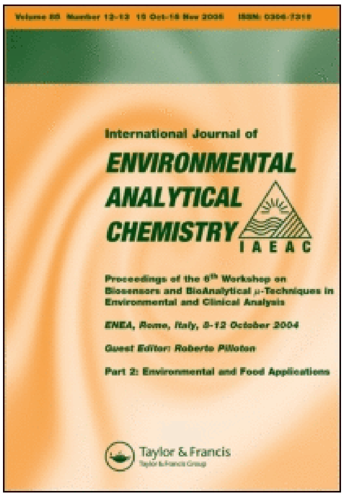

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Determination of Phenolic Compounds in Waste Waters by Sequential Injection Analysis and Spectrophotometry

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DETERMINATION OF PHENOLIC COMPOUNDS IN WASTE WATERS BY SEQUENTIAL INJECTION ANALYSIS AND SPECTROPHOMETRY

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A sequential injection analysis (SIA) system based on oxidative coupling of phenolic compounds with 4-aminoantipyrine (4-AAP) in alkaline solution and spectrophotometrical measuring of the absorbance at 510 nm has been developed for the determination of phenolic compounds in wastewaters. The proposed system is fully automatized and is able to monitor phenolic compounds in samples at a frequency of about 24 samples per hour with a relative standard deviation (RSD) better than 0.6%. The calibration graph is linear between 0.05 and 25 mg.dm^{-3}.

Keywords: Flow system; spectrophotometric; sequential injection analysis; phenolic compounds; wastewaters

INTRODUCTION

Phenolic compounds are often considered to be man-made organic pollution. They are present in the waste effluents of several industrial plants (p.e., petroleum, organic chemicals and steel) and have been extensively used as pesticides, herbicides and fungicides[1]. The environmental concern of phenol pollution results from the high toxicity of many substituted phenolics to mammals, fish and other aquatic lives[2].

Various methods have been reported for phenol determination, including spectrophotometry[3–5], fluorimetry[6], gas chromatography[7–9] and high perfomance liquid chromatography[8,10,11]. The spectrophotometric methods of analysis are the

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most frequently employed for the determination of the sum of compounds possessing a phenolic moiety. Moreover, the susceptibility to interferences should be low.

The official standard method commonly used in several countries [12,13] is based on oxidative coupling of phenol with 4-aminoantipyrine (4-AAP) in alkaline solution.

Automatic systems for on-line process control based on flow analyses were developed and used in the monitorization of chemical species in industrial effluents. Simplification of the system design for flow injection analysers yielding their application in process control is important. Robustness, reliability, long-term stability and low frequency of maintenance of process analysers is required. While manual reconfiguration of the flow channel, high reagent consumption due to continuous flow operation, frequent servicing of peristaltic pumps and frequent recalibration of the system is acceptable in laboratory applications, these are obstructive in terms of cost and manpower in a process environment. The sequential injection analysis (SIA) comprising only a single propulsor system, single valve and a single channel has been conceived and allowed to overcome the difficulties related to the conventional flow systems.

While in flow injection analysis (FIA) the sample zone is injected into a flowing carrier stream and auxiliary reagents are merged with it on the way to the detector, SIA is based on a different approach. Using a selector (rather than injection) valve, a washing solution, sample zone, and reagent zone(s) are sequentially injected into a channel. Therefore, a stack of well defined zones is obtained which is then injected through a reactor into a detector. The flow reversal as a result of the injection step creates a composite zone in which sample and reagent zone merge together due to combined axial and radial dispersion[14–17].

This paper describes a SIA system for the determination of phenolic compounds, using the oxidative coupling with 4-AAP, in wastewaters. The parameters that affect this determination were evaluated. The working charateristics of this system show to be rapid, sensitive and accurate, and easily adapted to on-line process measurements.

EXPERIMENTAL

Reagents and solutions

Solutions were prepared using high purity water, with a conductivity less than 0.1 $\mu S.cm^{-1}$. Analytical grade reagents were used.

A stock solution of phenol was prepared as usually done in the standards methods [12]. Phenol (1g.dm^{-3}) was initially dissolved in few milliliters of 0.1M sodium hydroxide and then with water. Working standards were daily prepared by appropriate dilution with water.

A buffer solution comprised 5.2g $NaHCO_3$, 5.8g H_3BO_3 and 6.2g KOH per dm^3 of water. One of the reagents was prepared by dissolution of 4-AAP (1 g) in buffer. The pH of this reagent solution was accurately adjusted to 10.2±0.2 by the addition of potassium hydroxide or hydrochloric acid. The oxidizing reagent was prepared by dissolution of 3 g $K_3[Fe(CN)_6]$ in 1dm^3 of water. The pH was adjusted to 11 with sodium hydroxide. Both reagent solutions had to be prepared at the beginning of each working day.

The wastewaters samples were from wood industry.

Equipment

The sequential injection system used was composed of individual components. A CRISON microBU 2031 (Crison instruments, Alella, Spain) with a 5 mL syringe was used as propulsor system. The liquids were propelled or aspirated at a constant flow-rate between 0.1–3 cm^3.min^{-1}.

A multiposition selection valve VICI (Valco Instruments Co. Inc.) with 8 inlets and 1 central outlet was used as injection system.

The manifolds were built from PTFE tubing (0.8 mm i.d.) with Gilson conectors. The confluence used was Perspex made.

A spectrophotometer UV/VIS JENWAY 6105, equipped with an 18µL flow-through cell of 1 cm path length was used for absorbance measurements at 510 nm. The detector output was recorded on a Kipp & Zonen recorder and signal evaluation was made by peak-height measurement.

The data acquisition control unity consisted of a microcomputer, whose software (written in QuickBasic) was developed for the manifold control. The comunication between the microcomputer and the burette was made by standard serial RS2321 protocol, whereas digital TTL signals, using an Advantech model 818 interface card was used for the connection with the valve. The same interface card was used for data acquisition.

Conventional procedure

The quality of the results obtained by the SIA system was assessed by comparison with those obtained by the conventional method. Therefore, the procedures suggested by the "Standard Methods for the Examination of Water and Wastewater"[12] (Direct Photometric Method) were applied.

RESULTS AND DISCUSSION

The simple manifold used for the phenolic compounds determination by SIA is depicted in Figure 1. The respective working parameters have been studied. Once established the optimal conditions of operation, the analytical features of the system have been determined and the quality of the results assessed.

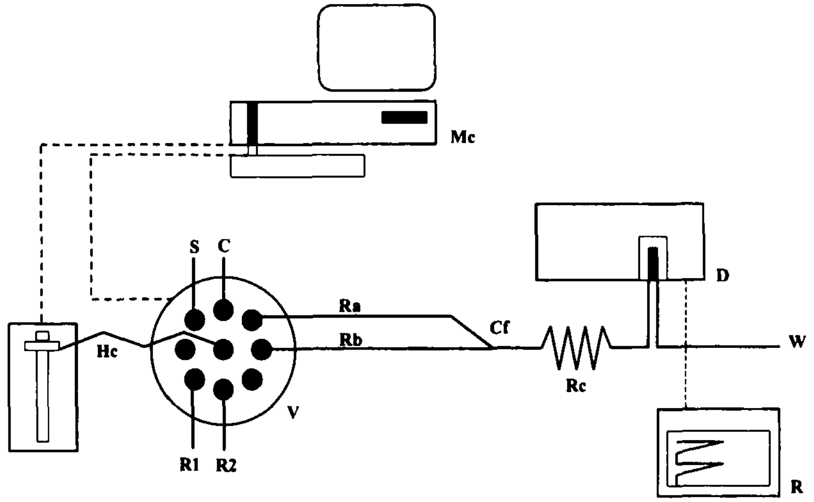

FIGURE 1 SIA manifold used in the determination of phenolic compounds in waters. S- sample; C- carrier; R1- 4-AAP (1 g.dm^{-3}), R2- $K_3[Fe(CN)_6]$ (3 g.dm^{-3}); B-automatic burette; V- valve; D- detector; R- recorder; Mc- microcomputer; Cf-confluence; Hc- holding coil; Ra= 40 cm; Rb= 80 cm; Rc= 100 cm

System optimization

The analysis by the proposed system consists basically in the sequential aspiration of well defined reagent and sample zones which are adjacent to each other in a holding coil. After the valve has been moved to the detector position, the flow is reversed and the zones mutually disperse and merge in each other as they pass through a reaction coil towards the detector. For the phenolic compounds determination with the developed system (Figure 1), a measuring cycle comprised the following operations: aspiration of carrier and introduction on the pathway to the detector, aspiration of sample and 4-AAP to the holding coil and, by reversing the flow, introduction of the mixture in Ra; aspiration of $K_3[Fe(CN)_6]$ to the holding coil and introduction in Rb. Sequentially, $K_3[Fe(CN)_6]$ from Rb, mixture from Ra and $K_3[Fe(CN)_6]$ from Rb, followed by carrier, was introduced in the pathway to the detector. The coloured compound formed during this sequential procedure was detected spectrophotometrically and recorded.

In order to optimize the proposed SIA manifold, the influence of the hydrodynamic and chemical parameters on the magnitude of the peak height, reproducibility and accuracy of the results were studied. Experimental parameters were optimized by an univariate approach.

The chemical conditions using 4-AAP in phenolic compounds determination have been reported before[5,12]. Accordingly, the oxidative coupling reaction was performed in alkaline buffer solution using $K_3[Fe(CN)_6]$ as oxidizing agent. Special attention was given to the sequence of the reagents introduction and to pH control. The pH of the buffer should be 10±0.2, and its strength had to be high enough to maintain this value during the mixing of the sample with the reagents, hence granting low pH interferences. The pH of the $K_3[Fe(CN)_6]$ solution had to be 11. The addition of 4-AAP to the sample for coupling reaction was prior to $K_3[Fe(CN)_6]$ addition to the oxidizing process.

$K_2S_2O_8$ and $K_3[Fe(CN)_6]$ were studied as oxidizing agents. $K_2S_2O_8$ showed slow oxidation kinetics that can only be compensated by using a very high oxidant concentration.

The optimal concentration of $K_3[Fe(CN)_6]$ was established and, therefore the baseline absorbance was low and stable. Using a high excess of oxidizing agent, to increase the reaction kinetics, some problems were observed namely Schlieren effect when the mixing of the sample and the two reagents was incomplete. A noisy baseline was obtained even when a long pathway to the detector (up to 200 cm) was used. Moreover, reaction of 4-AAP with excess of oxidizing agent could be observed in the absence of phenolic compounds causing a high blank value. Lower concentrations of oxidizing agent resulted in insufficient supply of reagent.

Optimization of the reagent composition was accomplished by varying the concentrations of 4-AAP and $K_3[Fe(CN)_6]$ and it was found that 1 $g.dm^{-3}$ 4-AAP was enough to promote the maximum response whereas the concentration of $K_3[Fe(CN)_6]$ should be in the range of 1–3 $g.dm^{-3}$.

The analytical signal was dependent on the changes of the length of the pathway to the detector. Lengths between 50 and 200 cm were tried, a decreasing in the analytical response being observed when longer pathways were used. A 100 cm pathway was chosen for further work.

A flow rate of 2.0 $cm^3.min^{-1}$ was selected for the measurement step, after having studied other flow rates. Under these conditions, a maximum response and a high sampling rate were attained.

Using this manifold the sample volume required to almost achieve the steady-state signal was 200 mm^3. With a 100 mm^3 volume more than 90% of this value was reached.

Furthermore, it was observed that the increase of the peak height and sensitivity of the measurements was better achieved by intercalating the product resulting from the reaction between sample and 4-AAP in equal volumes of oxidizing agent.

Calibration data obtained for the determination of phenolic compounds in the range 0.05–25 $mg.dm^{-3}$ showed a linear relationship between concentration and analytical signal with a correlation coefficient of 0.9995. The statistical limit of detection (3σ) was 0.01 $mg.dm^{-3}$. The precision of replicate injections was typically better than 0.6%. The sampling rate was about 24 $samples.h^{-1}$.

Interference study

Some cationic and anionic species normally found in wastewaters were studied as potencial interferents in the phenolic compounds determination.

Measurements of 10 $mg.dm^{-3}$ phenol were not affected by the presence of less than 1000 $mg.dm^{-3}$ of iodide, fluoride, bromide, phosphate, carbonate, sulphate, nitrite, nitrate, sodium, magnesium and potassium. If oxidizing agents, such as chloride, are present in the wastewaters the phenolic compounds will be oxidized partially. The interferences observed in this study were from chloride and calcium only when present in concentration above 400 and 200 $mg.dm^{-3}$, respectively. Therefore, these ions do not interfere with the phenolic compounds determination at levels which are normally present in this kind of wastewaters.

Application to wastewater analysis

The quality of the results obtained by the automatic system developed for the determination of phenolic compounds in wood industry wastewaters was evaluated comparing the results with those obtained by the conventional procedure.

A good agreement between both methodologies was obtained as show by the linear relation with a relative small intercept value (0.0247), slope near unity (1.0016) and correlation coefficient close to one (0.99995).

Table I present the results obtained using the two different methodologies, for 10 wastewater samples of wood industry. The maximum relative deviation between the results attained by the developed system and by the conventional procedure for the same samples was less than 1.2%.

TABLE I Results obtained, for 10 wastewater samples, in the determination of phenolic compounds

SIA (mg.dm^{-3})	*Conventional procedure (mg.dm^{-3})*	*Absolute deviation (mg.dm^{-3})*	*Relative deviation (%)*
9.50	9.51	–0.0010	0.10
14.29	14.27	0.0014	0.14
11.51	11.53	–0.0017	0.17
6.73	6.74	–0.0015	0.15
5.80	5.79	0.0017	0.17
14.60	14.62	–0.0014	0.14
5.80	5.84	–0.0070	0.70
3.33	3.37	–0.0120	1.20
5.18	5.16	0.0040	0.40
3.95	3.98	–0.0080	0.80

CONCLUSIONS

A sequential injection analysis system, with a spectrophotometric detector, was developed to evaluate the phenolic compounds concentration in wood industry wastewaters.

Some aspects are clearly advantageous, like the use of small volumes of reagents and sample, what is important in continuous analysis as it means less maintenance and less waste disposal. Additionally, all components and solutions are clustered around the selection valve, thus facilitating the future minimization of the system and its total automatization, what means computer-controlled operations running for extended periods. The simplicity and robustness, characteristics of the system, fulfil the environmental process control requirements. Other greatest attribute of the system is probably the fact that the same manifold configuration can accommodate a variety of chemistries, without requiring physical reconfiguration.

Nevertheless, there are two drawbacks that must be mentioned. First, since the aspiration of the washing and sequencing of the zones in reaction coil takes some time, the sampling frequency of this system is presently lower than that of conventional FIA systems, in which the filling of the injection valve is a matter of a few seconds. Secondly, this system requires special software, as the sequencing and injection are entirely computer driven. This, however, is not an obstacle in using this technique. Its attributes are valuable for continuous monitoring and process control and overcome its drawbacks in a practical and readly accessible form in wastewater analysis.

The application of the developed system in phenolic compounds determination shows to be an inexpensive and rapid technique that yields results in good agreement with those provided by conventional methodologies, with high sensitivity, accuracy and relative deviations lower than 0.6%.

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