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Spectrophotometric determination of formaldehyde with chromotropic acid in phosphoric acid medium assisted by microwave oven

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Abstract

In the present study, a spectrophotometric method for the determination of formaldehyde by using chromotropic acid was devised, in which the use of potentially hazardous and corrosive concentrated sulfuric acid was eliminated and advantageously replaced by a mixture of H_3PO_4 and H_2O_2. The reaction between formaldehyde and chromotropic acid (CA) in a concentrated phosphoric acid medium was accelerate by irradiating the mixture with microwave energy for 35 s (1100 W), producing a violet–red compound ($\lambda_{max}=570$ nm). Beer's Law is obeyed in a concentration range of 0.8–4.8 mg l^{-1} of formaldehyde with a good correlation coefficient ($r=0.9968$). The proposed method was applied in the analysis of formaldehyde in commercial disinfectants. Recoveries were within 98.0–100.4%, with standard deviations ranging from 0.03 to 0.13%.

Keywords: Formaldehyde; Chromotropic acid; Spectrophotometry; Microwave oven

1. Introduction

The uses of formaldehyde cover a wide range of fields. In the food chemistry, it is used as a food additive and it is also employed as chemical intermediate in the industrial synthesis of a large number of organic compounds. Moreover, formaldehyde is commonly used in the production of plastics and it can be added to some pharmaceutical products as a preservative. Formaldehyde kills viruses, bacteria, fungi and parasites and has found wide use as a disinfectant with a broad efficiency. Otherwise, it is considered one of the most significant industrial hazard and air pollutants [1]. The toxicity of formaldehyde to man and animals has been reported [2–4]. The International Agency for Research on Cancer has concluded that formaldehyde is a potential carcinogen for animals and that there is a limited evidence for the carcinogenicity of formaldehyde in human beings [1].

An efficient disinfectant should contain an adequate formaldehyde level. In order to assure the efficient use of disinfectants containing formaldehyde with regard to its toxicity and antiseptic activity, suitable analytical techniques are required. The most widely used methods for the determination of formaldehyde are based on spectrophotometry [5–8] and the chromotropic acid (CA) method has been recommended by NIOSH [9,10] in its P&CAM 125, 235 and 3500 reference methods. In the NIOSH method formaldehyde is detected by warming it with chromotropic acid, in the presence of concentrated sulfuric acid, yielding a soluble violet–red colour [6,11]. The spectrophotometric measurements are highly selective and other aldehydes do not interfere according to the literature [11]. The major drawback presented by the NIOSH method has been the use of concentrated H_2SO_4, which is potentially hazardous and corrosive, and the heating of the resulting solution for approximately 1 h in a steam bath (100 °C), making your utilization little attractive in routine analysis.

In previous study [12], modifications to the NIOSH procedure were described based on investigations concerning of the oxidation step of the reaction between formaldehyde and CA, in which the use of concentrated H_2SO_4 was eliminated and replaced by a mixture of HCl and H_2O_2. However, the aforementioned method even so requires a long heating time of the reaction mixture under strongly acidic conditions.

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Microwave heating has been widely used for sample digestion [13], acceleration of some chemical reactions [14–17] and for gravimetric determination [18]. The present work describes a new spectrophotometric method using CA for the determination of formaldehyde in disinfectants. In this method, a fast and efficient heating of the reaction medium was obtained by using a domestic microwave oven for 35 s (1100 W). Moreover, the use of concentrated H_2SO_4 or mixture of concentrated HCl and H_2O_2 was advantageously replaced by a mixture of H_3PO_4 and H_2O_2. Factorial experiments [19,20] were carried out to verify the existence of optimum levels for concentrated phosphoric acid volume and irradiation time. The proposed method was successfully applied in the analysis of commercial samples of disinfectants.

2. Material and methods

2.1. Apparatus

A Hewlett Packard Model HP8453 spectrophotometer with 1 cm matched silica cells was used for all absorbance measurements. Micropipettes Brand and Eppendorf were used to measure the smaller volumes in the experiment. A domestic microwave oven, Panasonic 1100 Watts Model Junior Intelligent Chaos was used for heating. The distribution of radiation in the oven cavity was realized similarly to a literature procedure [13,21].

2.2. Reagents

All reagents utilized were of analytical-reagent grade (Merck and Mallinckrodt Co.). For the preparation of the solutions and samples, deionised water and grade 'A' glassware were used throughout. Formaldehyde stock standard solution, 1000 mg l^{-1}, was prepared by dilution of commercially available analytical-reagent grade formaldehyde solution (37%, Mallinckrodt Co.) and standardized by a AOAC method [22]. Working standard solutions were obtained by appropriate dilution of this stock solution. Chromotropic acid (disodium salt dehydrate, $C_{10}H_6O_8S_2$ $Na_2.2H_2O$) was used to freshly prepare a 5% (w/v) aqueous solution. Concentrated phosphoric acid (85%) was purchase from Mallinckrodt Co. A 2.5×10^{-2} mol l^{-1} hydrogen peroxide solution was prepared from perhidrol 30% (w/v) (Merck) by a convenient dilution and standardized as described in the literature [23].

2.3. Methods

2.3.1. Calibration curve

The calibration curve was prepared as following: 1 ml of formaldehyde working standard solutions (comprising 0.80–4.80 mg l^{-1} of formaldehyde) was transferred separately into a 50 ml beaker. Then 300 μl of 5% CA solution were added followed by addition of 3.00 ml of concentrated H_3PO_4 and 70 μl of 2.5×10^{-2} mol l^{-1} H_2O_2. The beaker was covered with a glass cover, positioned in the center of the oven cavity and heated in the microwave for 35 s, at maximum power (1100 W). Afterwards, they were cooled at 25 °C. The absorbances are recorded at 570 nm ($b=1$ cm) against the reagent blank. Calibration graphs were prepared by plotting absorbance against formaldehyde concentration. These graphs or the corresponding linear least square equations were used to convert absorbance into formaldehyde concentration, for any analyzed sample.

2.3.2. Analysis of commercial disinfectants preparations

Commercial disinfectants preparations containing approximately 8.2% (w/v) (liquid form) and 3.0% (w/w) (solid form) of formaldehyde were assayed. For the liquid samples, 1.0 ml of each one was diluted with deionised water to 1.0 l and then 1.0 ml of this solution was diluted to 25 ml. For the solid samples, 0.1 g of each one was dissolved with approximately 500 ml of deionised water and 3.0 ml of concentrated H_2SO_4, then this solution was shaken and stayed in rest for 30 h. After this period, the volume was completed to 1000 ml with deionised water, and it was sonicated for 30 min. Aliquots of 1.0 ml of the both liquid and solid solutions were taken for analysis, following the procedure described for calibration curve.

2.3.3. Reference method

In order to compare the results obtained by the proposed method, the basic National Institute for Occupational Safety and Health (NIOSH) procedure using concentrated H_2SO_4 and heating for one hour in a steam bath (100 °C) was followed with modifications as described by Georghiou et al. [11].

3. Results and discussion

The absorption spectrum of the reaction product shows that the best analytical wavelength is located at 570 nm (Fig. 1).

Factorial experiments [19,20] were used to verify the optimum reaction conditions for determination of formaldehyde and to understand the effect of the factors upon the response. Variable parameters affecting the coupled reaction of the formaldehyde with CA were investigated by the evolutionary operation (EVOP). The absorbance response for fixed amounts of formaldehyde, CA and H_2O_2 can be optimized as a function of concentrated H_3PO_4 volume and irradiation time in the domestic microwave oven (maximum power). The conditions tested are summarized in Table 1.

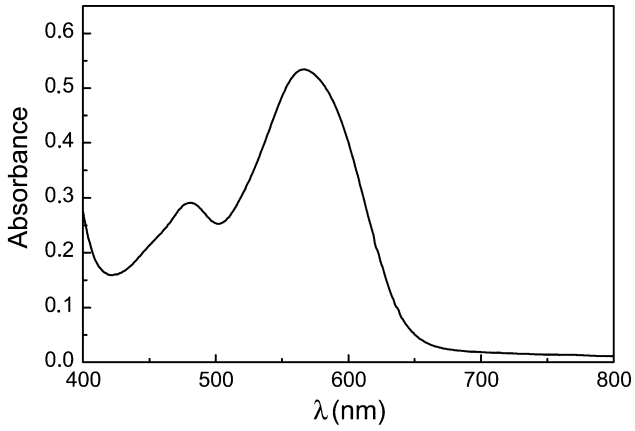

Fig. 1. Absorption spectrum of the reaction product obtained from formaldehyde (4.8 mg l^{-1}) and CA in a concentrated phosphoric acid medium; optical path = 1 cm; measurements were taken after heating for 35 s as described in Section 2.3.1.

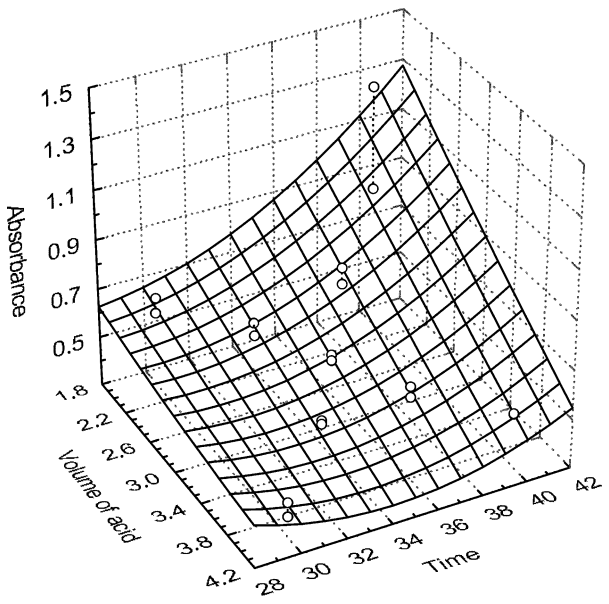

Fig. 2. Surface response obtained for the establishment of the optimum conditions.

The maximum absorbance response, without loss of sample or carbonization and with reproducibility, was reached with 3.0 ml of concentrated H_3PO_4 and 35 s of irradiation in the microwave oven. Fig. 2 shows the three-dimensional graph obtained from the experimental data and fitted to a response surface model. Analyzing the fitted surface, we determined the conditions of optimum response. As it can be seen in surface response graph other conditions showed absorbances values higher than the chosen conditions but they cannot be used because acid volumes higher than 3.0 ml and heating times higher than 35 s gave problems in regard to sample carbonization and decreased reproducibility. Another fact considered in our study was that the radiation absorbed by samples in the oven depends on their position in its cavity. The distribution of microwave radiation was determined as described in the literature [13,21] and the samples were strategically positioned in the center of the oven cavity, point where the microwave energy is more intense.

The possible interference of compounds commonly present in commercial formulations of disinfectants was carefully investigated. It was found that sodium dodecylbenzenesulfonate and eucalyptus essence do not interfere with the determination of formaldehyde by the presently proposed method.

Beer's Law is obeyed in a concentration range of 0.8–4.8 mg l^{-1} of formaldehyde ($r = 0.9968$) and this useful range was considered good for this kind of test. The slope of calibration curve leads to apparent molar absorptivity of $(1.63 \pm 0.08) \times 10^4$ mol l^{-1} cm^{-1} for the chromogen, which is close to that reported for the reaction developed with concentrated H_2SO_4, i.e. 1.8×10^4 mol l^{-1} cm^{-1} [11] or $(1.83 \pm 0.03) \times 10^4$ mol l^{-1} (this laboratory) [12], showing that the proposed method is quite competitive.

In order to assess the utility of the developed method it was applied to the determination of formaldehyde in commercial preparations. The results obtained by the proposed method were compared with the official method [11] (Table 2). For all the disinfectant preparations assayed the results obtained by the official and proposed methods were compared by applying the *F*-test and the *t*-test at the 95% confidence level. The results indicated that there is no significant difference between the official and proposed methods. The average recoveries obtained by the proposed method ranged from 98.0–100.4% for the commercial preparations; the standard deviations were within 0.04–0.13% (w/v) for liquid samples, and 0.03–0.13% (w/w) for solid samples, indicating good precision.

Table 1
Heating time in the microwave oven and volume of H_3PO_4 used to establish the optimum conditions for determination of formaldehyde by the proposed method

Volume of conc. H_3PO_4 (ml)	2.0	2.0	2.5	2.5	3.0	3.5	3.5	4.0	4.0
Heating time (s) (maximum power)	40	30	33	37	35	33	37	30	40

Table 2
Determination of formaldehyde in commercial disinfectants

Samples[a]	Nominal value[b,c]	Proposed method		Official method [9,10]	
		Found[c,d]	Rec (%)	Found[c,d]	Rec (%)
A	8.2	8.22 ± 0.13	100.2	8.24 ± 0.12	100.5
B	8.2	8.23 ± 0.08	100.4	8.18 ± 0.04	100.2
C	8.2	8.10 ± 0.04	98.8	8.03 ± 0.09	98.2
D	8.2	8.05 ± 0.10	98.2	8.00 ± 0.07	97.6
E	3.0	2.99 ± 0.13	99.7	2.88 ± 0.18	96.0
F	3.0	2.94 ± 0.03	98.0	2.87 ± 0.12	95.7

[a] A, B, C and D are liquid samples; E and F are solid samples.
[b] Nominal value supplied by the manufacturer.
[c] Concentration values: % (w/v) for liquid samples and % (w/w) for solid samples.
[d] Average ± S.D. of three determinations.

4. Conclusion

The proposed method for the determination of formaldehyde was considered simple and effective. The use of highly corrosive acid as the H_2SO_4 and heating in steam bath at 100 °C for lengthy time was avoided and replaced by a mixture of H_3PO_4 and H_2O_2 assisted by microwave oven. The application of microwave irradiation accelerated considerably the reaction among formaldehyde and CA in a concentrated H_3PO_4 medium. The colored compound is completely formed within 35 s of microwave irradiation. Our results demonstrate that the use of microwave oven irradiation can lead to substantial saving in time for this determination. This method was applied with success to the analysis of formaldehyde used as the active ingredient in commercial disinfectants.

Acknowledgments

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