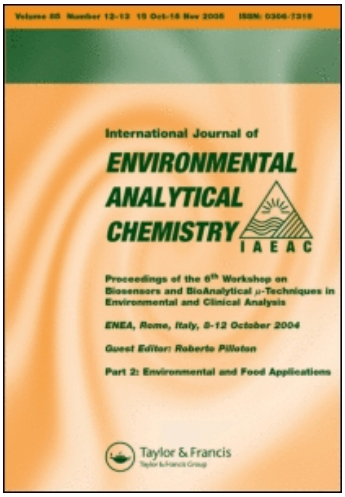

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FLOW INJECTION ANALYSIS OF FORMALDEHYDE AND SULPHITE USING THE OXIDATION OF p-PHENYLENEDIAMINE BY HYDROGEN PEROXIDE

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A spectrophotometric stopped-flow injection method for the determination of formaldehyde based on its catalytic property to oxidize *p*-phenylenediamine by hydrogen peroxide is described. The calibration graph is linear over the range 3–300 mg l^{-1} of formaldehyde. A sampling-rate of 35 samples h^{-1} was achieved. The effect of several organic and inorganic species was studied. The method was applied to the determination of formaldehyde in air in work environments and its accuracy was confirmed by comparing the results with those obtained using the standard acetylacetone method. The presence of sulphite decreases the catalytic effect of formaldehyde and this is the base for a new stopped-flow injection method for determination of sulphite. The proposed method for SO_3^{2-} shows a working range of 5–60 mg l^{-1} with a sampling-rate of 25 samples h^{-1}. The usefulness of the method was tested in the determination of sulphite in white wines.

KEY WORDS: Formaldehyde, sulphite, flow injection analysis , spectrophotometry, air, wine.

INTRODUCTION

Formaldehyde is considered to be one of the major pollutants present in air. It is widely used in several industries concerned with the manufacture of fertilizers, rubber, cotton, explosives and in the synthesis of organic compounds. In addition, it is a constituent of cigarette smoke and of combustion products from many sources. Recently, it has been described by the U.S. Environmental Protection Agency as a probable human carcinogen. Consequently, numerous analytical procedures for formaldehyde determination have been developed[1] and the introduction of new methods for monitoring its presence in biological systems and air are of great interest from a toxicological viewpoint.

A number of spectrophotometric methods have been developed for the determination of

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formaldehyde based mainly on its reaction with chromotropic acid[2], Schifft's reagent[3–4] and the formation of formazan dyes[5]. Some of the spectrophotometric reagents can also be used for the fluorimetric determination of formaldehyde[6–7]. Other methods used are chromatography[8–9], electrochemical techniques[10–11] and kinetic and enzymatic methods[12–14]. Flow injection analysis has also been applied to formaldehyde using strongly reducing agents, V(II) or U(III)[15–16], the rosaniline-sulphite system[17–18], and ammonium acetate and 2,4-pentanedione[19].

p-Phenylenediamine is oxidized by hydrogen peroxide in acid or neutral solutions to give a quinoidal compound known as Bandrowski's base. The oxidation is significantly accelerated by aldehydes. This effect was described by Worker[20] and proposed by Feigl as a sensitive spot test for aldehydes[21]. Several studies on the formation and stability of Bandrowski's base in the presence of aldehydes have shown this reaction to be applicable to the quantitative determination of aldehydes by spectrophotometric[22–23] and kinetic methods[12,22–24] with a relatively high selectivity.

In this paper a stopped-flow injection model is described for determining formaldehyde, based on its "catalytic" effect in the oxidation of *p*-phenylenediamine by hydrogen peroxide.

On the other hand, taking into account that sulphite is a suitable inhibitor of the "catalytic effect" of formaldehyde, the reaction has also been applied to a flow injection determination of this anion. Many methods suitable for the determination of sulphite have been reported and some of these are based on flow injection analysis (FIA) with the aim of developing fast, reliable and simple methods for routine analysis[25–33]. This paper reports a new method for the determination of sulphite using a reverse FIA mode.

EXPERIMENTAL

Apparatus

A Pye Unicam SP8-100 was used for recording spectra and a Philips PU-8625 spectrophotometer connected to a Hewllett Packard HP-3394 A, was used as the detector with a Hellma flow cell with inner volume of 18 μl.

A Gilson Minipuls HP4 peristaltic pump and an Omnifit injection valve were used. PTFE tubing of 0.5 mm i.d. was used for the mixing coil and for all connections.

Reagents

All chemicals used were analytical reagent grade and doubly distilled water was used throughout.

A 10^{-2}M aqueous formaldehyde solution was prepared by diluting 37% stock formaldehyde solution (Merck) with water and standardized using the hydrogen peroxide method[34]. Working solutions of lower concentrations were prepared by diluting with water.

A 10^{-2}M sulphite solution was prepared daily from the product (Merck) and standardized with iodine. Working solutions were obtained by adequate dilution of the stock solution.

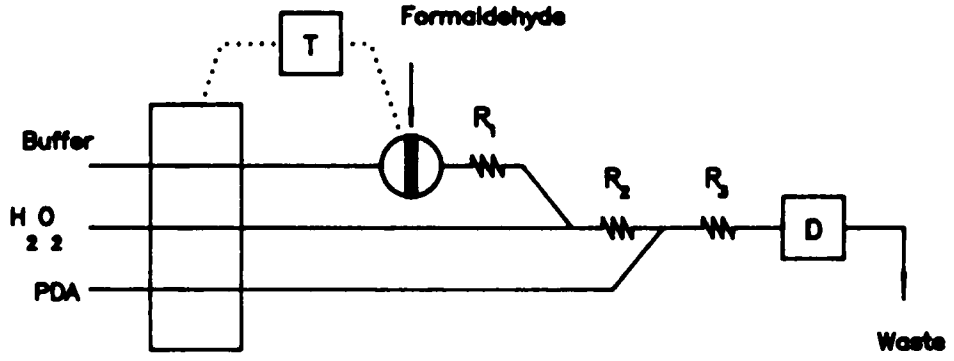

Figure 1 Schematic diagram of the manifold used for the determination of formaldehyde.

A 1% w/v aqueous *p*-phenylenediamine solution was prepared daily by dissolving *p*-phenylenediamine dihydrochloride (Merck) in water and diluting to 100 ml. Working solutions of lower concentrations were prepared by appropriate dilution of the stock solutions.

Hydrogen peroxide solutions were prepared by dilution of a 30% stock solution (Merck).

Phosphate buffer solutions, were prepared from 0.2 M disodium or dipotassium hydrogen phosphate and sufficient 5M potassium hydroxide to give the desired pH.

Manifolds

The manifolds used for the determinations of formaldehyde and sulphite are shown in Figures 1 and 2, respectively. Except for the pump tubing (Tygon), PTFE tubing (0.5 mm i.d.) was used throughout the manifold. However, the Tygon tubing was previously washed with a diluted solution of nitric acid. A timer synchronized to the injection system allowed the reagent streams to be stopped at any delay time and for as long as required.

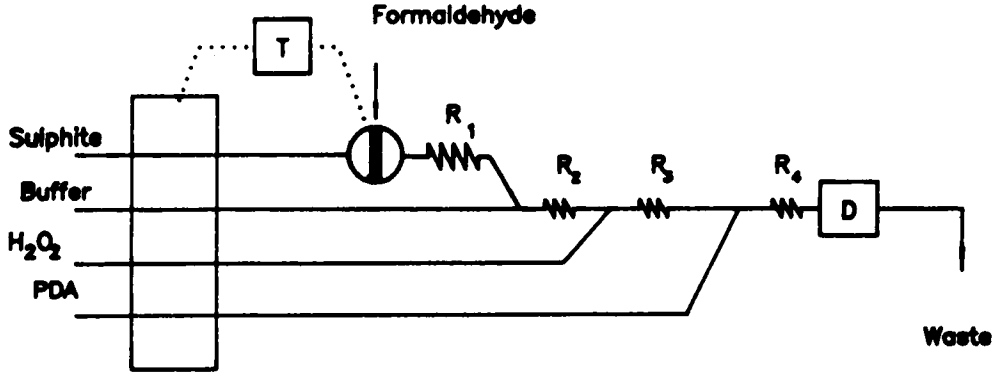

Figure 2 Schematic diagram of the manifold used for the determination of sulphite.

Procedure for the determination of formaldehyde

Samples containing between 3 and 300 mg l^{-1} of formaldehyde were sucked into the sample loop (120 ml) of the injection valve by means of the peristaltic pump and injected into the buffer stream of the FIA manifold (see Figure 1). The timer was programmed so that 30 s after the injection of formaldehyde, i.e. when the sample zone was in the flow cell, the flow was stopped for 60 s and then the pump started again. The absorbance was measured at 530 nm and the concentration of formaldehyde was evaluated from peak increase during the stop interval by using a graph based on freshly prepared formaldehyde standard.

Procedure for the determination of sulphite

120 µl of formaldehyde 3.2×10^{-3}M was injected into the sample stream, and the above described procedure was also followed for the determination of sulphite. The curve is linear between 5 and 60 mg l^{-1} of sulphite.

RESULTS AND DISCUSSION

Study of reagent concentrations

The oxidation of *p*-phenylenediamine (PDA) by hydrogen peroxide catalyzed by formaldehyde was sensitive to changes in pH. To select the optimum detection wavelength and the optimum pH, absorption spectra were recorded at several pH values. Figure 3 shows that the pH which gave the greatest absorbance was 6.5, and the absorption peak was centered at 530 nm. In subsequent experiments, pH 6.5 was always used and the absorbance measured at 530 nm.

The influence of the concentration of H_2O_2 and PDA on the signal was studied. The peak height increased with PDA concentration up to 1.5×10^{-2}M, after which it decreased. The recommended concentration of the PDA stream was 1.5×10^{-2}M.

The effect of the concentration of hydrogen peroxide was studied in the range 0.02–2.0M. Increasing the H_2O_2 concentration increased substantially the peak height while the base line increased only slightly. A 1.0 M hydrogen peroxide concentration was sufficient to achieve sensitive responses.

The effect of temperature was studied in the range 15–50°C. The peak height increased with increasing temperature up to 30°C (6% per °C), above which it decreased. The temperature adopted in the procedure was 30 ± 0.5 °C.

Optimization of manifold parameters

The variables studied were sample volume, length and inner diameter of the mixing coils and the flow rate of each reagent line. The concentrations used in these experiments were

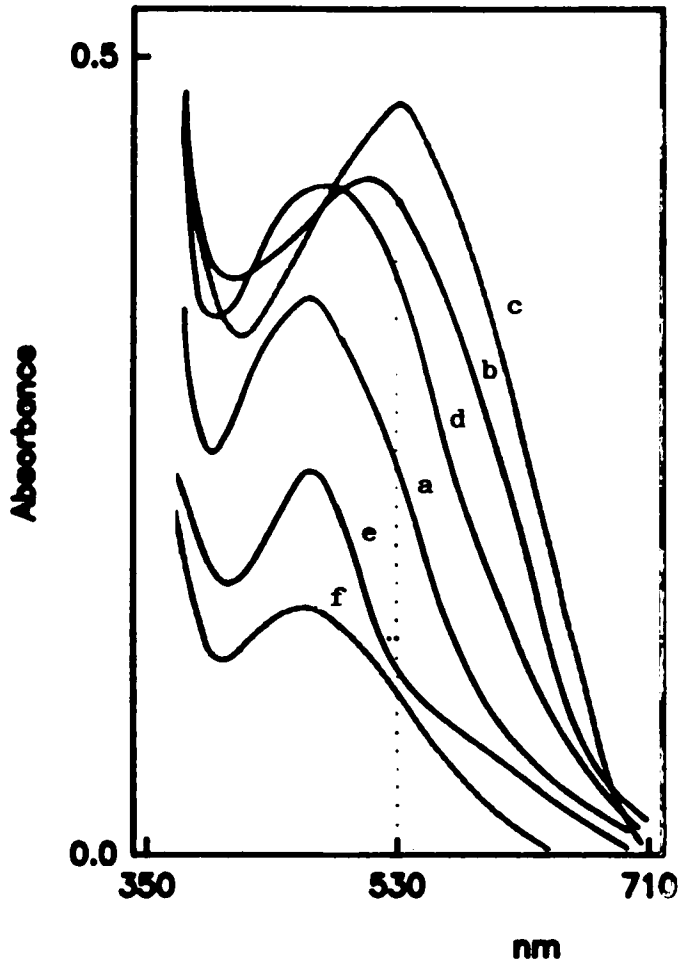

Figure 3 Absorption spectra for the oxidation of PDA by H_2O_2 in the presence of formaldehyde at several pH. Conditions: PDA, 1.5×10^{-3}M; H_2O_2, 4.5×10^{-2}M, formaldehyde, 2×10^{-4}M. Curves a-f correspond to pH 4; 5; 6.5; 7; 8 and 9.

as follows: buffer line, 0.2 M phosphate buffer pH 6.5; hydrogen peroxide line 1.0 M; PDA line, 1.5×10^{-2}M; sample solution, 15 μg ml^{-1}. The manifold parameters used in the optimization procedure were mixing coils of 30 cm length with an inner diameter of 0.5 mm and a stop time of 45 s.

The sample volume was varied between 35 and 235 μl. The volume of formaldehyde injected in the range 85–140 μl yielded and almost constant signal, which decreased outside this range ; a volume of 120 μl was chosen for further experiments.

The tube diameters studied were 0.30, 0.50 and 0.70 mm. The signal decreased when the diameter was increased, as a consequence of the lower concentration of sample plug reaching the detector cell. An internal tube diameter of 0.5 mm was chosen as a compromise between the flow resistance and sensitivity.

The flow rate of the reagents was varied over the range 0.4 to 2.0 ml min^{-1}. The maximum peak height was observed at a flow rate of 0.7 ml min^{-1} for each channel.

The timing sequence and time intervals used were chosen so as to give a high absorbance increase during a reasonably short constant interval of time after the flow had been stopped. A 30 s delay time after injection and measurement of the absorbance for 60 s gave the best results. The delay time was slightly longer than the residence time, i.e., the samples were stopped shortly after the peak maximum had been passed. As the stop time was identical in all cases (60 s) the analytical results correspond to the peak increase during the stop interval.

The optimum length of the mixing coils (R_1, R_2 and R_3) was examined over the range 0–60 cm. The highest peak height was obtained when R_1, R_2 and R_3 were 30–60 cm. The length chosen for each mixing coil was 30 cm.

Calibration graph and reproducibility

A series of standard solutions of formaldehyde were pumped in triplicate to test the linearity. Calibration graphs were linear for 3.0–300 mg l^{-1} with correlation coefficients of 0.9992. The sampling rate was about 35 samples h^{-1}. The statistical study performed on 10 samples of triplicate pumping containing 13.7 and 20.4 mg l^{-1} of formaldehyde yielded a r.s.d. of 0.48 and 0.67 %, respectively. The detection limit, calculated as the value corresponding to three times the standard deviation of the blank, was 0.5 mg l^{-1}.

Interferences

The investigation of interferences was conducted with regard to possible chemical interferences and the problem of selectivity. The results of this study are shown in Table 1. A substance was considered not to interfere if the variation in the analytical signal of formaldehyde was less than ± 3% in its presence.

Table 1 Tolerance of the other substances in the formaldehyde method.

Substance	*Tolerable molar ratio substance/formaldehyde*[+]
Nitrate, chloride, sulphate, phenol	100*
Methanol, ethanol, acetone	50
Acetaldehyde, benzaldehyde	10
Carbonate, glyoxal, sulphide Co^{II}, Zn^{II}, Hg^{II}	5
Cu^{II}, Mn^{II}	0.1

*Maximum tested
[+] 3.10^{-4}M (10 mg l^{-1}) of formaldehyde.

Table 2 Determination of formaldehyde in air.

	Formaldehyde content[a] mg/m^3	*Formaldehyde found*[b] mg/m^3
Sample 1	2.01	1.98
Sample 2	1.52	1.49
Sample 3	2.60	2.57

[b]FIA method. Average of three determinations.
[a]Acetylacetone method. Average of three determinations.

Oxidizing or reducing agents which exits as atmospheric contaminants (sulfur dioxide, nitrogen dioxide and hydrogen sulphide) were also examined. Of these, only sulfur dioxide showed interference, but his interference is readily removed by treatment with dilute hydrogen peroxide prior to the injection of sample into the manifold.

Analysis of air samples

The proposed flow-injection method in the stopped-flow mode has a great potential for the determination of formaldehyde in real samples. This is confirmed by the results obtained in the analysis of formaldehyde in air from a research laboratory handling formaldehyde. Water was used to collected the formaldehyde[1]. The results obtained for three samples were in good agreement with those obtained using the acetylacetone method[7] (Table 2).

Determination of sulphite

The oxidation of *p*-phenylenediamine by hydrogen peroxide catalyzed by formaldehyde was also applied to flow-injection determination of sulphite. The method was based on the decrease of the catalytic effect of formaldehyde in the presence of sulphite.

Of all FIA configurations tested, the best results were obtained with the reverse mode diagrammed in Figure 2. The stopped-flow mode was also used.

Effect of the concentration of reagents and manifold parameters

The study of the chemical variables showed identical results to those obtained for the determination of formaldehyde. A 200 cm reactor coil (R_1) was used so that formaldehyde injected (2×10^{-3} M, 120 µl) and sulphite reacted before reaching the buffer chanel (Figure 2).

Calibration graph

Under the recommended conditions, the calibration graph was linear over the range 5.0–60.0 mg l^{-1}. The regression coefficient was 0.9991 and the sampling rate was 25 samples h^{-1}. The

Table 3 Tolerance of other substances in the sulphide method.

Species added	*Tolerance*[a] *molar ratio substance/sulphite*
Nitrate, sulphate, chloride, perchlorate	100*
Sulphide, Co^{II}, Hg^{II}, Zn^{II}	10
Nitrite, Mn^{II}	1

*Maximum tested.
[a]1.25×10^{-4} (10 mg l^{-1}) of sulphite

reproducibility of the method was studied with ten replicate injections at two levels of sulphite, 9.2 and 38.3 mg l^{-1}; the relative standard deviations were 0.85 and 0.56, respectively. The detection limit was 1.0 mg l^{-1}.

Interferences

An interference study was performed on several anions and cations with a permitted change in the signal of ± 3%. The results obtained are summarized in Table 3.

Determination of sulphite in wines

The stopped-flow method was used for the determination of sulphite in white wines. The sample of wine was diluted with double distilled water and then sucked into the sample line by the peristaltic pump. (see Figure 2). The results were checked by the *p*-rosaniline method[34]. The results obtained by both techniques are in good agreement as shown in Table 4.

Table 4 Determination of sulphite in wines.

	Sulphite content[a] *mg/l*	*Sulphite found*[b] *mg/l*
Wine 1	7.9	8.0
Wine 2	8.2	8.4
Wine 3	10.3	10.5

[a]Rosaniline method. Average of three determinations.
[b]FIA method. Average of three determinations.

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