of ammonium and nitrate using gas phase molecular absorption spectrometry. Talanta 64, 688–694 (2004)

[29] Oms, M.T., Cerdà, A., Cerdà, V.: Sequential injection analysis of nitrites and nitrates. Analytica Chimica Acta 315, 321–330 (1995)

[30] Cerdà, A., Oms, M.T., Forteza, R., Cerdà, V.: Speciation of nitrogen in wastewater by flow injection. Analyst 121, 13–17 (1996)

[31] Oms, M.T., Cerdà, A., Cerdà, V.: Preconcentration by flow reversal in conductometric sequential injection analysis for ammonium. Electroanalysis 8, 387–390 (1996)

[32] Oms, M.T., Cerdà, A., Cladera, A., Cerdà, V., Forteza, R.: Gas diffusion techniques coupled sequential injection analysis for selective determination of ammonium. Analytica Chimica Acta 318, 251–260 (1996)

[33] Bauzá de Mirabó, F.M., Forteza, R., Cerdà, V.: A multisyringe sequential injection method for monitoring water in the energy cogeneration system of a municipal waste incinerator. Talanta 79, 1011–1020 (2009)