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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 $3s_{blank}$ detection limits of 0.01 mg l^{-1} N_2H_4, 0.13 mg l^{-1} NH_4^+, 0.04 mg l^{-1} Fe, 0.03 mg l^{-1} SiO_2 and 0.05 mg 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 $\mu S\,cm^{-1}$ to 8.0–9.0 $\mu S\,cm^{-1}\,ppm^{-1}$ 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 $\mu g\,ml^{-1}$ 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