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A multisyringe sequential injection method for monitoring water in the energy cogeneration system of a municipal waste incinerator

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ABSTRACT

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 but can be avoided by proper management and control of the water supply. In this work, we developed a multiparameter monitor based on multisyringe sequential injection for the sequential determination of up to eight important parameters, namely: pH, specific and acid conductivity, hydrazine, ammonium, phosphate, silicate and total iron.

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. Use of the optimum chemical and physical operating conditions provided $3s_{\mathrm{blank}}$ detection limits of 0.01 mg $\mathrm{l^{-1}}$ N_2H_4, 0.13 mg $\mathrm{l^{-1}}$ NH_4^+, 0.04 mg $\mathrm{l^{-1}}$ Fe, 0.03 mg $\mathrm{l^{-1}}$ SiO_2 and 0.05 mg $\mathrm{l^{-1}}$ PO_4^{3-}, and relative standard deviations not greater than 2.5%. The methods integrated in the proposed monitor were successfully applied to real samples from the water–steam cycle at the Son Reus ashing plant in Palma de Mallorca (Spain).

1. Introduction

Water supplied to energy cogeneration boilers usually comprises condensate or boiler steam passing through the turbine or heat exchangers and externally supplied water. The latter is usually subjected to various treatments including filtering, decarbonation and demineralization in order to remove impurities. In fact, an appropriate treatment of the water in combination with efficient control of the recycled condensate and purge helps prevents corrosion, scaling and other potential sources of deterioration and shortening of the useful life of boilers.

Corrosion is no doubt the detrimental phenomenon most strongly affecting maintenance costs. In order to minimize its impact, a chemical reaction inside boilers is forced prior to first use in order to obtain a protective coating usually referred to as *magnetite* or *ferrous–ferric oxide*; this involves using pure or slightly alkaline water with a controlled oxygen content at a high temperature. Under these conditions, magnetite is poorly soluble and precipitates as a coherent, tough surface coating capable of strongly hindering ion and electron diffusion.

One of the factors leading to rapid decomposition of magnetite is an inappropriate pH in the supplied water. In fact, water pH is a crucial analytical variable with a view to ensuring proper functioning of boilers. Boiler corrosion can be efficiently minimized by using a water pH of 9.5–10.5, a small deviation from which can have substantial deleterious effects that increase rapidly as water acidity rises and eventually causes an *acid attack*. Corrosion also increases above pH 10 by effect of the formation of hydrogen, iron oxide and causticizing substances through reaction of alkaline water with boiler steel. Accurately measuring the pH of boiler water is far from easy since the water is usually very highly pure and has very low ion concentrations and a high resistivity as a result.

One other major variable here is the dissolved oxygen concentration. Properly adjusting and maintaining an appropriate oxygen level (*ca.* 20 ppb) requires the addition of hydrazine; this compound decomposes into ammonia, which acts as a volatile alkalizer. The water is also usually supplied with trisodium phosphate, which acts as a non-volatile alkalizer and simultaneously reduces water hardness by precipitating Ca and Mg as non-scaling salts that can be easily removed by purging [1,2].

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By virtue of its high sensitivity to the presence of electrolytes, conductivity is the most important factor with a view to ensuring efficient monitoring and control of water purity in the water–steam cycle. However, it is poorly selective; also, some gases present in steam (e.g. ammonia) are easily ionized at very low concentrations and can interfere with measurements of dissolved solids. The interference can be quite substantial with highly pure water. Thus, the presence of ammonia can raise the conductivity of water from 1.0–2.0 μS cm^{-1} to 8.0–9.0 μS cm^{-1} ppm^{-1} ammonia.

Ammonia can be removed by passing the water through a cation-exchange resin in order to retain ammonium ion and release protons (which will additionally reduce the alkaline pH of the medium):

$$NH_3 \leftrightarrow NH_4{}^+ + OH^- \overset{resin-H^+}{\longleftrightarrow} resin - NH_4{}^+ + H_2O$$

The outcome is therefore a reduced conductivity by effect of ammonia and a number of cations being removed, and an also reduced concentration of hydroxyl ions, which are neutralized by protons. The conductivity thus measured is known as *acid conductivity* and deemed the most accurate indicator of dissolved solids in boiler water [3].

In summary, the parameters to be controlled in order to ensure proper functioning of a boiler system are SiO_2, $PO_4{}^{3-}$, Fe, pH, N_2H_4, $NH_4{}^+$, conductivity and acid conductivity. Because their monitoring is a labour-intensive, time-consuming process, we thought it of interest to develop a dual sequential injection analysis (SIA) system for their joint determination. We chose to use SIA for this purpose on the grounds of its robustness and low reagent consumption.

The analytical methods used to determine the previous eight parameters were as follows: iron, hydrazine and ammonium with *o*-phenanthroline, *p*-dimethylaminobenzaldehyde and salicylate, respectively; phosphate and silica by formation of a molybdoheteropoly blue dye in the presence of ascorbic acid as reductant – the former with an ammonium molybdate–potassium antimonyl tartrate mixture – and conductivity and acid conductivity by using a flow-cell designed by our group—the latter parameter was determined following passage through a cation-exchange resin.

The purity of boiler water used in the water–steam systems of power plants can be controlled by using various types of analytical methods. Ion chromatography, which is among the most common choices for this purpose [4], has the advantage that it affords simultaneous determinations. Law [5] used it to determine F^-, Cl^-, $PO_4{}^{3-}$, $NO_3{}^-$ and $SO_4{}^{2-}$. Also, Kusch et al. [6] used solid-phase extraction in combination with gas chromatography and mass spectrometry for the determination of corrosion-inhibiting long-chain primary alkyl amines employed in the chemical treatment of boiler water. Flame atomic absorption spectrometry, FAAS, was used following separation and preconcentration on Amberlite XAD-1180 chelating resin chemically modified with *o*-aminophenol for the determination of Cd(II), Co(II), Cu(II), Ni(II), and Pb(II) ions [7]. George et al. [8] proposed a spectrophotometric method for determining hydrazine based on the formation of a dinitro derivative that obeys Beer's law over the concentration range of 0–0.28 μg ml^{-1} and Mori et al. [9] reported a sensitive ion-exclusion chromatographic method for determining hydrazine with a detection limit of 0.64 ng ml^{-1}. Finally, Li et al. [10] proposed the simultaneous determination of silicate and phosphate by using flow injection spectrophotometry with serially arranged flow cells; the ensuing method allowed the determination of concentrations over the range of 0.05–22 mg l^{-1} for silicate and 0.1–24 mg l^{-1} for phosphate.

Flow-based multiparameter determinations for water samples are widely documented in the bibliography. Typical examples as regards the species targeted in this work include the simultaneous determination of ammonia and phosphate proposed by Frank et al. [11], which uses sequential injection analysis, and that of Fernandes and Reis [12], based on a flow system that uses multicommutation to increase sample residence times for improved sensitivity. Cerdà et al. [13] developed an FIA system for nitrate, nitrite and total nitrogen in waster water; Thomas et al. [14] reported a wastewater monitor affording the sequential determination of up to 12 parameters including total organic carbon (TOC), chemical oxygen demand (COD) or biological oxygen demand (BOD) and particulate pollution as total suspended solids (TSS), among others; and Grudpan et al. [15] proposed a method for the simultaneous stopped-flow injection determination of phosphate and silicate using molybdenum blue. Gómez and Callao [16] recently produced a review of multicomponent analysis using flow systems where they discussed various strategies based on solid-phase extraction, sequential injection chromatography and miscellaneous approaches, multichannel manifolds, selective detectors and combinations of flow systems with chemometric processing of multivariate data.

2. Experimental

2.1. Reagents

All chemicals used were analytical-reagent grade and all solutions made in distilled water purified by passage through a Millipore apparatus. The solutions were prepared as follows:

- 4% *p-dimethylaminobenzaldehyde* by dissolving an appropriate amount of Sigma–Aldrich product in 1.5 M H_2SO_4 and storing in dark-coloured flasks.
- 0.05% *hypochlorite* by using 1 ml of domestic bleach containing 50 g active Cl_2 per litre – the solutions were standardized iodimetricaly and all bleach brands containing less than 47 g Cl_2 l^{-1} were previously discarded –, 7 ml of 1 M NaOH and 20 ml of 0.05 M sodium tetraborate decahydrate, and diluting the mixture to 100 ml with distilled water.
- 1.5 M *sodium salicylate* containing 0.8 M NaOH and 3.2×10^{-3} M sodium nitroprusside from the corresponding Sigma–Aldrich products.
- 5% hydroxylamine from hydroxylammonium chloride (Sigma–Aldrich) in distilled water.
- 0.1 M *o-phenanthroline* by dissolving the required amount of 1,10-phenanthroline hydrochloride monohydrate (Merck) in 2 M acetic acid–acetate buffer at pH 4.8.
- 0.075 M *ammonium molybdate* by dissolving ammonium heptamolybdate tetrahydrate (Merck) in 0.4 M HCl.
- 0.5 M *ascorbic acid* by dissolving the required amount of Sigma–Aldrich product in distilled water.
- 0.08 M *oxalic acid* by dissolution of oxalic acid dihydrate (Merck) in distilled water.
- 0.005–0.006 M *antimonyl tartrate–oxalic acid* by diluting a 0.1 M solution of potassium antimonyl tartrate trihydrate (Sigma–Aldrich) as required, adding 0.075 g of oxalic acid dihydrate (Merck) and diluting to 100 ml with distilled water.
- 500 mg l^{-1} *hydrazine standard* from hydrazine sulphate (Merck).
- 500 mg l^{-1} *ammonium standard* from ammonium chloride (Merck).
- 1000 mg l^{-1} *iron standard* by dissolving iron wire (Sigma–Aldrich) in HCl.
- 1000 mg P l^{-1} from potassium dihydrogen phosphate (Sigma–Aldrich).
- 1000 mg l^{-1} *silicon standard* from sodium metasilicate pentahydrate (Fluka).

In addition, we used 1 M HCl to regenerate the cation resin and 1 M NaCl as carrier solution in order to correct the effect of

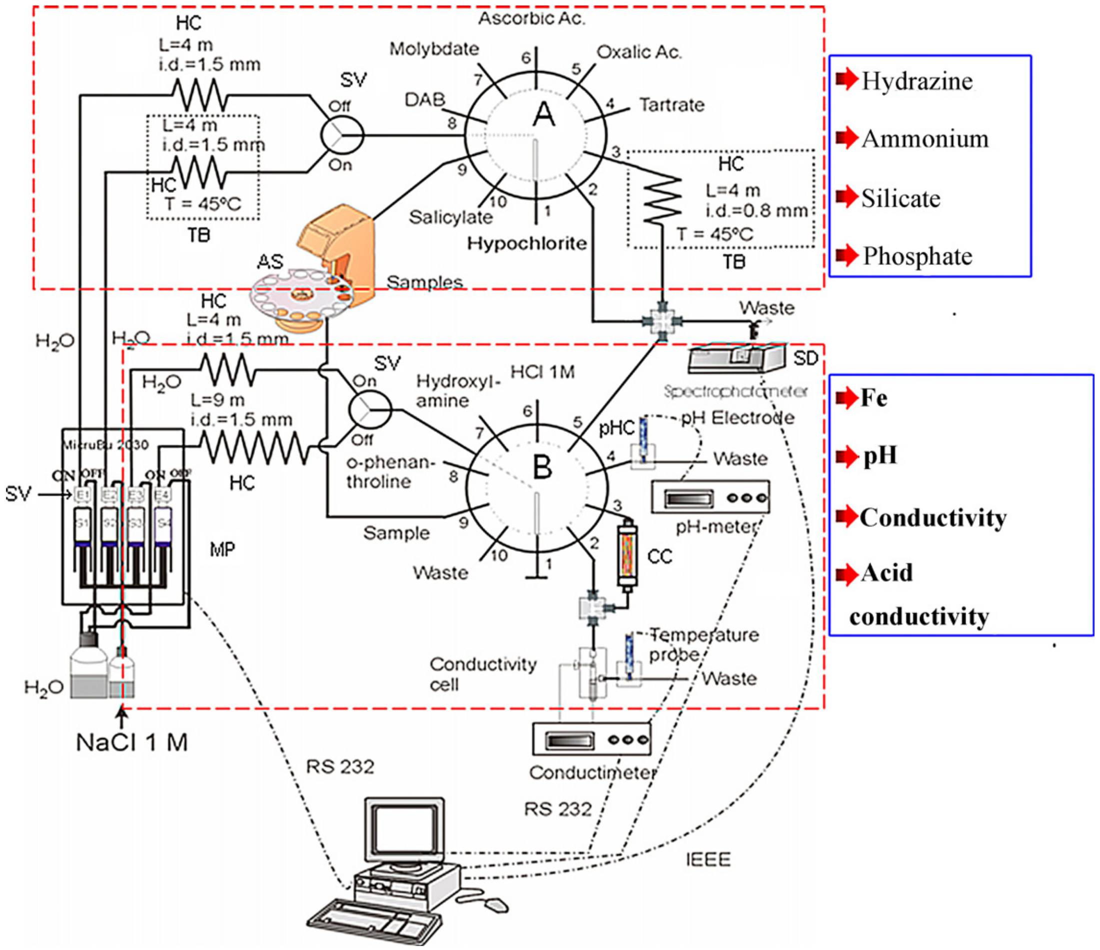

Fig. 1. Schematic depiction of the proposed monitor for the determination of eight different parameters in water from the water–steam cycle at an energy cogeneration plant. DAB: *p*-dimethylaminobenzaldehyde solution; MP: multisyringe pump; A and B: 10-way multiposition valves; SV: three-way solenoid commutation valve; HC: holding coil; TB: thermostatic bath; AS: autosampler; SD: spectrophotometric detector; CC: cationic column; pHC: pH-meter cell; S1, S3 and S4 syringes filled with H_2O; S2 syringe filled with 1 M NaCl. Inner diameter of PTFE tubing at positions 1, 4, 5, 6, 7, 8, 9 and 10 of valve A and positions 2, 3, 4, 6, 7, 8, 9 and 10 of valve B 1.5 mm; i.d. of PTFE tubing at other positions of both valves 0.8 mm. Position 1 of valve B was closed.

changes in refractive index (Schlieren effect) in the determinations of ammonium and silica.

The resin used was Dowex 50W-X8, 20– 50 mesh, from Aldrich, which is a strongly acidic gel-type cation-exchange resin (H^+ form, styrene–divinylbenzene skeletal structure).

2.2. Apparatus

Fig. 1 depicts the proposed multiparameter monitor, the main components of which are as follows:

- A multisyringe burette (*MicroBu 2030*, Crison, Alella, Barcelona, Spain) furnished with four 10-ml syringes, a module consisting of two 10-way valves (*Val 2 SV*, Crison, Alella, Barcelona, Spain), a sampler holding up to 15 samples (*MicroSampler 2040*, Crison, Alella, Barcelona, Spain), a conductimeter equipped with a temperature probe (*Model 525*, Crison, Alella, Barcelona, Spain). The conductivity cell (Fig. 2) was laboratory made from poly(methyl)methacrylate and gold-coated bronze tubular and wall-jet electrodes. The column used to measure acid conductivity was 53 mm long × 4 mm i.d. and made from poly(methyl)methacrylate as well; it was packed with cation-exchange resin by means of a Pasteur pipette. A small amount of glasswool was placed at the column ends in order to avoid resin losses. A Crison Basic 20 pH-meter equipped with a cell closely mimicked the batch system involving immersion of the electrode in solution, so it was not liquid-tight. It had an inlet channel and an outlet channel, and was 5 ml in volume. We used a glass–Ag/AgCl microelectrode 3 mm in diameter from Crison in such a way that contact with the cell walls was avoided. A Hewlett–Packard

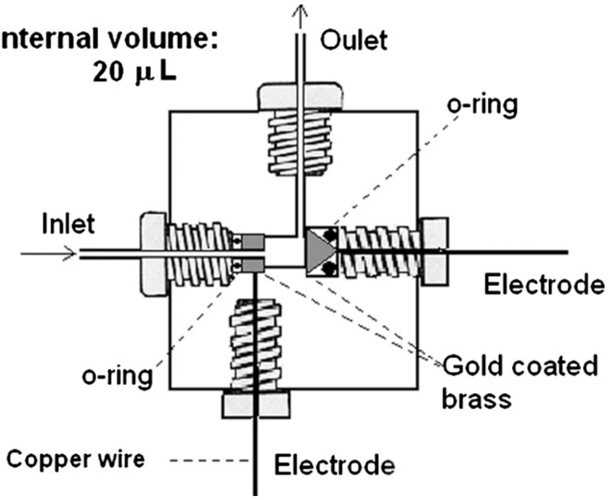

Fig. 2. Laboratory-made poly(methyl)methacrylate tubular and wall-jet conductivity cell.

HP 8452A diode array spectrophotometer equipped with a 18 μl flow-cell of 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 and an HP-IB parallel port): one serial channel was used to acquire pH readings and the other to control or acquire data from the multisyringe, sampler, conductimeter and valves; on the other hand, the HP-IB channel was employed to govern the spectrophotometer and acquire data from it. The instruments were governed and data acquired with the aid of the software AutoAnalysis (Sciware) [17], which can be very easily programmed via a graphical user interface to implement the analytical methods required for various determinations or instruments. Each method is implemented by running the command sequence needed by each individual system component. To this end, each line of the method can be opened in a separate window in order to select the instrument to be programmed. This, for example, allows the volume to be handled by the multisyringe and its flow-rate to be set. It should be noted that only one syringe volume can be set, all others being a function of their size ratios. The operator must also set the flow direction (aspiration or propulsion) and whether the flow is to be driven to the system or the reagent reservoir—this choice can be programmed separately for each syringe. The software also affords control of the supplementary three-way valves. Because it has multitasking capabilities, it allows the simultaneous implementation of analytical methods, and the acquisition and processing of data from instruments—or even interfacing to other, commercially available software.

All manifold tubing was polytetrafluoroethylene.

2.3. Procedure

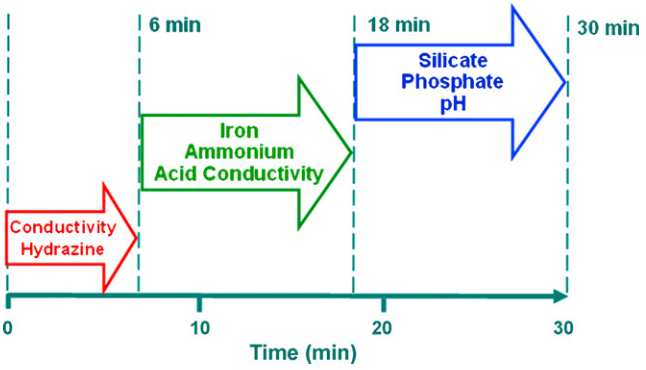

Fig. 3. Time sequence for three replicate determinations of each target parameter.

Fig. 1 depicts the proposed multiparameter determination system. The two dotted boxes contain the components used to monitor the target parameters. While all determinations could obviously have been performed simultaneously, this would have complicated the system to a great extent. Rather, we chose to conduct determinations in groups according to similarity in analysis time for practical convenience. Thus, conductivity and hydrazine were determined jointly in the first step; iron, ammonium and acid conductivity in the second; and silicate, phosphate and pH in the third. The system afforded three replicate determinations of each parameter within 30 min (Fig. 3). Hydrazine was the sole spectrophotometrically determined parameter measured in isolation; this provided three consecutive spectral peaks. On the other hand, the peaks for Fe and ammonium, and those for phosphate and silica, appeared alternately (Fig. 4).

Briefly, the conductivity and acid conductivity procedure involved using switching valve B and burette 4 in the multisyringe to flush the sample channels and measuring cell. This was followed by filling of the sample loop with 7 ml of sample and sending 9.8 ml to the measuring cell. Conductivity measurements were made under continuous-flow conditions since they gave better results than batchwise operation – they avoided baseline drifts – provided the flow-rates were kept within an acceptable range. Acid conductivity was determined similarly except that the sample aspirated and delivered volumes were 5 and 3.5 ml, respec-

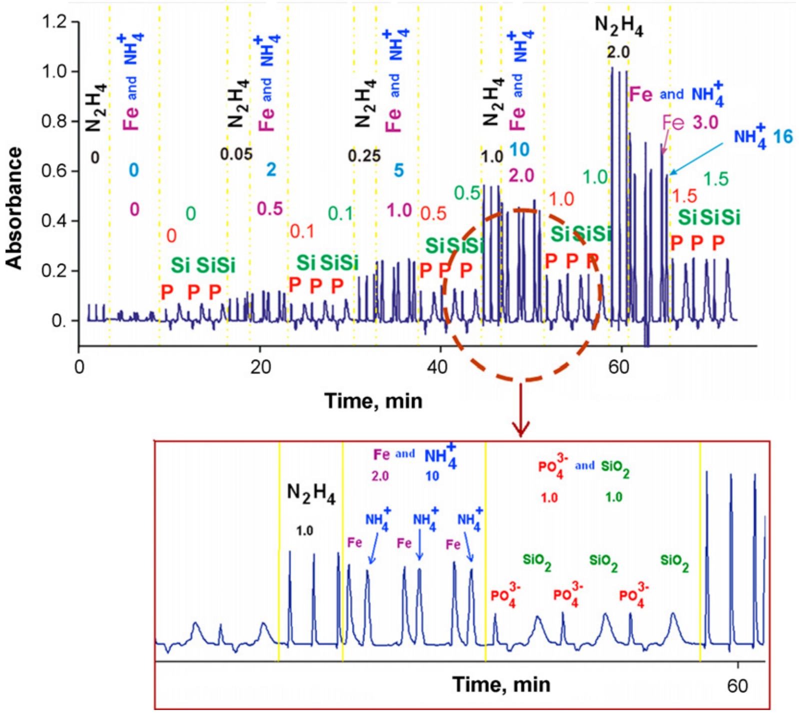

Fig. 4. SIA graph obtained in the spectrophotometric determinations. All concentrations in mg l^{-1}.

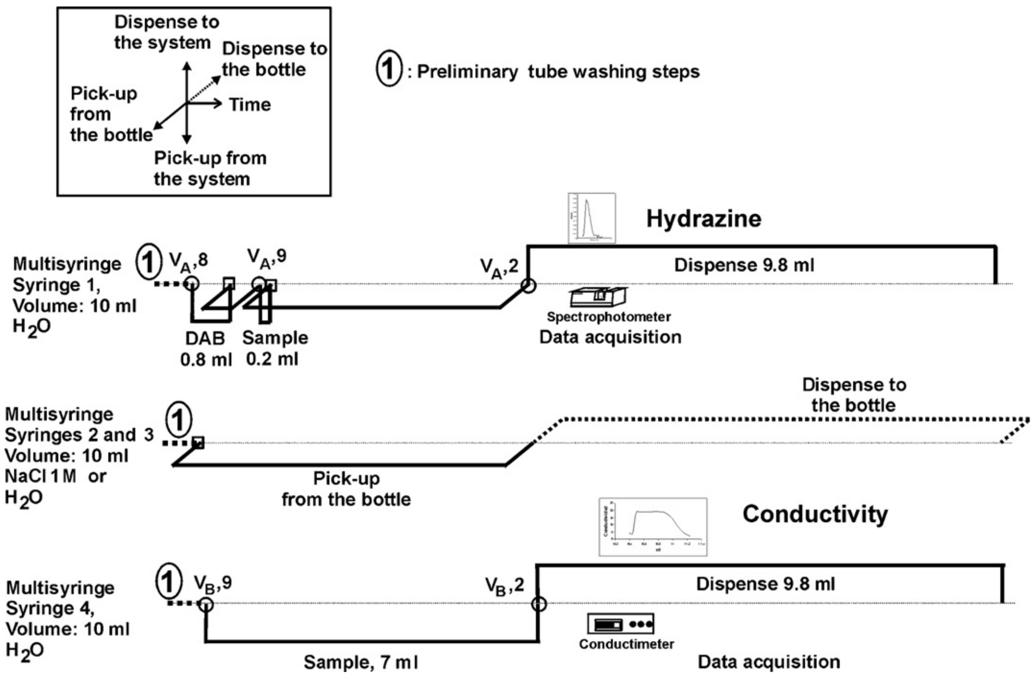

Fig. 5. Solution processing sequence for the determination of hydrazine and conductivity. The letter V followed by a number denotes the position of the 10-way multiposition valve and the solution volume handled is stated.

tively, and the sample 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 after each working day in order to ensure that the system would always operate under optimum conditions. The regeneration procedure involved passing 7 ml of 1 M HCl through the column and then flushing it with 10 ml of distilled water 10 times.

Hydrazine was determined by reaction with *p*-dimethylaminobenzaldehyde [18]. To this end, switching valve A and burette 1 in the multisyringe were used to aspirate 0.8 ml of reagent, which was followed by actuation of the valve to aspirate 0.2 ml of sample, waiting for 30 s to allow a yellow quinone to form and propelling of the coloured compound to the detector for measurement of its absorbance at 455 nm—with correction at 650 nm in order to minimize the effect of changes in refractive index (Schlieren effect). When one of the two switching valves had to be actuated, the valve mounted on the syringe head was switched off and the syringes were filled from the reservoirs in order to avoid stopping the multisyringe and prevent contamination by the reagents contained in its attached lines.

Fig. 5 shows the solution processing sequence for the determinations of hydrazine and conductivity. As can be seen, both involved using syringes 1 and 4 while 2 and 3 were emptied or filled from the reservoirs; in fact, they moved jointly with the four syringes as they were connected as a whole to the same stepper motor.

Iron was determined by reaction with *o*-phenanthroline [19]. To this end, switching valve B and syringe 3 were used to aspirate 0.1 ml of hydroxylamine, 0.3 ml of sample and 0.05 ml of *o*-phenanthroline, the mixture being driven to the spectrophotometer for measurement of the absorbance difference (A_{510}–A_{650}).

The determination of ammonium was based on the modified Berthelot reaction (viz. the use of salicylate instead of phenol) [20,21]. In the first step, ammonium was reacted with hypochlorite to form chloramine, which was then reacted with a 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 °C. The aspirated volumes (switching valve A and syringe 2) were 0.2 ml hypochlorite, 0.35 ml sample and 0.35 ml salicylate. Because it took a long time, this determination was performed in parallel with those of acid conductivity and iron. Absorbance measurements of the reaction product were made at 640 nm – spectral oscillations caused by changes in refractive index were corrected for by subtracting the absorbance at 800 nm – using a delivered volume of 8 ml. Such a volume, which clearly exceeded that needed to monitor the ammonium signal, was also used to flush the column employed to determine acid conductivity.

Fig. 6 shows the solution processing sequence for the determinations of acid conductivity, iron and ammonium. The labelling “Loading of syringes” means that the syringes were nearly empty after the previous operations and should be refilled in order to propel the ammonium solution to the detector for measurement.

The determinations of silicate and phosphate were based on kinetic differences in the rates of formation of their molybdoheteropoly blue derivatives [22–24]. Both required using switching valve A; in addition, that of silicate entailed aspirating the reagents and propelling the resulting products via appropriate coils immersed in a thermostated bath at 45 °C. The procedure started by using syringe 2 to aspirate the reagent for silicate, 0.35 ml of molybdate, and 1 ml of sample via a thermostated coil where they were allowed to stand for 1 min. This program sequence was used to proceed with parallel steps in the simultaneous determinations of pH and phosphate, albeit with the switching valve mounted on syringe head 2 OFF; this forced the carrier to come from or go to its reservoir rather than enter the system, and hence the sample and molybdate to be retained in the thermostated bath. As can be seen from Fig. 7, this lapse was used to complete the determination of phosphate by using syringe 1 and performing the following operations: flushing the tube connecting the three-way valve to switching valve A, and aspirating 0.25 ml of antimonyl tartrate–oxalic acid buffer, 0.30 ml of ascorbic acid, 0.2 ml of ammonium molybdate and 0.75 ml of sample. Finally, a reaction mixture volume of 4 ml was propelled to the detector for measurement of the absorbance difference (A_{650}–A_{774}). This was followed by the determination of silicate, which involved aspirating 0.7 ml of ascorbic acid and 0.35 ml of

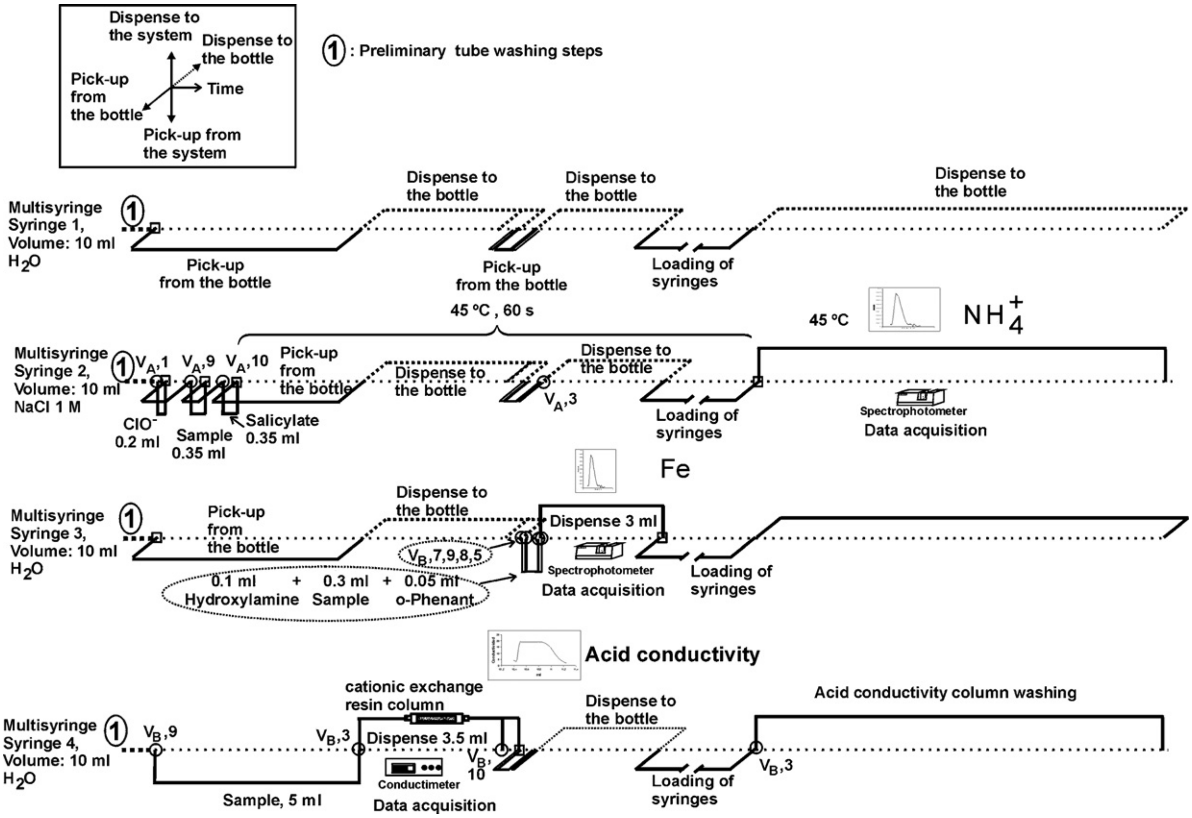

Fig. 6. Solution processing sequence for the determination of ammonium, iron and acid conductivity.

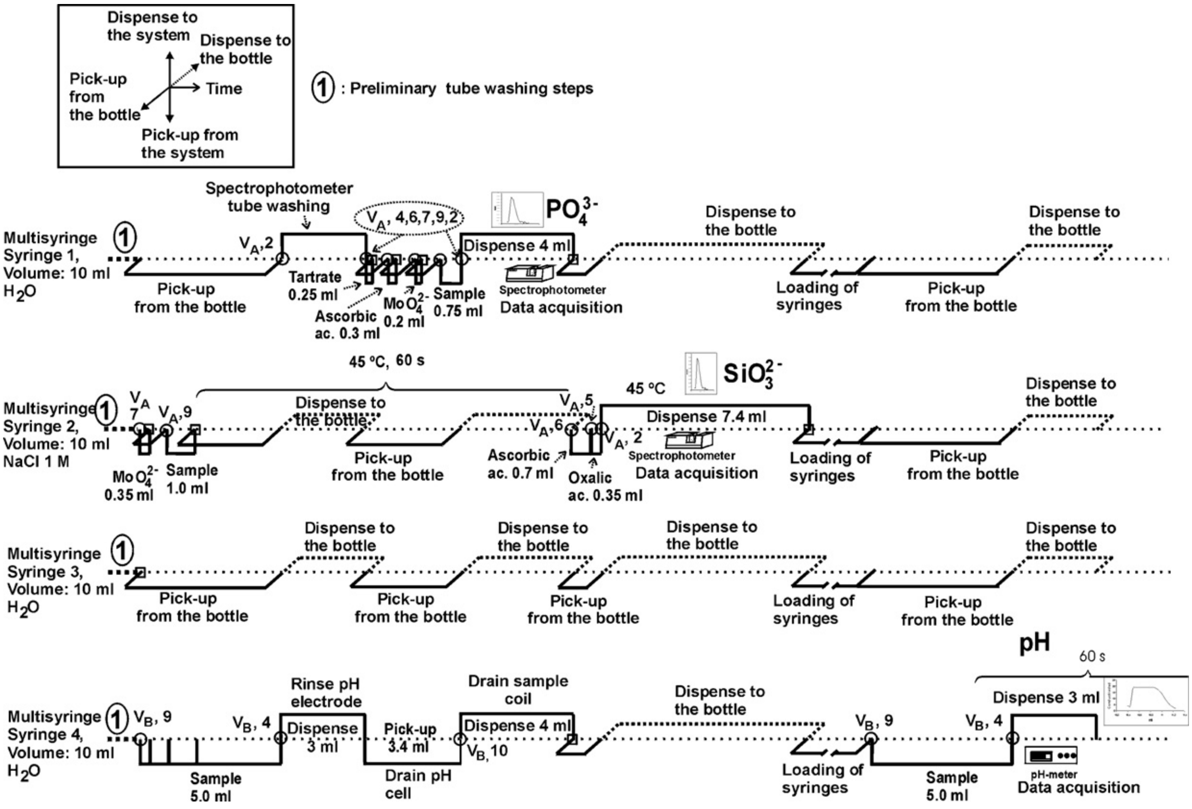

Fig. 7. Solution processing sequence for the determination of phosphate, silicate and pH.

oxalic acid, and driving 7.4 ml of the mixture, at 45 °C, to the detector for spectrophotometric measurement (A_{810}–A_{550}).

pH was determined simultaneously with silicate and phosphate, using switching valve B and syringe 4. Care was exercised to ensure that the sample would not be diluted on its way to the measuring electrode and that the cell holding it would be properly rinsed with sample. To this end, a volume of 5.0 ml of sample was aspirated and one of 3.0 ml passed through the cell holding the combined pH electrode; then, a volume of 3.4 ml was aspirated from the cell in order to ensure that it was fully emptied and 4.0 ml was sent to waste. Once the phosphate and silicate signals were acquired, a further 5.0 ml of sample was aspirated and 3.0 ml propelled to the pH electrode for measurement.

3. Results and discussion

3.1. Construction of the SIA system

We chose to use sequential injection analysis as the monitoring technique on the grounds of its robustness and automatability. Sequential injection analysis as implemented in a multiparameter monitor using a multisyringe (viz. four simultaneously moving syringes) to aspirate and propel solutions, afforded greater reagent handling flexibility than did employing a single burette and was thus a more suitable choice.

The most salient advantages of the proposed system can be summarized as follows: because it uses four syringes, it can handle four different streams simultaneously; this, in combination with the switching valves used, provides a wide range of possibilities as regards handling of reagents and mixtures. The ability to perform simultaneous determinations obviously saves time as it allows one to perform lengthy determinations together, separately from more expeditious determinations. Also, using PTFE piston heads allows both aggressive chemicals and organic solvents to be used and the restrictions of flexible tubes for peristaltic pumps in FIA avoided.

The syringes and autoburette require no maintenance; also, they can be operated for months without recalibration. This saves reagents compared to FIA as switching valves allow the analytical solutions to be introduced into the system exactly when required for a determination rather than in a continuous manner. When not needed, the solutions are sent back to their respective reservoirs instead of waste as in FIA.

The methods used to determine the target parameters in highly pure water were chosen in accordance with the following criteria:

(a) They should afford implementation of an SIA multiparameter system and the use of an acceptable number of detectors. We used a spectrophotometer, a potentiometer and a conductimeter for our determinations.
(b) They should be sensitive and selective enough for use at control laboratories in energy cogeneration plants.
(c) The methods should be simple in order to maximize robustness, minimize maintenance requirements, and use readily prepared, common analytical laboratory reagents.

Once the specific procedures for determining the target parameters were chosen, the factors potentially affecting the reactions involved were examined with provision for the fact that they would occur by diffusion of some solutions into others. The factors studied here included the geometry of the reaction tubes [length, inner diameter and shape (coiled or knotted)], hydrodynamic characteristics of the flow streams (flow-rate, waiting time, merging points), aspiration and delivery sequence, aspirated and delivered volumes, temperature and solution concentrations.

Table 1
Influence of temperature on conductivity measurements as a function of the type of sample delivered by the water–steam cycle.

Sample	Temperature coefficient (%/°C)
Boiler input	4.71
Feed tank	4.60
Reboiler 1	4.49
Reboiler 2	4.90
Steam 1	6.34
Steam 2	5.89
Condenser	5.97

After each determination was optimized separately, a set of compromise conditions was established with a view to ensuring acceptable results with as simple an analytical system as possible. Such conditions allowed the eight target parameters to be reliably determined as regards traceability to reference methods, precision and application range, all within an acceptable time. Adopting such conditions obviously led to characteristics slightly different from those for the optimal individual determinations.

3.2. Optimization of variables

This section describes some of the more salient results obtained in the process of optimizing the different determinations [25].

The conductivity and acid conductivity of samples from the water–steam cycle usually range from 0 to 25 μS cm^{-1}. We examined the influence of the following variables on them: temperature, sample volume, flow-rate per column, dimensions and volume of the ion-exchange resin, volume and concentration of HCl used to regenerate the ion exchanger, resin regeneration frequency, volume of distilled water used to rinse the column after regeneration, flow-cell arrangement and electrode material. Because ensuring that the hydrodynamic conditions in the system would result in unity dispersion at peak maxima, conductivity had to be measured in undiluted samples.

We tested tubular, wall-jet, laminar and Z-shaped conductimetric cells made of poly(methyl)methacrylate. Electrodes were constructed from graphite mixed with two-component adhesive (Ceys ARALDIT®), pressed graphite, stainless steel and gold-coated bronze. We examined the impact of the previous factors as regards sensitivity, memory effects, and bubble formation, and concluded that the best results were provided by tubular and wall-jet cells, and gold electrodes (Fig. 2).

The effect of temperature changes was examined by calculating a temperature coefficient as the percent change per degree centigrade which was found to depend on the nature of the particular ions present in solution:

$$\text{temp. coeff. } (\%/^\circ\text{C}) = \frac{\kappa_i - \kappa_{25}}{\kappa_{25}} \frac{100}{(T_i - 25)^\circ\text{C}}$$

where κ_i is the conductivity of the solution at the measurement temperature, T_i (°C), and κ_{25} that at 25 °C. Table 1 shows the temperature coefficients for the studied samples. As can be seen, they differed from one another, but were all in the region of 5%. Conductivity corrections for temperature as measured with the monitor itself were made via the software; in fact, AutoAnalysis affords input of variable values and calculation of mathematical formulae.

The column used to determine acid conductivity was packed with two different resins, namely: Dowex 50W-X8 and Amberlite IRC-50, with sulphonate and carboxyl active groups, respectively. We adopted the former for subsequent use as it exhibited a higher exchange rate.

Fig. 8 shows the influence of the regeneration frequency of the cationic column on the determination of acid conductivity as established by repeatedly using a standard to identify the point where

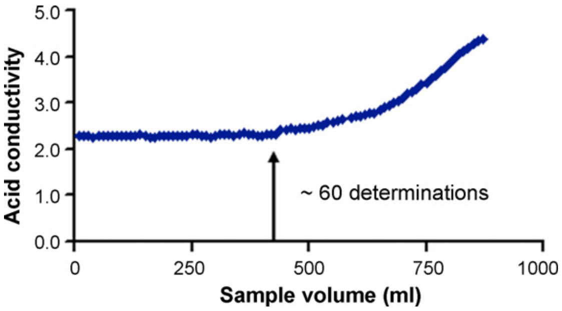

Fig. 8. Assessment of the capabilities of the column for acid conductivity measurements.

Table 2

Composition of the mixtures used to study potential interferences with the determinations of silicate and phosphate. The results for several replicates were compared via analysis of variance.

Interferences with the determination of silicate	Interferences with the determination of phosphate
1 ppm SiO_2	1 ppm PO_4^{3-}
1 ppm SiO_2 + 0.15 ppm NH_4^+	1 ppm PO_4^{3-} + 0.15 ppm NH_4^+
1 ppm SiO_2 + 0.5 ppm PO_4^{3-}	1 ppm PO_4^{3-} + 0.5 ppm SiO_2
1 ppm SiO_2 + 1 ppm PO_4^{3-}	1 ppm PO_4^{3-} + 1 ppm SiO_2
1 ppm SiO_2 + 1.5 ppm PO_4^{3-}	1 ppm PO_4^{3-} + 1.5 ppm SiO_2
1 ppm SiO_2 + 2 ppm N_2H_4	1 ppm PO_4^{3-} + 2 ppm N_2H_4
1 ppm SiO_2 + 0.05 ppm Fe^{2+}	1 ppm PO_4^{3-} + 0.05 ppm Fe^{2+}
ANOVA significance level, $p = 0.08$ (NS)	ANOVA significance level, $p = 0.18$ (NS)

NS: not significant.

the results started to exhibit substantial deviations. The column was found to be unaltered after as many as 60 determinations.

Hydrazine, ammonium and iron were determined with the usual, widely documented methods and were easily optimized and integrated into the proposed multiparameter monitor.

The determination of hydrazine – the concentration of which in the studied sample type is usually lower than 2 mg l^{-1} – was based on its reaction with *p*-dimethylaminobenzaldehyde in the presence of sulphuric acid to obtain a yellow-coloured quinone. The variables most markedly increasing the sensitivity of the reaction included the aldehyde concentration, the effect of which was examined over the range of 0.5–5% and found to increase the absorbance up to five times. The reagent solution was prepared in three different media (viz. 1 M H_2SO_4, 1 M HCl and 60% methanol); no appreciable differences between the signals thus obtained were observed.

We examined the potential interferences of iron, silicate, phosphate and ammonium. Silicate and phosphate concentrations up to 10 mg l^{-1} resulted in no signal change. No higher concentrations were studied since silicate levels in the studied sample type are usually in the microgram-per-litre 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.

The determination of iron, which is typically present at concentrations below 2 mg l^{-1} in the studied sample type, was based on the reaction between ferrous ion and *o*-phenanthroline, which required no reaction coil in the detector channel or thermostatic bath to accelerate it—in fact, the analytical reaction is very fast. No waiting time in the loading coil was necessary either; thus, increasing the waiting time was found to diminish the signal through increased dispersion of the solutions in the system. Potential interferents were studied at concentrations up to 50 mg l^{-1} for ammonium, and 10 mg l^{-1} for both silicate, phosphate and hydrazine; none was found to have an appreciable effect on the analytical reaction.

Ammonium, which normally occurs at concentrations below 7 mg l^{-1} in the studied sample type, was determined with the modified Berthelot reaction, which was preferred to the Nessler reaction [26]; in fact, the latter was interfered with by hydrazine, which gave a gray-coloured precipitate possibly resulting from the reduction of HgI_4^{2-} to mercury(I) chloride or elemental mercury. While the Nessler reaction is quite simple – it uses a single reagent – and sensitive, the modified Berthelot reaction is slow; thus, it required inserting a reaction coil in the detector channel, using a thermostatic bath in order to facilitate use of a higher temperature – the signal increased up to 50 °C – and lengthening the waiting times—the signal peaked at 70 s. Also, the impact of changes in refractive index (Schlieren effect) was minimized by replacing the original carrier (distilled water) with 1 M NaCl; this resulted in increased repeatability through decreased signal noise. 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 analyte were found not to interfere, and so was hydrazine at concentrations not exceeding those of ammonium—which is usually the case with water from energy cogeneration plants.

The simultaneous determination of phosphate and silicate, both of which typically occur at concentrations below 2 mg l^{-1} in the studied sample type, involved the reaction of both ions with molybdate in an acid medium to obtain yellow molybdophosphate and molybdosilicate, further reduction of the Mo(VI) giving the respective molybdenum blue compounds. Selectivity towards each ion was accomplished by carefully conditioning the medium in order to explore differences in the formation kinetics of the two heteropolyacids. 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

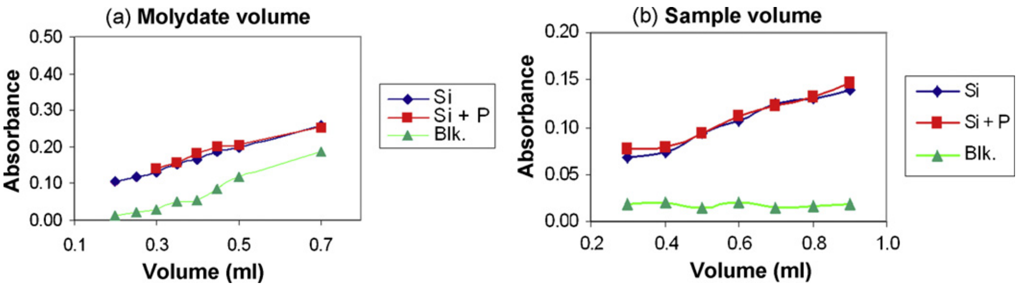

Fig. 9. Influence of the presence of phosphate on the determination of silicate. Study of the effect of the volume of (a) molybdate and (b) sample used in the determination of silicate. Si: silicate signal; Si + P: silicate + phosphate signal, Blk: blank signal.

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. The previous reactions were very similar, so they required careful optimization of the working conditions in order to avoid mutual interferences.

Fig. 9 shows the results of tests aimed at establishing the influence of the presence of phosphate on the determination of silicate. The graph compares the absorbance obtained in the presence of silicate alone and the two ions. As can be seen, increasing the volume of molybdate caused the analyte signal – and also, to a substantial extent, the blank signal – to rise. Also, increasing the sample volume by a factor of 3 caused the signal to double. Additional tests were conducted with a view to establishing the influence of the reagent volumes and concentrations, flow-rates, waiting times and absorbance wavelengths used, and also to correcting the Schlieren effect.

Finally, potential interferences of other ions with the determinations of silicate and phosphate were examined by replicate analysis of various solutions and mixtures. An ANOVA of the results revealed a significance level, p, of 0.08 for silicate and 0.18 for phosphate (i.e. greater than 5% in both cases) [27] (Table 2).

pH measurements were far from easy as the samples consisted of highly pure water containing very low ion concentrations and exhibiting a low conductivity. We used both a combined glass–Ag/AgCl electrode fitted with a planar membrane in a air-tight cell [28] and a batch, stopped-flow regime involving the use of an open cell and a glass–Ag/AgCl microelectrode 3 mm in diameter that was supplied with an appropriate volume of sample in order to ensure negligible sample dispersion ($D = 1$). The better results were provided by the latter choice, which was that more closely resembling manual measurements.

3.3. Features of the determinations of the five chemical parameters

The most salient features of such determinations are summarized in Table 3. As can be seen, the determinations integrated in the proposed monitor departed slightly from individual and separate SIA determinations under their corresponding optimal conditions used in this work by effect of 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 plant. Also, the precision was acceptable.

The proposed monitor affords a triplicate determination of the eight target parameters within 30 min.

Fig. 4 shows the SIA signals for various standard solutions of hydrazine, iron, ammonium, phosphate and silicate as obtained using the above-described procedure.

Table 3
Analytical figures of merit of the spectrophotometric determinations.

	Monitor determination	Separate SIA determination[a]
Hydrazine		
Linear range[b]	0.03–2 mg l^{-1} N_2H_4	0.15–10 mg l^{-1} N_2H_4
Detection limit[c]	0.01 mg l^{-1} N_2H_4	0.05 mg l^{-1} N_2H_4
%R.S.D. ($n = 10$)	1.2% (0.25 mg l^{-1} N_2H_4)	3.6% (1 mg l^{-1} N_2H_4)
Ammonium		
Linear range[b]	0.4–8 mg l^{-1} NH_4^+	3.3–20 mg l^{-1} NH_4^+
Detection limit[c]	0.13 mg l^{-1} NH_4^+	1 mg l^{-1} NH_4^+
%R.S.D. ($n = 10$)	1.6% (2.5 mg l^{-1} NH_4^+)	0.9% (5 mg l^{-1} NH_4^+)
Iron		
Linear range[b]	0.13–1 mg l^{-1} Fe	0.13–12.5 mg l^{-1} Fe
Detection limit[c]	0.04 mg l^{-1} Fe	0.04 mg l^{-1} Fe
%R.S.D. ($n = 10$)	1.7% (0.5 mg l^{-1} Fe)	2.6% (5 mg l^{-1} Fe)
Silicate		
Linear range[b]	0.1–1.5 mg l^{-1} SiO_2	
Detection limit[c]	0.03 mg l^{-1} SiO_2	
%R.S.D. ($n = 10$)	2.5% (2.5 mg l^{-1} SiO_2)	
Phosphate		
Linear range[b]	0.2–1.5 mg l^{-1} PO_4^{3-}	
Detection limit[c]	0.05 mg l^{-1} PO_4^{3-}	
%R.S.D. ($n = 10$)	2.2% (1 mg l^{-1} PO_4^{3-})	

[a] Results obtained by initial optimization performed in this work.

[b] Lower limits equal to the concentration of substance providing signals equal to 10 times the standard deviation of the blank and upper limit equal to the concentration deviating by more than 3% from linearity [29].

[c] Detection limits were calculated as the concentrations of the respective substances providing signals equal to three times the standard deviation of the blank [30].

Table 4
Comparison of the results obtained in the determination of the eight target parameters with the proposed monitor and the reference method.

Sample	Conductivity (μS cm^{-1})		Acid conductivity (μS cm^{-1})		Hydrazine (mg ml^{-1})		Fe (mg ml^{-1})	
	Monitor	Reference method	Monitor	Reference method	Monitor	Reference method	Monitor	Reference method
Boiler input	17.5	17.1	2.8	2.7	0.010	0.017	<DL	<DL
Feed tank	19.8	20.0	2.9	3.4	0.486	0.457	0.04	0.03
Reboiler 1	14.4	15.4	5.1	4.0	0.150	0.127	0.04	0.02
Reboiler 2	13.3	14.1	4.8	3.6	0.064	0.066	0.06	0.05
Steam 1	17.7	19.2	2.3	2.8	<DL	<DL	<DL	<DL
Steam 2	17.5	18.9	2.6	3.7	<DL	<DL	<DL	<DL
Condenser	17.8	19.8	2.8	3.0	0.067	0.082	<DL	<DL
n		48		48		50		10
p		0.18		0.40		0.66		0.73

Sample	Ammonium (mg ml^{-1})		SiO_2 (mg ml^{-1})		Phosphate (mg ml^{-1})		pH	
	Monitor	Reference method	Monitor	Reference method	Monitor	Reference method	Monitor	Reference method
Boiler input	18.56	18.80	<DL	<DL	<DL	<DL	9.55	9.52
Feed tank	22.13	21.70	<DL	<DL	<DL	<DL	9.53	9.65
Reboiler 1	5.69	4.90	1.32	1.22	0.10	0.06	9.28	9.25
Reboiler 2	6.14	5.90	0.67	0.53	0.80	0.86	9.24	9.07
Steam 1	18.94	15.30	<DL	<DL	<DL	<DL	9.66	9.77
Steam 2	19.39	18.30	<DL	<DL	<DL	<DL	9.56	9.55
Condenser	17.41	17.50	<DL	<DL	<DL	<DL	9.58	9.67
n		50		16		18		44
p		0.20		0.60		0.24		0.13

p: significance level of the t-test of means for paired samples. n: number of paired samples.

3.4. Analytical applications

The studied samples were obtained from TIRME, an urban solid waste (USW) ashing plant near the city of Palma de Mallorca (Spain) that uses an energy cogeneration system. The plant can process up to 300 000 tons of USW and produce up to 34 MW of electrical power each year. The facilities include two operating ashing lines and elements shared by both. Analyses are performed on seven different samples: one from the water feeding tank – which receives externally supplied water or water from the condensate – one from the boiler input, two from each reboiler – the point where the phosphate was added – two of steam from the boiler and one from the air condenser.

Table 4 shows selected results obtained in the determination of the eight target parameters with the proposed monitor and the reference method used at the plant laboratory [1]. The data include the results of hypothesis tests conducted in order to compare the means for paired samples (*t*-tests). As can be seen from the *p* values obtained, the differences between the results provided by the proposed monitor and reference method were not significant at $p = 0.05$.

4. Conclusions

The proposed monitor allows the determination of eight important physico-chemical parameters in water from water–steam systems in cogeneration plants with a high degree of automation, which saves much time relative to conventional batch determinations; in fact, the monitor can perform a triplicate determination of the eight target parameters within only 30 min—by contrast, their batch determination would have taken several hours. The monitor surpasses conventional alternatives in simplicity, expeditiousness and precision; also, it minimizes reagent consumption – and can thus be deemed environmentally friendly – by using an SIA configuration, and maximizes flexibility and robustness by use of a multisyringe. The ability to easily, expeditiously obtain the results allows any corrective actions to be immediately applied.

Finally, we should emphasize the high operational flexibility afforded by software such as AutoAnalysis, which features open, hardware-independent design, and multisyringe flow systems, and can be readily adapted for determining additional parameters of interest in water from water–steam systems.

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