

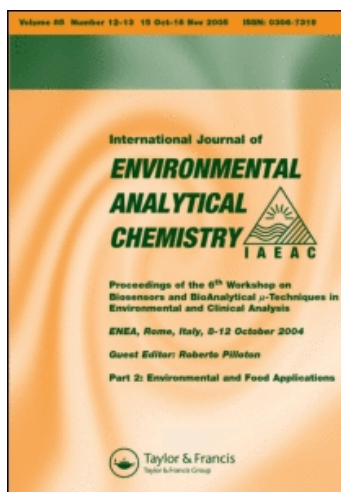
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SELECTIVE MONITORING OF FORMALDEHYDE IN AIR BY USE OF THE STOPPED-FLOW TECHNIQUE

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Two kinetic methods based on the stopped-flow technique are proposed for the determination of formaldehyde in air by reaction with 3-methyl-2-benzothiazolone hydrazone (MBTH), followed by photometric detection at 620 nm, and with acetylacetone, followed by fluorimetric detection at $\lambda_{\text{ex}} = 410$ nm and $\lambda_{\text{em}} = 510$ nm. Kinetic methodology considerably shortens the formaldehyde analysis time (measurements can be obtained within a few seconds) relative to existing methods based on these reactions and equilibrium measurements (ca. 30 and 60 min are needed for equilibrium to be reached in the photometric and fluorimetric method, respectively). One additional advantage of the kinetic methodology is its high selectivity, which was checked by studying the effect of various organic and inorganic species. Calibration graphs were linear over the ranges 20–600 and 20–1000 ng ml⁻¹ formaldehyde for the photometric and fluorimetric methods, respectively. Both methods were applied to the determination of formaldehyde in air from urban areas; the accuracy of the results was confirmed by comparing them with those provided by the standard chromotropic acid method. The proposed kinetic methods were found to be more sensitive, rapid, reproducible and easier to use than the widely accepted standard method.

KEY WORDS: Formaldehyde determination, 3-methyl-benzothiazolone hydrazone reaction, acetylacetone reaction, kinetic method, stopped-flow technique, air, spectrophotometry, fluorimetry.

INTRODUCTION

Formaldehyde is widely used at present for a variety of purposes including manufacturing resins for plywood, particle board and insulation, in plastics, cosmetics and vaccines, and in permanent press textiles and paper products. In addition, it is a natural by-product of smoke and exhaust from common everyday sources such as cigarettes, power plants and automobiles¹.

There is no single optimum method for the determination of formaldehyde in air. Major methods for this purpose are based on photometry, fluorimetry, gas and liquid chromatography, and polarography². Although column liquid chromatography is becoming a standard laboratory technique because of the sensitivity and short analysis time it affords in the determination of formaldehyde, the most common methods currently used are photometric. Among these, the standard chromotropic acid method³ remains the most popular in spite of its limited sensitivity and the fact that it requires using concentrated sulphuric acid, which is difficult to handle. As an alternative, many other photometric and fluorimetric methods featuring a high sensitivity have been

reported². However, they are scarcely used owing to serious drawbacks such as a lack of selectivity and/or colour stability, and/or the long standing time required before measurements can be made.

In this work, kinetic methodology was used to minimize or avoid some of the above mentioned drawbacks in order to improve the analytical features of previously reported photometric and/or fluorimetric methods for the determination of formaldehyde in air. Since reaction rate data are obtained in a considerably shorter time than those required for equilibrium data, the overall analysis time for formaldehyde can be substantially reduced. On the other hand, kinetic methods introduce a high selectivity as a result of the kinetic behaviour differences between aldehydes.

Two reactions were selected for this study, viz (i) the formation of a formazan dye ($\lambda_{\max} = 670$ nm) from 3-methyl-2-benzothiazole hydrazone hydrochloride (MBTH) and formaldehyde in the presence of an Fe(III)–sulphamic acid mixture as oxidant⁴, and (ii) the Hantzsch reaction between acetylacetone, ammonia and formaldehyde to form the fluorescent 3,5-diacetyl-1,4-dihydrolutidine ($\lambda_{\text{ex}} = 410$ nm, $\lambda_{\text{em}} = 510$ nm)^{5,6}. Both methods are highly sensitive and the reactions proceed under mild conditions. However, equilibrium is only reached after a long standing time (ca. 30 and 60 min, respectively); besides, the reactions essentially involve the aldehyde group, so they are good candidates for application of kinetic methodology.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade and employed as supplied. Distilled water was used throughout. A formaldehyde stock solution (ca. 1 g l^{-1}) was prepared by diluting 2.5 ml of 37% formaldehyde solution (Merck, Darmstadt, Germany) to 11 with water and standardized by the sulphite method^{7,8}; the solution remained stable for at least 3 months. More dilute solutions ($20 \mu\text{g ml}^{-1}$) were prepared daily by direct dilution of appropriate aliquots of the stock solution. Aqueous solutions of 3-methyl-2-benzothiazolone hydrazone (MBTH, Aldrich, 0.15 M) and acetylacetone (Carlo Erba, 0.025 M) were prepared daily. A 3.6×10^{-2} M Fe(III) solution was made from $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{ H}_2\text{O}$ (Merck) in 8×10^{-3} M sodium hydroxide in order to get a final pH value of 2.1 (the pH of a 3.6×10^{-2} M aqueous Fe(III) solution was 1.9). An ammonium acetate–acetic acid buffer (pH 6.2) was made by mixing the reactants at final concentrations of 2.8 M and 0.05 M, respectively.

Apparatus

A Model 650-10S fluorescence spectrophotometer and a Model Lambda 5 UV/visible spectrophotometer (Perkin-Elmer, Norwalk, CT, USA) were used for kinetic measurements. A stopped-flow module⁹ (Quimi-Sur Instrumentation, Seville, Spain) was fitted to the spectrophotometers for application of the stopped-flow technique. The module, which contained an observation cell of 0.3 cm path length, was controlled by the associated electronics and a 40 K commodore computer. The solutions in the stopped-flow module and cell compartment were thermostated to within $\pm 0.1^\circ\text{C}$ by circulating water through it.

The air sampling equipment consisted of a constant-flow pump (Dupont Model S2500), 30-ml impingers, and cellulose ester filters (37 mm diameter, 0.8 μm thick).

Procedure for the stopped-flow photometric determination of formaldehyde

Two solutions, A and B, were used to fill the two 10-ml reservoir syringes of the stopped-flow module. Solution A contained 6 ml of MBTH solution (0.15 M), appropriate volumes of formaldehyde standard solution (20 $\mu\text{g ml}^{-1}$) to give a final concentration between 20 and 600 ng ml^{-1} , and distilled water to a final volume of 10 ml. Solution B contained 3.6×10^{-2} M iron(III) at pH 2.1. After the two 2-ml drive syringes were filled with the corresponding solutions from the reservoir syringes, 0.15 ml of each solution was mixed in the mixing chamber in each run. The reaction was monitored at 620 nm by recording the variation of the absorbance as a function of time while keeping the system at $20 \pm 0.1^\circ\text{C}$. The reaction rate was calculated by the initial-rate method from the absorbance–time curves after subtraction of the rate corresponding to a blank solution containing no formaldehyde.

Procedure for the stopped-flow fluorimetric determination of formaldehyde

In this procedure, solution A contained 4 ml of ammonium acetate (2.8 M)–acetic acid (0.05 M) buffer (pH 6.2), the volume of 20 $\mu\text{g ml}^{-1}$ formaldehyde solution required to give a final concentration between 20 and 1000 ng ml^{-1} , and distilled water to a final volume of 10 ml. Solution B contained 0.025 M acetylacetone. The reaction was monitored at $\lambda_{\text{ex}} = 410$ nm and $\lambda_{\text{em}} = 510$ nm by recording the variation of the fluorescence intensity as a function of time while keeping the system at $58 \pm 0.1^\circ\text{C}$. The reaction rate was calculated by the initial-rate method. Blank solutions were prepared in the same way as the samples but containing no formaldehyde; their signals were subtracted from those for the samples.

Formaldehyde air sampling

The air samples used were collected from typically urban areas. Formaldehyde was collected by drawing air through two serially arranged impingers, each containing 10 ml of distilled water, at a rate of 1.5 l min^{-1} for 2 h. A cellulose ester filter was inserted in the sampling line to retain particulate matter. After sampling, the solutions were quantitatively transferred to a 25-ml standard flask and made up to the mark with water. The formaldehyde content in a sample volume not greater than 1.5 ml was determined by both the stopped-flow photometric and the fluorimetric method. When analyses were not immediately performed, samples were stored at 4°C for a time never exceeding 24 h.

RESULTS AND DISCUSSION

Kinetics curves for the determination of formaldehyde by both the photometric-MBTH and the fluorimetric-acetylacetone method were run under the experimental equilibrium conditions described elsewhere^{4,5} using the conventional kinetic (batch) technique. Signal stabilization took ca. 30 and 60 min, respectively (Figure 1, curves A2, and B2).

Reaction rate measurements were obtained within a few minutes from the kinetic curves corresponding to the photometric-MBTH method (Figure 1, curve A2); however, the kinetic curves obtained with the fluorimetric-acetylacetone method exhibited an induction period, (Figure 1, curve B2), so measurements could only be obtained ca. 30–40 min after the reaction was started.

Increasing the speed of these procedures was intended to fulfill two aims, namely to increase the sensitivity of the formaldehyde determination and/or shorten the standing time before measurements. For this purpose, we studied two alternatives that had previously proved effective with other reactions: micellar catalysis¹⁰ and stopped-flow analysis¹¹. Various types of micelles were found not to significantly increase the rate of the two reactions studied. However, substitution of conventional kinetic methodology by the stopped-flow technique had a marked effect on the rate of both reactions (Figure 1, curves A1, and B1), particularly that involving the formaldehyde-acetylacetone system (Figure 1B, curves 1 and 2). Thus, the rate was increased by a factor of 45 and 100 for the MBTH–formaldehyde and acetylacetone–formaldehyde system respectively, by using the stopped-flow technique, under identical experimental and instrumental conditions, relative to conventional kinetic methodology. Therefore, kinetic data for both systems could be collected in a few seconds. Also, the sensitivity of the formaldehyde determination was enhanced as a direct result of the increased reaction rate.

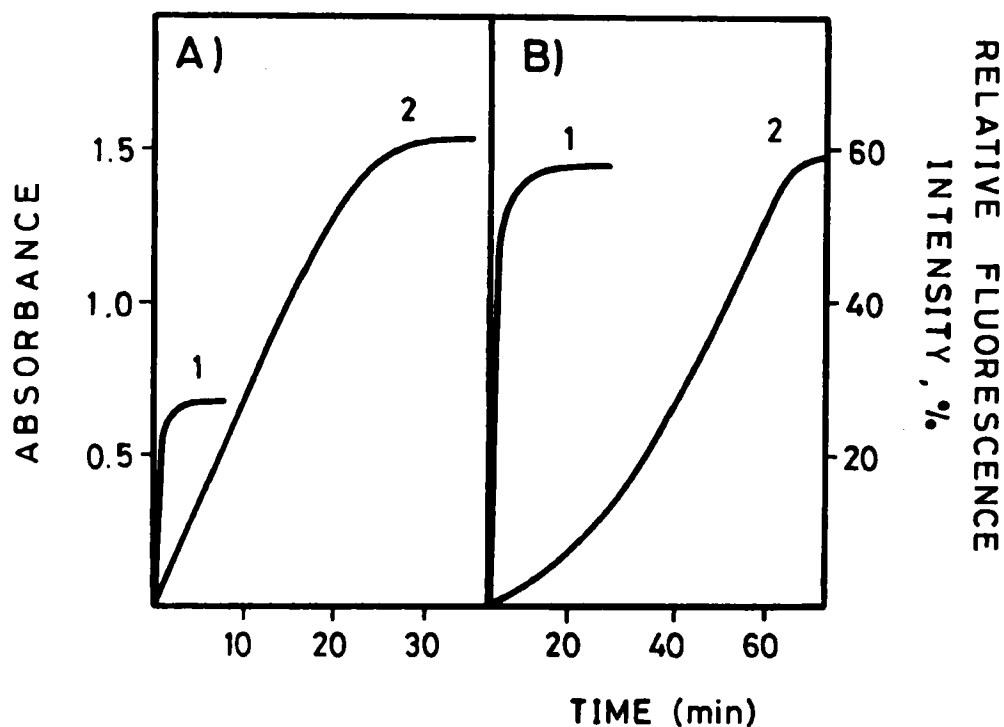


Figure 1 Kinetic curves for (A) the MBTH–formaldehyde and (B) the acetylacetone–formaldehyde system obtained by (2) conventional kinetic methodology and (1) the stopped-flow technique.

Optimization of the reaction conditions for the MBTH-formaldehyde system

The reactants involved in the reaction, the Fe(III)–sulfamic acid complex, MBTH and formaldehyde, were mixed in various sequences in order to determine their optimum distribution in each syringe of the stopped-flow module. Only Fe(III) and MBTH were found to react to some extent, so mixing them in the same syringe was avoided. The reaction rate was maximal when MBTH and formaldehyde were mixed in one syringe, and Fe(III)–sulfamic acid was put in the other. That is, the formation of the addition compound between MBTH and formaldehyde before condensation with another MBTH molecule⁴ accelerated the formation of the formazan dye. The mixing time for the solution held in each syringe was not significant as curves obtained for the same solutions over a span of 1 h were similar.

All concentrations stated here are initial concentrations in the syringes (twice the actual concentrations in the reaction mixture at time zero after mixing). Conditions were optimized for maximum initial rate V_0 and minimum variations of this parameter with the assayed concentration.

The hydrogen ion concentration was found to affect the formation of the formazan dye (Figure 2A). pH values above 2.5 were avoided as they caused iron (III) hydroxide to precipitate, which was not prevented by the addition of sulfamic acid. For this reason, various oxidants (iodate, periodate, Ce(IV) and peroxodisulphate) were tested as an alternative to Fe(III). The final product yield in the presence of iodate and periodate was found to be different from that obtained in the presence of iron (III). This product was analytically inadvisable as it resulted in a very low sensitivity to formaldehyde. Both yielded a reaction product seemingly identical with that obtained in the presence of Fe(III); however, the formation of the formazan dye was considerably slower. Therefore, Fe(III) was selected as the most suitable oxidant and precipitation was avoided by using a pH value of ca. 2.

The influence of the Fe(III) concentration is shown in Figure 2B. Concentrations of this reagent above ca. 40 mM could not be used because they resulted in precipitation of iron (III) hydroxide in the reaction medium. Sulphamic acid had no influence on the reaction rate, at least below 0.1 M. Also, the reagent did not alter the experimental conditions where the iron (III) precipitate was formed, so no iron(III)–sulfamic acid was produced at the working pH value. Therefore, its presence in the reaction medium was considered unnecessary.

The effect of the MBTH concentration on the reaction rate (Figure 2C) was studied over the range 0–0.104 M. Pseudo-zero order conditions were never obtained in this interval, although the effect of increased concentrations of MBTH could not be determined owing to its precipitation in the reaction medium.

The temperature had a marked effect on the rate of formation of the formazan dye (Figure 2D). Above ca. 25°C the formation of bubbles in the reaction medium gave rise to irreproducible measurements. A temperature of 20°C was thus selected. From Arrhenius plots of $\ln K$ against the reciprocal of the absolute temperature, the activation energy for the reaction was calculated to be 4.3 ± 0.1 Kcal/mol.

The influence of the ionic strength on the initial rate of the reaction was examined up to about 2 M and was found to depend on the electrolyte used to adjust it. Thus, potassium nitrate had no effect, while sodium sulphate inhibited the reaction completely at an added concentration of ca. 1 M. This inhibition is possibly caused by the formation of a bisulphite adduct from formaldehyde and sulphite which is a typical contamination in sulphates¹². Sodium chloride increased the initial rate ca. 2-fold at an

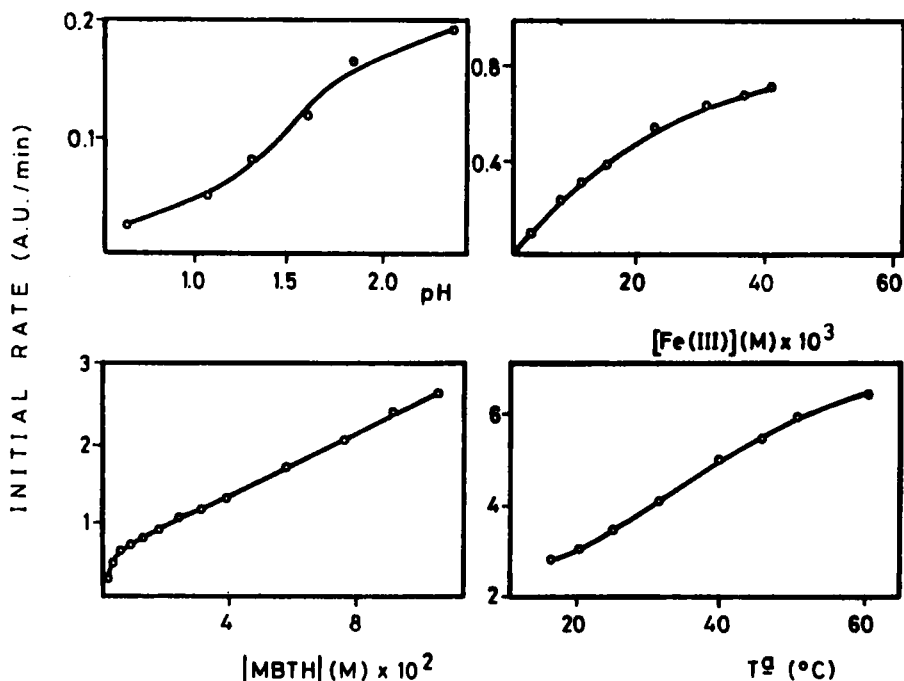


Figure 2 Influence of (A) pH, (B) the iron(III) concentration, (C) the MBTH concentration and (D) temperature on the rate of the MBTH-formaldehyde system.

added concentration of 1.3 M. Since the effect was not significant and the dependence of initial rate on the sodium chloride concentration was linear, which might result in imprecise measurements, potassium nitrate was finally chosen to adjust the ionic strength whenever necessary.

Absorbance vs. time curves at different formaldehyde concentrations were recorded; their initial slopes were consistent with a first-order reaction in formaldehyde. The various kinetic dependences on pH and the iron (III) and MBTH concentrations are summarized in Table 1. The following equation is proposed for the formation of the formazan dye from MBTH (9×10^{-2} M) and formaldehyde in the presence of Fe(III) (3.6×10^{-2} M) as oxidant agent, at pH 2.1:

$$v = k [H^+]^{-1/2} [MBTH]^{1/2} [Fe^{+3}]^{1/2} [formaldehyde] + k' \quad (1)$$

where v is the overall rate and k' the contribution of the blank reaction.

Optimization of the reaction conditions for the acetylacetone-formaldehyde system

The optimum distribution of reactants (acetylacetone, formaldehyde and ammonium acetate-acetic acid buffer) in the two syringes of the stopped-flow module was determined by mixing them in various sequences. It was advisable to keep acetylacetone and the buffer in separate solutions since, although they hardly reacted at room temperature within 24 h, some reaction occurred at higher temperatures. Based on the results, the initial rate did not depend on the way the reactants were distributed over the syringes.

Table 1 Summary of kinetic data.

	Dependence of v_0 on*	Concentration range (M)
MBTH–formaldehyde	$[H^+]^{-1/2}$	$4.4 \times 10^{-3} - 2.5 \times 10^{-1}$
	$[Fe^{+3}]$	$7.4 \times 10^{-3} - 2.2 \times 10^{-2}$
	$[Fe^{+3}]^{1/2}$	$2.2 \times 10^{-2} - 5.2 \times 10^{-2}$
	$[MBTH]^{1/4}$	$1.8 \times 10^{-3} - 1.5 \times 10^{-2}$
	$[MBTH]^{1/2}$	$1.5 \times 10^{-2} - 9.1 \times 10^{-2}$
Acetylacetone–formaldehyde	$[H^+]^2$	$1.8 \times 10^{-9} - 2.0 \times 10^{-7}$
	$[H^+]^0$	$2.0 \times 10^{-7} - 1.0 \times 10^{-6}$
	$[H^+]^{-3}$	$1.0 \times 10^{-6} - 2.6 \times 10^{-6}$
	$[NH_4Ac]$	$1.6 \times 10^{-1} - 6.3 \times 10^{-1}$
	$[NH_4Ac]^0$	$6.3 \times 10^{-1} - 1.2$
	$[Acac]^2$	$8.0 \times 10^{-3} - 2.0 \times 10^{-2}$
	$[Acac]^0$	$2.0 \times 10^{-2} - 3.1 \times 10^{-2}$
$[Acac]^{-3}$	$3.1 \times 10^{-2} - 5.2 \times 10^{-2}$	

* v_0 is the initial reaction rate

The net effect of pH on the reaction rate could not be determined since ammonia was required to form the product: 3,5-diacetyl-1,4-dihydrolutidine. Therefore, changing the pH value also changed the NH_4OH/NH_4^+ and HAc/Ac^- ratio. At a constant buffer concentration, the optimum pH working was found to be about 6.2 (Figure 3A), at which value the initial rate was found to depend linearly on the ammonium acetate concentration up to ca. 0.7 M. At higher values it rapidly dropped to a zero-order dependence (Figure 3B).

A zero-order dependence of the initial rate on the acetylacetone concentration was found over a reagent concentration range from ca. 0.02 to 0.03 M (Figure 3C). A 0.025 M acetylacetone concentration was selected in order to ensure maximum sensitivity and reproducibility.

The temperature had a significant effect on the reaction between formaldehyde, ammonia and acetylacetone. Above ca. 40°C, the kinetic curves exhibited an induction period the length of which decreased with increasing temperature. This induction period disappeared above ca. 40°C. Figure 3D shows the variation of the initial rate with temperature. As can be seen, the optimum working temperature was between 55 and 60°C. From Arrhenius plots of $\ln K$ against the reciprocal of the absolute temperature, the activation energy for the reaction was calculated to be 8.2 ± 0.1 Kcal/mol.

Up to at least 0.4 M, the reaction was not affected by the ionic strength, when adjusted with sodium chloride, potassium nitrate or sodium sulphate, provided that the electrolytes were added to solution A, which contained formaldehyde and the ammonium acetate–acetic acid buffer. Adding the electrolytes to solution B, which contained acetylacetone, considerably reduced the initial rate at a salt concentration above ca. 0.08 M. Since the sample to be analysed was added to solution A, the ionic strength was assumed not to affect the initial rate up to 0.4 M electrolyte.

A first-order dependence on the formaldehyde concentration was found over the range 20–1000 ng ml⁻¹. The various kinetic dependences on pH, ammonium acetate and acetylacetone are summarized in Table 1. The following equation is proposed for the formation of 3,5-diacetyl-1,4-dihydrolutidine from acetylacetone (0.025 M), ammonium (1.12 M) and formaldehyde, at pH 6.2:

$$v = k [\text{formaldehyde}] + k' \quad (2)$$

where v is the overall rate and k' the contribution of the blank reaction.

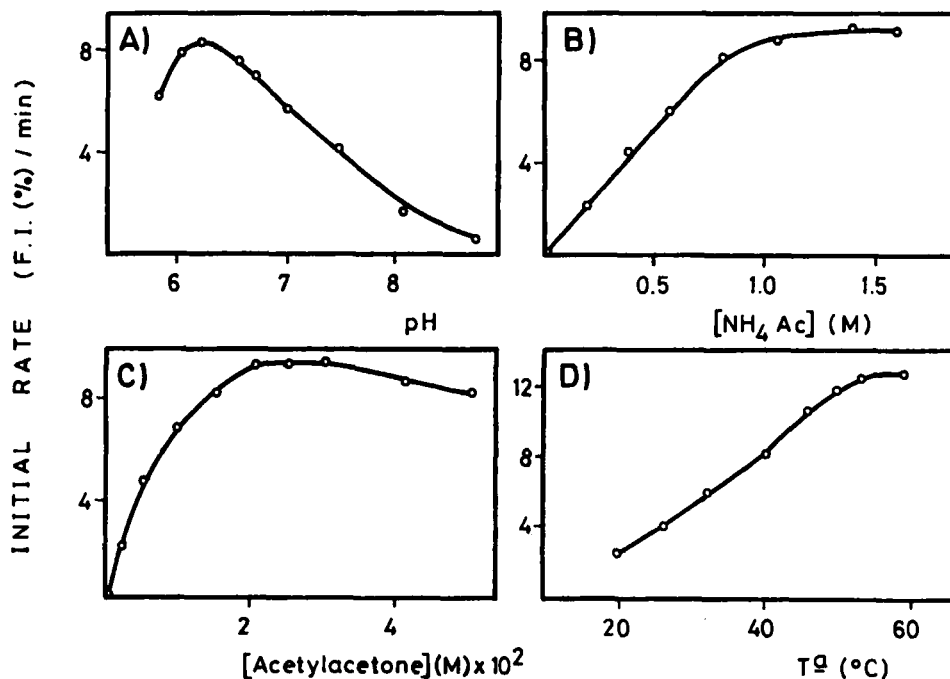


Figure 3 Influence of (A) pH, (B) the ammonium acetate concentration, (C) the acetylacetone concentration and (D) temperature on the rate of the acetylacetone-formaldehyde system.

Calibration

Calibration graphs for the determination of formaldehyde by both the MBTH and the acetylacetone method were run under the optimal conditions described above. By using the stopped-flow photometric method based on MBTH, this analyte could be determined over the range 20–600 ng ml⁻¹. The corresponding calibration equation was

$$Y = (0.064 \pm 0.001)[X] + (1.8 \pm 0.5) \quad (3)$$

where Y is the initial rate (AU min⁻¹) and X the formaldehyde concentration (ng ml⁻¹). The standard error of the estimate and correlation coefficient were 0.996 (UA min⁻¹) and 0.998, respectively. The detection limit (3σ) was 14 ng ml⁻¹. The precision of the proposed method was evaluated by using 11 samples encompassing the concentration range for which the method was intended (50, 250 and 500 ng ml⁻¹). The relative standard deviations were 5.1%, 3.4% and 3.0%, respectively.

By using the stopped-flow fluorimetric method based on acetylacetone, the dependence of the initial rate on the formaldehyde concentration was linear over the range 20–1000 ng ml⁻¹. The corresponding calibration equation was

$$Y = (0.063 \pm 0.002)[X] - (1.4 \pm 1.2) \quad (4)$$

where Y is the initial rate (FI min⁻¹) and X is the formaldehyde concentration (ng ml⁻¹). The standard error of the estimate and the correlation coefficient were 2.58 (FI min⁻¹) and 0.995, respectively. The detection limit (3σ) was 13 ng ml⁻¹. The precision, evaluated at three formaldehyde concentrations (100, 200 and 500 ng ml⁻¹) and

expressed as the relative standard deviation, was 6.1%, 4.7% and 4.0%, respectively, for 11 replicates.

Selectivity

In order to assess the selectivity of the proposed stopped-flow photometric and fluorimetric method, various organic and inorganic species were tested by adding them to solutions containing 100 ng ml⁻¹ formaldehyde and applying both procedures. Table 2 summarizes the results. The maximum ratio of compound to formaldehyde tested was 50. A given species was considered not to interfere with the determination if the interferent plus analyte mixture yielded a signal comprised in the range $S_x \pm \sigma$, where S_x is the signal provided by the analyte in the absence of the interferent, and σ the standard deviation of the method.

Low-molecular-weight aldehydes caused too high results at concentrations above that of formaldehyde. The selectivity of the kinetic methods towards these compounds was much higher than with the equilibrium methods. Since formaldehyde is usually in a substantial excess over any other individual aldehyde in urban atmospheres, interferences from other aldehydes should pose no problem in real-life air sampling applications. Alcohols and other organic compounds only contributed to the photometric or fluorimetric signal when present in greater amounts than formaldehyde. Also, inorganic species such as sulphite, sulphide, nitrite and cyanide, which interfere with most of the colorimetric and fluorimetric methods available for determining formaldehyde, were found not to interfere appreciably with the proposed stopped-flow photometric and/or fluorimetric method. Overall, the method using the MBTH-formaldehyde system was found to be more selective than that based on the reaction between acetylacetone, ammonium and formaldehyde.

Table 2 Effect of inorganic and organic species on the determination of 100 ng ml⁻¹ formaldehyde.

Added compounds	Tolerated limit (ng ml ⁻¹)	
	Photometric method	fluorimetric method
Acetaldehyde	150	500
Propionaldehyde	1500	500
Benzaldehyde	3000	500
Acrolein	500	500
Crotonaldehyde	5000	500
Acetone	1000	5000
Acetate*	5000	—
Ethanol	5000	5000
Methanol	5000	1000
Phenol	3000	1000
Hydroxylamine	5000	—
Sulphite	5000	120
Sulphide	1000	5000
Bicarbonate	5000	1000
Nitrite	2000	500
Cyanide	1000	5000
Ammonium*	1000	—
Hydrogen peroxide	5000	2500

*Added as ingredients of the acetylacetone reaction.

Determination of formaldehyde in air

The proposed methods were applied to the determination of formaldehyde in air samples taken from typically urban areas. The analyte was collected in water. The collection efficiency was evaluated by using an apparatus similar to that developed by Rayner and Jephcott¹³. Briefly, known amounts of formaldehyde of 40–60 µg, dissolved in 25 ml of distilled water, were added in a purified air stream from a microburette at a rate of 0.2 ml/min. To ensure continuous evaporation, the incoming air was heated to a temperature of ca. 35°C. The formaldehyde borne on the air stream was collected in the absorbing solution, which was held in three impingers each containing 10 ml of distilled water. The results of seven determinations carried out at a flow rate of 1.5 l min⁻¹ for about 2 h showed the average collection efficiency to be ca. 80%. Most of the analyte was collected in the first (ca. 90%) and second (ca. 10%) impingers.

The accuracy of the proposed methods was evaluated by comparing their results and those provided by the standard chromotropic acid method³ for ten different urban air samples. The sampling site was located at street level, near a busy crossroads in a shopping area in Córdoba, Spain. Correlation coefficients of 0.958 and 0.956 were obtained for the stopped-flow photometric and fluorimetric methods, respectively. The corresponding linear regression equations were

$$Y_1 = (1.0 \pm 0.1)X - (0.4 \pm 1.4) \quad (5)$$

$$Y_2 = (1.0 \pm 0.1)X + (0.07 \pm 0.90) \quad (6)$$

where Y_1 , Y_2 and X are the results obtained from the MBTH, acetylacetone and chromotropic acid method, respectively. The results suggest the absence of systematic errors in the proposed methods. The formaldehyde levels found in the urban area analysed, ca. 0.1 mg/m³, were lower than those legally allowed in several European countries.

CONCLUSIONS

Both the MBTH–stopped-flow and the acetylacetone–stopped-flow method allow a straightforward determination of formaldehyde and can be used for monitoring occupational and environmental exposure to this toxic compound. The two proposed methods minimize some of the disadvantages of equilibrium MBTH-photometric and acetylacetone-fluorimetric methods. Their main advantages include a dramatically reduced analysis time (measurements can be obtained after a reaction time of 3 s and 3 min rather than 30 and 60 min for the MBTH and acetylacetone method, respectively), and a greater selectivity towards low molecular weight aldehydes (the results obtained for urban air samples were highly correlated with the standard chromotropic acid method). These improved features make these modified classical methods competitive with the chromotropic acid method, which they surpass in terms of sensitivity, rapidity and operational convenience.

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