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Determination of formaldehyde in Brazilian alcohol fuels by flow-injection solid phase spectrophotometry

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Abstract

In this work, a solid phase spectrophotometric method in association with flow injection analysis for formaldehyde determination has been developed with direct measurement of light-absorption in C_{18} material. The 3,5-diacetyl-1,4-dihydrolutidine produced from the reaction between formaldehyde and fluoral P was quantitatively retained on C_{18} support and the spectrophotometric detection was performed simultaneously at 412 nm. The retained complex was quickly eluted from C_{18} material with the eluent stream consisting of a 50% (v/v) ethanol solution. The results showed that the proposed method is simple, rapid and the analytical response is linear in the concentration range of 0.050–1.5 mg L^{-1}. The limit of detection was estimated as 30 μg L^{-1} and the R.S.D. 2.2% using a sample volume of 625 μL. The system presented an analytical throughput of 20 determinations per hour. The method was successfully applied in the determination of formaldehyde in ethanol fuel.

Keywords: Formaldehyde; Solid phase spectrophotometric; Fluoral P; Ethanol fuel

1. Introduction

Formaldehyde enters the environment from natural sources (including forests fires) and from direct human sources such as fuel combustion, industrial on-site uses, and off gassing from building materials and consumer products. Thus, formaldehyde is uniquely important because of its widespread use and toxicity and it is recognized as one of most important environment pollutant [1]. This compound is widely present in the environment and is classified as "a probable human carcinogen", identified by the US Environmental Protection Agency and International Agency for Research on Cancer as a Class 2A carcinogen [2]. Also, it has known irritant properties, such as dermatitis, eye irritation, respiration irritation, asthma, and pulmonary edema [3,4].

Although formaldehyde is not present in gasoline, it is a product of incomplete combustion and is released, as a result, from internal combustion engines. The amount generated depends primarily on the composition of the fuel, type of engine, operating conditions and age and state of the vehicle [1,5]. In metropolitan areas, formaldehyde is almost always the predominant aldehyde emitted by automobiles. Meanwhile, there is evidence that the use of oxygenated fuels, including methanol, ethanol and blended fuels, can change the aldehyde profile emissions [5,6].

Brazil is the country that has attempted the large-scale use of alcohol as an automobile fuel by the use of ethanol–gasoline blended fuel (gasohol, mixture of 75% gasoline and 25% anhydrous ethanol). In addition, in Brazil, there are light duty cars exclusively driven using hydrated ethanol as fuel [7] and it is known that formaldehyde contamination in hydrated ethanol can be found because this compound can be formed during ethanol production by alcoholic fermentation process [8]. Indeed, it is necessary sensitivity and accuracy analytical methods for determination of this compound in this kind of matrix.

Small amounts of formaldehyde are commonly analyzed by spectrophotometric methods [9]. The spectrophotometric determination of formaldehyde with chromotropic acid

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(CA), for example, is a sensitive and selective method, however the major drawback present by CA method has been the use of hot concentrated sulphuric acid [10] or the use of a less harmful mixture of HCl and H_2O_2 [9]. Others drawback involving spectrophotometric methods are low color stability [11,12], interference of many substances [13,14] or preconcentration step [15]. Dimedone and 1,3-cyclohexanedione have been proposed as the detection reagents for trace amounts of aldehydes in previous paper, however, the procedure by batchwise method needs long reaction and high temperature [16–18].

Solid phase spectrophotometry, coupled with continuous flow system (FI-SPS) has been employed to determine low concentration of several chemical species in different kinds of sample solutions [19]. In FI-SPS, the solid support is placed into the light path of the flow cell and detection is performed simultaneously with the analyte retention [20]. This approach permits to achieve a high sensitivity and provides a low reagent and sample consumption. On the other hand, the FI-SPS approach permits the achievement of better performance than the flow systems that involve preconcentration and measurement of the analyte in the eluent or direct measurements in solution. Systems involving preconcentration/elution are usually designed to attain high enrichment factors. Nevertheless, an inherent dilution is observed during the elution step, which can cause an undesirable reduction of sensitivity [21].

In this work, a simple and sensitive method was developed for determination of formaldehyde in ethanol fuel by FI-SPS. The method is based in the reaction between formaldehyde and fluoral P producing 3,5-diacetil-1,4-dihidrolutidine (DDL) and their retention onto C18. This reaction was first applied for determination of microamounts of formaldehyde more than 50 years ago by Nash [22], who pointed out that the reaction product, DDL, fluoresce when properly ligh-excited. This last remark was advantageous used as a quantitative fluorimetric method for formaldehyde determination [23] and in more recent articles, others procedures based on DDL formation has been developed [8,24].

In the present paper, the DDL absorbance measurement is done in the solid phase by using a continuous flow system, thus integrating preconcentration and detection on a sorbent material packed in a flow cell. The FI-SPS proposed method is sensitive, selective and fast. Additionally, the method has a low sample and reagents consumption and low cost since measurements may be carried out with the help of conventional spectrophotometers. The method was successfully applied in the determination of formaldehyde in ethanol fuel.

2. Experimental

2.1. Apparatus

The set-up consisted of a Cary 1E spectrophotometer (Varian, Australia) with a homemade glass flow cell with 1.5 mm optical path [25]. A Gilson (Villiers-le-Bel, France) Minipuls 2 peristaltic pump equipped with flexible polyvinyl chloride tubes was employed as propeller device. The flow manifold was assembled with a homemade sliding-bar commutator [26], employing sample loops and flow lines of 0.8 mm i.d. PTFE tubes.

2.2. Reagents and solutions

All reagents were of analytical grade quality and freshly distilled and deionized water was used. Ethanol absolute (Merck, min. 99.8%) was used to prepare the ethanolic solutions. The fluoral P was prepared by reaction of 0.3 mL of acetic acid, 0.2 mL of previously distilled acetylacetone, and 15.4 g of ammonium acetate (which serves as a source of NH_3 and buffering agent). The volume was then filled to 100 mL with ethanol solution (50%, v/v) in water.

A 1000 mg L^{-1} solution of formaldehyde was prepared by diluting 2.7 mL of 37% formaldehyde solution to one liter with water and was standardized by the sulfite method. Working solutions were prepared daily by appropriate dilution of the stock solution with 50% (v/v) ethanol solution.

Ethanol solution (50%, v/v) in water was used as carrier stream.

A 15 mg amount of C18 bonded silica (60–100 μm) obtained from a Sep-Pak cartridge (Waters) was used as solid support for complex retention in the flow cell.

2.3. Samples

Eleven hydrated ethanol fuel samples were randomly collected from different gas stations in Salvador, Bahia State, Brazil (Safra, Texaco, Shell, Total, Esso, Hora, Petrobahia, Satélite, Esso, CBPI, BR). So 5 mL portion of each sample was transferred to 10 mL volumetric flasks and the volume was filled to 10 mL with water.

2.4. Flow diagram and procedure

The flow cell was filled with ca. 15 mg of C18 beads and glass wool was placed at the inlet and outlet of the cell to avoid removal of the solid phase by carrier stream. Then, the flow cell was inserted in the optical path of the spectrophotometer.

The flow diagram system is presented in Fig. 1. In this situation, the commutator is in the position where the loop L (625 μL) is being filled with 3,5-diacetyl-1,4-dihydrolutidine (DDL). DDL is obtained on-line from the reaction between formaldehyde present in the samples (or standards solution) and Fluoral P previously mixed in the confluence *x*. Both solutions are flowing at a flow rate of 1.0 mL min^{-1}. The carrier stream, C, (ethanol solution 50%, v/v) flows through the analytical path at 1.5 mL min^{-1}.

By sliding the commutator central bar, the reaction product between formaldehyde present in the sample (or standards) and Fluoral P, previously formed in the loop

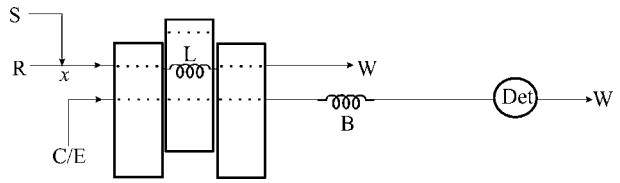

Fig. 1. Flow diagram of the system employed for flow-injection solid-phase spectrophotometric determination of formaldehyde. S, sample or standard solution at 0.75 mL min^{-1}; R, reagent, Fluoral P solution at 0.75 mL min^{-1}; C/E, carrier and eluent stream, ethanol solution 50% (v/v) at 1.5 mL min^{-1}; L, sample loop (625 μL); B, 50 cm flow line; W, waste; *x*, confluence; DET: spectrophotometer equipped with flow cell loaded with C_{18}, 412 nm.

L, is inserted into the analytical path. Subsequently, the 3,5-diacetyl-1,4-dihydrolutidine (DDL) formed was retained in the flow cell, filled with C18, positioned in the optical pathway. Absorbance signals were continuously recorded at 412 nm. After reaction and detection, the carrier stream, which also acts as the eluent stream, removes the DDL from the solid-phase. In the flow manifold, the flow line B is maintained as short possible (ca. 20 cm). The overall system was operated at room temperature (22 ± 2 °C).

3. Results and discussion

3.1. Chemical variables

The mechanism of the reaction between formaldehyde and Fluoral P involves steps of condensation and cyclization of two molecules of formaldehyde with one molecule of Fluoral P. The rate of the analytical reaction is too slow to be conveniently adapted to conventional spectrophotometric flow injection analysis [27]. However, the association between solid phase spectrophotometry and continuous flow system (FI-SPS), used in this work, provided an adequate system for trace measurement of formaldehyde, because the FI-SPS approach permits the achievement of good sensitivity due to in situ accumulation of the analyte in a small volume of solid phase. In addition, it is unnecessary to attain equilibrium conditions when FI-SPS is employed.

The spectrum of the DDL retained on C_{18} bonded silica was measured after baseline correction established with the solid support treated with 50% (v/v) ethanol solution. On the solid phase, the dye presented an absorption maximum at 412 nm. C_{18} support was very stable in aqua and ethanolic solutions, allowing its use for more than 200 measurements without affecting the retention of DDL. Fifty percent (v/v) ethanol solution, employed as carrier stream and eluent solution, allowed proper DDL elution without change the retention characteristics of the solid phase. The retained complex was quickly and completely eluted from C_{18} material and the baseline was stable during the measurements.

The influence of the pH on the formation of DDL and on its retention onto C_{18} support was investigated within the range of pH 4.0–12.0 adjusting the pH of the fluoral P solution with acetic acid or ammonium hydroxide. No significant variation in the retention efficiency was observed in the pH range of 5.5–7.0. Thus, in further experiments, fluoral P solutions were previously buffered at pH 6.0 with acetic acid/ammonium acetate buffer solution.

The reagent composition used in this work was adapted from the values reported by de Andrade et al. [8]. However, the analytical sensitivity is not significantly dependent on the reagent concentration. Changing the concentrations, one at a time, of acetic acid, acetylacetone or ammonium acetate upward or downward as a factor of 2 from the concentrations stated in the experimental section changed the responses of the system to formaldehyde determination by less than 5%.

3.2. FI variables

The total flow rate of the system was maintained at 1.5 mL min^{-1} because at higher values fluid leakage was observed due to the increase of the pressure inside the system. Fluoral P and sample carrier flow rates were divided equally in order to the final flow rate in the confluence *x* to be 1.5 mL min^{-1}.

The removal of DDL from the solid-phase was performed after each measurement to avoid the saturation of the adsorption sites. This procedure was carried out by employing the carrier solution as eluent. Thus, a transient signal was obtained after each sample insertion, due to DDL retention and removal by the ethanolic carrier. Different concentrations of ethanol in the samples and the others solutions cause a formation of intense refractive index gradients in sample zone (Schlieren effect). The usual way to overcome this perturbation is to employ a carrier with physical and chemical characteristics as similar as possible to the samples [28]. So, the concentration of ethanol in the samples, standard solutions, reagent and carrier/eluent stream was maintained in 50% (v/v) in order to overcoming the Schlieren effect.

The effect of the flow rate on the desorption of DDL retained on C_{18} was investigated using the 50% (v/v) ethanol solution as cleaning solution. A change in flow rate from 0.5 to 1.5 mL min^{-1} did not affect the DDL desorption. Flow rates >1.5 mL min^{-1} caused fluid leakage in the joints due the increase in back pressure. Therefore, a flow-rate value of 1.5 mL min^{-1} was selected as a compromise between sample throughput and system stability.

An important advantage of solid phase spectrophotometry is the potentiality of improving sensitivity by increasing the sample volume from which the analyte is concentrated in the solid support [21]. This fact is important since it can provide different alternatives for varying the sensitivity of the procedure as a function of the formaldehyde concentration in the samples. This effect can be assessed by measuring the absorbance intensity on C_{18} with different volumes of solution containing the same concentration of formaldehyde injected through the flow cell. So, the volume of the loop L located after mixing the samples and reagents was varied between 150 and 850 μL. As shown in Table 1,

Table 1
Effect of the volume on the sensitivity and sample throughput

Loop volume (μL)	Sensitivity ($L\,mol^{-1}\,cm^{-1}$)	Sample throughput, determinations per hour
150	0.38×10^4	31
300	0.71×10^4	25
450	1.00×10^4	23
625	1.55×10^4	20
850	1.82×10^4	14

sensitivity ($L\,mol^{-1}\,cm^{-1}$) had increased with the loop volume (mL). On the other hand, by increasing the sample volume, an inherent decrease in the sampling rate was also observed. Thus, a 625 μL sample volume was chosen as a compromise between sensitivity and sample throughput.

3.3. Features of the method

Under the conditions described, in the proposed procedure, the Beer's law was obeyed from 0.050 to 1.5 $mg\,L^{-1}$ when a sample volume of 625 μL was employed, according to the equation: $A = 0.516C + 0.002$ ($r = 0.9981$), where A represents the absorbance signals measured as peak height and C the concentration of formaldehyde in $mg\,L^{-1}$. The coefficient of variation for 10 independent measurements was 2.2% and the detection limit, calculated as three times the standard deviation of the blank solution, was 30 $\mu g\,L^{-1}$. The apparent molar absorptivity of the proposed method was estimated as $1.55 \times 10^4\,L\,mol^{-1}\,cm^{-1}$. This value is ca. two-fold higher than that obtained for pure DDL in ethanol–aqueous solution ($8.0 \times 10^3\,L\,mol^{-1}\,cm^{-1}$) reported in previously work [23]. This fact occurs because the use of solid phase spectrophotometry permits the achievement of better sensitivity due the concentration of the complex and measurements of the absorbance signal on a solid support.

The recording of an analytical run obtained by duplicate injections of formaldehyde standards is shown in Fig. 2,

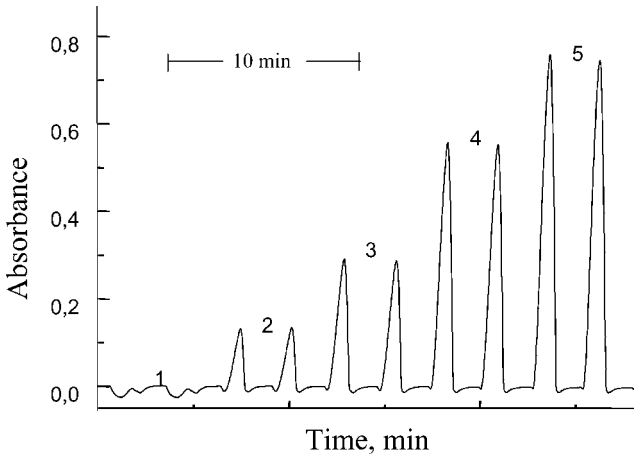

Fig. 2. Recorder output obtained for the solid phase determination of formaldehyde as DDL. Injected standards of formaldehyde correspond to (1) 0.0 $mg\,L^{-1}$, (2) 0.30 $mg\,L^{-1}$, (3) 0.60 $mg\,L^{-1}$, (4) 1.2 $mg\,L^{-1}$ and (5) 1.5 $mg\,L^{-1}$.

Table 2
Comparison of the analytical characteristics of the proposed procedure and previously work [24]

Analytical characteristic	Proposed method	Previously method [24]
Variation coefficient (%R.S.D.)	2.2	4
Detection limit ($\mu g\,L^{-1}$), 3σ	30	3
Correlation coefficient (r)	0.9981	0.9999
Temperature of reaction (°C)	At room temperature (22 ± 2 °C)	51
Time of analysis for sample (min)	3	6[a]
Acetaldehyde tolerance (concentration of acetaldehyde/concentration of formaldehyde, mol/mol)	1000	1

[a] Time of sample analysis by HPLC after derivatization reaction of 12 min and cooling to room temperature.

from it can be deduced that a sample throughput of 20 determinations per hour can be achieved with good baseline stability and precision.

The proposed method was developed for determination of formaldehyde in ethanol fuel and this matrix presents no majors interferences. In addition, the reagent used in the method is well-know and it is a specific reagent for determination of formaldehyde. This reagent does not react with ketones, and the only aldehydes it reacts with are formaldehyde and acetaldehyde [24]. So the interference study was performed in several mixtures containing both aldehydes under the optimum working conditions. For this purpose, variable amounts of aceldehyde were added to a 0.1 $mg\,L^{-1}$ solution of formaldehyde up to a maximum aceltadehyde/formaldehyde ratio of 1000:1 (molar:molar). It was found that, in the conditions of this study, acetaldehyde does not interfere even when present in molar concentrations 1000 times higher than formaldehyde. Additionally, acetaldehyde reaction with fluoral P is more slowly than DDL formation and no significant absorbance signal was observed from this reaction after 24 h in off-line measurements at 412 nm.

A previously work [24] used the same reaction followed by HPLC analysis for determination of formaldehyde. A comparison of the analytical characteristics of the proposed procedure and the previously work is summarized in Table 2. As can be seen, the HPLC method has good sensitivity; however, the proposed method displays advantages over the already published methods as time saving, automation, acetaldehyde tolerance as well as simultaneous preconcentration and determination of the analyte on a sorbent material packed in a flow cell.

3.4. Application

The proposed method has been applied to the determination of formaldehyde in hydrated ethanol fuel from different fuel distributors. Results are showed in the Table 3.

Table 3
Determination of formaldehyde in hydrated ethanol fuel ($mg\,L^{-1}$)

Sample	Comparative method [8]	Proposed method
Distributor 1	0.22 ± 0.03	0.18 ± 0.02
Distributor 2	0.35 ± 0.05	0.39 ± 0.04
Distributor 3	0.32 ± 0.04	0.31 ± 0.02
Distributor 4	0.46 ± 0.06	0.50 ± 0.02
Distributor 5	0.31 ± 0.04	0.28 ± 0.03
Distributor 6	0.57 ± 0.08	0.66 ± 0.04
Distributor 7	0.57 ± 0.08	0.55 ± 0.03
Distributor 8	0.21 ± 0.03	0.25 ± 0.02
Distributor 9	0.24 ± 0.03	0.31 ± 0.02
Distributor 10	0.31 ± 0.04	0.26 ± 0.03
Distributor 11	0.51 ± 0.07	0.55 ± 0.04

Each result was obtained as the average of three replicates of each fuel. The results obtained by the proposed method were compared with spectrofluorimetric method [8]. The application of the paired *t*-test (95% confidence level) did not show significant differences between the values obtained.

4. Conclusions

The developed procedure provides a sensitive and simple approach for the determination of formaldehyde by the retention of product of the reaction between the analyte and fluoral P onto C_{18} without any sample pretreatment. The FI-SPS proposed method is rapid, robust and it has low cost since the measurements may be carried out with the help of conventional spectrophotometers. Small amounts of sample, resin and reagent are required. Another advantage of the method is the possibility of working at different formaldehyde concentration levels by selecting the sample volume depending on the analyte concentration. The method was successfully applied in the determination of formaldehyde in ethanol fuel.

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