

INTEGRATED RETENTION/SPECTROPHOTOMETRIC DETECTION METHOD FOR THE DETERMINATION OF FORMALDEHYDE

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ABSTRACT

An integrated-sensor method for the determination of formaldehyde based on retention of the reaction product of the analyte with p-rosaniline and sulfite in a flow-cell packed with Dowex 1-X-8 anion exchange resin was developed. The method has a good selectivity with a detection limit of $0.3 \mu\text{g ml}^{-1}$ (1 ml sample) or 75 ng ml^{-1} (2 ml sample), and a linear range between $1\text{-}30 \mu\text{g ml}^{-1}$. The relative standard deviations ($n = 11$) were 2.8 and 1.3% for 2 and $20 \mu\text{g ml}^{-1}$ formaldehyde, respectively. Depending on the working conditions, the sampling frequency ranged between 10 and 18 h^{-1} . The method was applied to the determination of formaldehyde in well water.

INTRODUCTION

Despite the toxic nature of formaldehyde, it is one of the most important industrial chemicals for the manufacture of synthetic resins, fertilisers, explosives and others. It is found in a great variety of consumer products such as cosmetics, and permanent press fabric and also as a combustion product from many sources including automobile exhausts and cigarette smoke.

Studies on its toxicity have revealed important health-related complaints. It has been established as a primary irritant and as mutagen, and it has been investigated as a suspected carcinogen.

Concern over environmental pollution by release of HCHO from consumer products has led to the need to develop reliable analytical methods for its determination. Although most of the methods are related to atmospheric samples, several methods have been evaluated for measurement of formaldehyde in complex water samples¹.

The most widely used and recommended spectrophotometric methods for determination of formaldehyde are those based on the usage of chromotropic acid², and the modified *p*-rosaniline (PRA) procedure^{3,4}. The use of concentrate H₂SO₄ in the chromotropic acid method is potentially hazardous, but it has the practical advantage that the heat of mixing with the aqueous medium facilitates the completion of the derivatization reaction. The modified PRA method, which is an adaptation of a method for sulfur dioxide⁵, is one of the most sensitive and selective, but its main drawbacks are the long standing time required for the reaction development and the need for strict temperature control.

Continuous flow injection (FI) methods including conventional, multidetection⁶, and stopped-flow⁷, using the same analytical reaction (HCHO-SO₂-PRA), minimise some of the disadvantages of the batch spectrophotometric method (e.g. it affords for a higher sampling-rate, easy control of temperature, small sample volumes and reduction of human participation).

On the other hand, increasing attention is being paid to the advantages of flow-through sensors in flow injection systems⁸⁻¹⁰, which are based on the transient or permanent immobilization of one of the components of a (bio)chemical reaction. This approach is compatible with automated systems and also calls for enhancement of valuable analytical features such as sensitivity and selectivity due to the *in situ* concentration and separation processes taking place simultaneously with detection on a solid support which packed the flow-cell of a non-destructive spectroscopic detector. According to this and using the reaction above mentioned, the purpose of this work was to develop a flow spectrophotometric method for the determination of formaldehyde

based on the temporary retention of the reaction product in the flow-cell of a conventional photometric detector packed with Dowex 1-X-8 anion exchange resin.

EXPERIMENTAL

Reagents

All chemicals used were analytical-reagent grade. Bidistilled water was used throughout.

Formaldehyde stock solution ($1\ 000\ \mu\text{g ml}^{-1}$) was prepared daily by diluting 1 to 1 with water 2.5 ml of 37% formaldehyde solution (Merck). More diluted solutions were prepared by appropriate dilution.

A 0.2% p-rosaniline solution in 1M hydrochloric acid was prepared and purified according to Scaringelly et al.¹¹

The sulfite solution was also prepared daily and consisted of 0.1000 g of anhydrous sodium sulfite dissolved in 100 ml of water. The eluting solution used was 2M hydrochloric acid equilibrated with 1-butanol.

The anion-exchange material in the chloride form was conditioned as required¹².

Apparatus and instruments

A Unicam 8625 UV/VIS spectrophotometer equipped with a flow-cell and connected to a Knauer xt recorder was used. A Hellma 138-OS flow-cell ($40\ \mu\text{l}$ inner volume) was packed with resin up to 8 mm from the bottom. A laboratory made assembly including a planar lens (glass BK7 PCX lens) driven by two micrometric screws was placed in the cell compartment in order to focus the light beam precisely in the exact position of the resin.

A four-channel Gilson Minipuls-2 peristaltic pump furnished with a rate-selector, a Rheodyne 5041 injection valve, a Rheodyne 5060 rotary switching valve and two Tecator TM III chemifolds were also used.

Manifold and procedure

Figure 1 shows the manifold used for the determination of HCHO. The sample (1 or 2 ml, depending on the concentration of the analyte in the sample) was inserted into a bidistilled water stream (flow-rate $-q_1$ - $0.5\ \text{ml}^{-1}$). Then, this stream merged with a reagent stream ($0.08\%\ \text{PRA}-0.4\ \text{M HCl}-0.1\%\ \text{Na}_2\text{SO}_3$, flow-rate $-q_2 + q_3$ - $1\ \text{ml min}^{-1}$) at M_1 . PRA in acid medium and sulfite solutions were previously mixed at M_2 in order to avoid

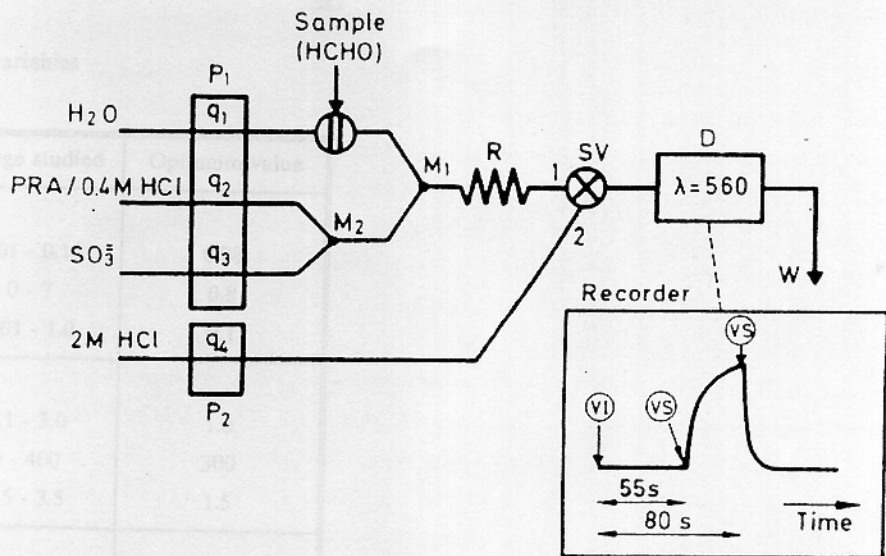


Fig. 1 Manifold and recording obtained by the flow-through photometric sensor for the determination of formaldehyde. PRA denotes p-rosaniline, q flow-rate, P peristaltic pump, M mixing point, R reactor, SV and IV switching and injection valve, respectively, D detector and W waste.

the instability of sulfite in acid medium. The reaction product formed in the reactor R (300 cm long, 0.5 mm id) started to be retained in the flow-cell packed with Dowex 1-X-8 anion-exchanger 55 seconds after injection as the selecting valve SV was switched to position 1. The retention signal was monitored at 560 nm. When the signal reached the maximum height (i.e., the tail of the sample plug), the concentrated reaction product was eluted with 2 M HCl saturated with 1-butanol, which was inserted via position 2 of SV 80 seconds after injection, thus restoring the baseline.

RESULTS AND DISCUSSION

Optimization of the proposed method

The variables affecting the performance of the proposed method were divided into three groups: a) chemical, b) FIA, and c) typical of the retention/detection unit. Table 1 shows the optimal values found and the ranges over which they were studied.

Table 1. Optimization of variables

Variable	Range studied	Optimum value
Chemical		
PRA, %	0.01 - 0.16	0.08
pH	0 - 7	0.8
Na ₂ SO ₃ , %	0.01 - 1.0	0.1
FIA		
Injected volume (IV), ml	0.1 - 3.0	1.0
Length of reactor (R), cm	0 - 400	300
Flow rate, ml min ⁻¹	0.5 - 3.5	1.5
Retention/detection unit		
Path length, mm	1 - 2	1
Particle size, mesh	50 - 400	100 - 200
Eluting agent (HCl), M	10 ⁻³ - 3	2
Flow rate of eluting agent, ml min ⁻¹	0.5 - 2	1

a) Chemical variables

The most influencing chemical variables for both the analytical and the blank signals were the PRA concentration and the pH of the reagent stream.

Both the analytical signal and the blank absorbance increased with increasing concentrations of PRA. Prior to optimization it was mandatory to purify the PRA solution¹¹ because adsorption of dye impurities on the resin significantly increased the blank signal. A PRA concentration of 0.08% was selected as optimum. Similarly, intensity of the color of both the reaction product and p-roaniline solution was enhanced with an increased pH of the reagent stream. The optimum pH was between 0.6 and 1.0. Lower pH values resulted in lower signals because high acid concentrations hindered adsorption of the reaction product on the resin.

The absorbance also increased with the concentration of SO₂ to reach a maximum value over 0.07%. An increase in the concentration of this reagent had not influence in the blank signal. A concentration of 0.1% was selected as optimal.

b) FIA variables

The flow-rate had a strong influence in the analytical signal. Increased flow-rates decreased the signal because the retention of the reaction product on the resin was not instantaneous. A total flow-rate ($q_1 + q_2 + q_3$) of 1.5 ml^{-1} was selected as a compromise between sensitivity and sample throughput.

The length of the reactor R had also influence on the response as the reaction-rate was relatively slow. Over 190 cm the signal was kept constant. A reactor of 300 cm was selected in order to increase dispersion thus facilitating retention by fitting the concentration of the reaction product in the solution reaching the flow-cell to the retention kinetics. On the other hand, the sample volumes were selected depending on the concentration level of the analyte in the sample. For concentrations of formaldehyde lower than $1 \mu\text{g ml}^{-1}$ a 2 ml sample volume was used and 1 ml for higher concentration in order to increase the sampling frequency.

c) Variables of the retention/detection unit

Using the selected FIA and chemical conditions given above the reaction product was easily retained in an anionic Dowex 1-X-8 resin showing maximum absorption at 560 nm.

The absorbance increased proportionally to the path length of the flow-cell, but the resin itself saturated the detector capacity when cells of 2 mm were used. A 1.0 mm path length cell was chosen which produced a baseline absorbance of 1.300 absorbance units (AU).

Decreasing particle size of the support packed in the cell (50-400 mesh) resulted in increasing the signal of the resin through increased compaction of the solid, while the analytical signal remained constant. A resin of 100-200 mesh was selected as optimal for further studies.

Measurements were made by focusing the light beam 2.5 mm below the top of the resin level. Above this height the signal decreased dramatically because the light beam passed through the solution. Heights lower than 2.5 mm decreased the signal at a rate of 0.05 AU per mm because the reaction product was largely retained on the resin zone where the flow impinged.

In order to make the sensor regenerable, a study of the potential of different species as eluting agents was carried out. Dimethylformamide, ethanol, methanol and acetone were studied as eluting agents in water-organic solvent mixtures in which the organic solvent ranged between 5 and 40%. They were not efficient for fast elution of

the reaction product. However, increasing hydrochloric acid concentration improved the efficiency of the regeneration step providing faster baseline restoration when its concentration was equal or above 2 M.

On the other hand, it was necessary to use 2 M HCl solution saturated with 1-butanol as eluting agent because after long working periods the time required for the regeneration step increase owing to the sorption of impurity traces present in PRA even after purification. In this medium, the impurities were soluble and thus eluted in each regeneration step.

Features of the proposed method

Under the optimized working conditions given in Table 1, a series of standards with concentration ranging from 0.10 to 50 $\mu\text{g ml}^{-1}$ were injected into the manifold. The linear relation between peak height absorbance and formaldehyde concentration was expressed by the least-squares method as,

$$A = 0.030[\text{HCHO}]_{\mu\text{g/ml}} + 0.160 \quad (r = 0.9989)$$

The plot was linear in the range 1.0 to 30.0 $\mu\text{g ml}^{-1}$. The detection limit, calculated by using the 3σ recommendation, was 0.30 $\mu\text{g ml}^{-1}$. The precision, expressed as rsd, of 11 replicate injection of solution containing 2 and 20 $\mu\text{g ml}^{-1}$ for formaldehyde was 2.8 and 1.35%, respectively, and the sampling frequency was 18 h^{-1} by using the selected working conditions.

Increased sample volumes were injected into the manifold in order to make the method more sensitive. A sample volume of 2 ml afforded for a detection limit of 75 ng ml^{-1} , but the sampling frequency decreased to 10 h^{-1} .

The relatively high intercept of the calibration equation (0.160 AU) was owing to the adsorption of PRA simultaneously with the reaction product and it corresponded to the blank signal as the baseline was established when the eluting agent was passing through the flow-cell. Another possibility was to establish the baseline when reagents were flowing through the cell. In this instance the calibration graph had the same slope but zero intercept. However, this last mode was slower than the above established as it required waiting for stabilization of the signal by passage of the reagents before injection of the sample.

Study of interferences

As only relative low molecular mass aldehydes (glyoxal, propionaldehyde and acetaldehyde) and carbonate ion interfered in the FIA⁷ and stopped-flow method⁷ where

Table 2. Comparison of the selectivity of different continuous FI methods

Specie	Molar ratios allowed foreign specie/analyte		
	Conventional FIA method ^(a)	Stopped flow method ^(a)	Flow through sensor method ^(b)
Glyoxal	0.01 : 1	0.06 : 1	15 : 1
Propionaldehyde	0.8 : 1	7 : 1	50 : 1
Acetaldehyde	1 : 1	10 : 1	6 : 1
Carbonate	1 : 1	15 : 1	100 : 1

^(a)Ref. 7 ; ^(b)This work

Table 3. Determination of formaldehyde in spiked well water

Sample	Added, $\mu\text{g ml}^{-1}$	Standard method ^(a)		Proposed method	
		Found, $\mu\text{g ml}^{-1}$	Recovery, %	Found, $\mu\text{g ml}^{-1}$	Recovery, %
Well 1	1.50	1.57	104.7	1.46	96.6
Well 2	2.00	2.25	112.4	1.95	97.5
Well 3	2.00	1.95	97.7	1.95	97.5
Well 4	0.95	1.09	115.2	1.03	108.4
Well 5	3.00	3.25	108.4	3.09	103.3

^(a)Ref. 2

the same analytical reaction was used, the potential interference of these compounds was studied. As shown in Table 2, the interferences from these compounds were lower in the proposed flow-through sensor method.

The higher selectivity achieved by using the proposed method could be due to faster retention kinetics of the reaction product of the analyte, the products from other aldehydes being not retained or retained more slowly.

Application of the proposed method

The flow-through sensor method was applied to the determination of formaldehyde in spiked well water using the standard addition method. Five different samples were spiked with standards in the concentration range of 0.95 to 3.00 $\mu\text{g ml}^{-1}$. The recoveries were compared with those obtained by the chromotropic acid method. As can be seen in Table 3 the results obtained by both methods are quite consistent.

CONCLUSIONS

The proposed integrated sensor approach for the determination of formaldehyde based on immobilisation of the product of the well-known reaction of the analyte with PRA and sulfite in the flow-cell possesses valuable analytical features that allowed its application to real samples.

A comparison of the proposed method with other methods using the same analytical reaction shows the advantages and disadvantages involved in its use. The comparison with its conventional counterpart^{3,4} shows that the proposed method is much faster, simpler and offer a high reduction of human participation. The conventional modified PRA method is very sensitive and selective, but requires a long standing time before measuring (about 1 h).

On the other hand, the proposed sensor has many of the advantages afforded by the normal FI procedure⁷, but it is more sensitive and selective, although the sample frequency is lower. Compared with the stopped-flow method⁷, despite the sensitivities and sample throughput being similar, the use of the sensor method uses a simpler set up, as it requires no go-stop control of the propulsion system or automation of data collection.

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