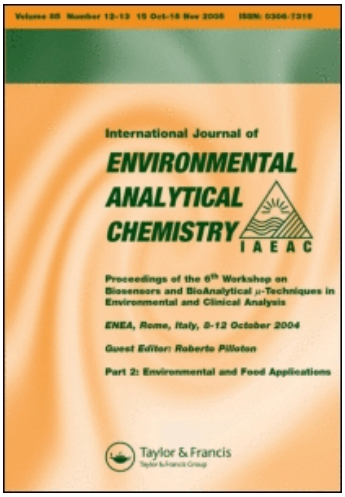

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Sensitivity Enhancement of the Formaldehyde Fluorimetric Determination by the use of a Surfactant

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SENSITIVITY ENHANCEMENT OF THE FORMALDEHYDE FLUORIMETRIC DETERMINATION BY THE USE OF A SURFACTANT

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A sensitive method for the formaldehyde determination in aqueous samples by Flow Injection Analysis has been developed. Formaldehyde reacts with acetylacetone, acetic acid and ammonium acetate to form diacetyldihydrolutidine, detectable by its fluorescence; the effects of various surfactants upon this spectrofluorimetric method have been assessed. Fluorescence enhancements from 15–70% were observed in comparison with that without surfactant. The developed method has a detection limit of 55 ng/l and a precision of 2.5% at 1 μg/l level. The calibration graph is linear in over the range 0.1–3000 μ/l. The sensitivity, speed, ease of use and small volume of sample make this method ideal for formaldehyde determination in precipitation samples with concentration from very low to very high by continuous or semicontinuous analysis.

Keywords: Formaldehyde; Flow Analysis; Fluorimetry; Triton X-100; Rain; Snow

INTRODUCTION

Carbonyls and thus formaldehyde play a central role in the chemical reactions taking place in the troposphere because they are generally the first stable intermediates in the photo-oxidation mechanism of organic compounds.

Formaldehyde is a labile compound involved in several important processes occurring in the troposphere. It affects the acid generating capacity of atmospheric waters because it inhibits oxidation of S(IV) to sulphuric acid, and because it is a precursor to formic acid[1,2]. Formaldehyde plays a relevant role in the oxidizing capacity of the troposphere because of its interactions with H_2O_2, OH and HO_2 radicals in solution[3]. Formaldehyde serves as an important free radical precursor (resulting from the combination of its fast photolysis rate and large atmospheric abundance), contributing for 25–30% of the radical production during midday by way of photolysis, and its contribution can be compared to that of O_3, the primary source of free radicals[4].

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Thus, accurate formaldehyde measurements are essential to further an understanding of various atmospheric cycles involving hydrogen- and carbon-containing species.

Carbonyl compounds are amongst the few species that are both emitted directly into the atmosphere and produced *in situ* (e.g. photodegradation of organic compounds). Primary emissions of formaldehyde are due to anthropogenic activities, such as incomplete combustion processes, and emissions from natural sources[5]. Aldehydes are produced directly in the combustion of hydrocarbon fuels[6] and thus motor vehicle emissions are the source of formaldehyde throughout the year[7]. The atmospheric level of formaldehyde in Salvador Bahia (Brazil) has a close relationship with the vehicular fleet[8]. Also from studies in Grenoble (France), formaldehyde appears to come mainly from exhaust car emissions[9].

The diurnal variation shows significant decrease of formaldehyde concentration in the night, indicating a decrease in primary source such as traffic emissions[7, 10]. Carbonyls (formaldehyde, acetaldehyde and acetone) are strongly correlated with CO during winter, suggesting an important motor vehicle source; a stronger correlation with O_3 concentration in summer suggest a net photochemistry carbonyl production[11].

It is possible that the vegetation in summer may play a role as a sink or as a biogenic source for the formaldehyde. In fact biogenic non-methane hydrocarbons are emitted into the atmosphere from the terrestrial vegetation; oxygenated compounds, among them organic acids as well as aldehydes, represent a substantial part of the released hydrocarbons[12]. The oxidation of biogenic hydrocarbons emitted, particularly isoprene and terpenes, represents an important source of formaldehyde[11]. Moreover, vascular plants do not only emit the precursors of carbonyl compounds but they are also found to emit directly aldehydes especially during the daytime with high light and temperature. Both coniferous and deciduous trees can emit formaldehyde[13].

There have been numerous studies of formaldehyde in the gas phase presumably because of formaldehyde's role in photochemical smog formation. Moreover the effects of this pollutant on the environment have generated intensive scientific and public concern due to possible deleterious effect on human, plant and animal life. Especially, formaldehyde has received attention as a very toxic urban pollutant because of its carcinogenic effect, its eye-irritating effect and its irritation of the respiratory tract resulting in asthma-like symptoms[14]. The "human dose of rodent carcinogen" (HERP) was evaluated: human dose $= 598\,\mu g$, HERP $= 0.4$[15].

Levels of formaldehyde in air as high as $32.7\,\mu g/m^3$ in very polluted areas are reported in the literature[16]. In Florence (Italy) were observed the mean/maximum formaldehyde concentrations $3.3/23.4\,\mu g/m^3$[10].

The high formaldehyde solubility in water ($K_H = 3400$)[17] produces precipitations with an elevated content of this compound. For example, Báez *et al.*, found concentrations of 1 mg/l at the beginning of a precipitation in Mexico City[18]. Formaldehyde was detected in 116 rain samples in Wilmington (USA) from 1996–1998 and its concentrations ranged from below 0.3 to 400 μg/l, in the range of formaldehyde levels reported at other locations worldwide[19]. The mean/maximum formaldehyde rain concentration of samples collected in Florence was $98/443\,\mu g/l$[10]. It is interesting to determine formaldehyde content also in the snow and in remote zones.

The oxidative capacity of the atmosphere determines the lifetime and ultimate fate of atmospheric trace species; it is controlled by the presence of highly reactive radicals, particularly OH radicals formed as a result of ozone photolysis[20]. The main formaldehyde source in the remote troposphere is oxidation chain of methane initiated

by reaction with OH radicals and followed by further reactions[21]. Formaldehyde archived in the ice, produced in the atmosphere by radical reactions closely linked to the OH budget, offers then the potential to constrain model estimates of OH concentrations in the past and thus the oxidative capacity of the past atmosphere[22]. Direct formaldehyde sources may be emission by algae contained in polar snow and photolysis of organic matter including marine biomolecules; thus formaldehyde originating from the snowpack constitutes an important local source. Under conditions of low ambient humidity, the radical production by ozone photolysis is inefficient and formaldehyde photolysis is likely to constitute the most important radical source in the lower polar troposphere[20].

The measurements of formaldehyde concentrations along the New Grip Ice Core from Summit (Central Greenland) showed a variability of about 0–12 μg/l[23]. Sumner and Shepson measured formaldehyde at Canada Forces Station Alert in Canada from February to April 1998[20]; during this period they also measured formaldehyde concentrations in melted snow samples collected within the study area. The snow-phase concentrations measured ranged from about 0 to 21 μg/l. Antarctica is the continent with the lowest environmental contamination and the formaldehyde concentration in the snow is very low: about 0–25 μg/l[22]. Our preliminary measurements show a larger concentration range: 0–67.8 μg/l, with 7.7 μg/l mean concentration, 5.8 μg/l median concentration and a background level of a few μg/l[24].

Because of this low formaldehyde concentrations, it is necessary to obtain an analysis method highly sensitive and with very low detection limit.

For several years surfactant molecules and their aggregates have been increasingly used in analytical techniques. The most significant characteristic of the amphiphilic molecules, containing both hydrophobic and hydrophilic moieties, is the tendency to adsorb very strongly at the interface between air and water. As the surfactant concentration increases, the adsorption at the air–solution interface becomes stronger. Saturation is reached when the molecules are packed close together, with strong lateral interactions occurring between the hydrophobic chains, which tend to stick up out of water[25]. Amphiphilic molecules associate in water above the critical micellar concentration (cmc) to form aggregates of colloidal dimensions called ''micelles''.

The normal micelle aggregate consists of from 40–200 monomers. The precise structure of the micelle depends upon the temperature and concentration and also on the molecular structure: size of head group, length and number of hydrocarbon chains, presence of branches, double bonds or aromatic rings, etc. Increasing the concentration of the surfactant leads to the formation of rodlike micelles and, subsequently, to liquid crystals[25]. The existence of premicellar assemblies was also confirmed[26].

The cmc depends on the surfactant structure (the longer the hydrocarbon tail, the lower the cmc) and on experimental conditions (ionic strength, temperature, etc.). The heterogeneous structure of micellar aggregates has a strong effect on the properties of partitioned solutes, including the photophysics of molecules[27].

The use of surfactants to improve determination schemes based on spectral methods was one of the first applications of organized systems in analytical chemistry. In most cases surfactant-modified procedures allow an improvement in the sensitivity and/or the selectivity of determination, whereas certain analytical methods can be exclusively conducted in organized media[25].

It was observed that the addition of surfactants to a fluorescent compound solution causes a remarkable fluorescence enhancement and/or minor interferences. The factors

that are responsible for the increased fluorescence intensity in micellar solution are still poorly understood. The micelle effect appears to result from the protection of the fluorescent compound from the quenching in the bulk solvent[25].

There is the possibility of more subtle effects due to molecular ordering in the micellar phase[28]. Also a more rigid structure would account for the observed florescence enhancement[29]. One of these factors or a combination of these, causes a diminution of deactivation processes (non-radiative) for the excited states. Thus, the micelle provides a favorable microenvironment so that the excited singlet state is stabilized and the efficiency of fluorescence improved[27, 29]. Moreover the presence of surfactants generally gives a higher selectivity than a conventional method[30]. The presence of micelles is also known to accelerate the rate of many organic reactions carried out in aqueous media. Micellar catalysis of thermal reactions is a well-established area of research (and the formation of DDL is known to be a reaction which occurs at high temperature). The micelle solubilizes reactants in the same micellar volume, thereby increasing their local concentrations, and hence increasing the reaction rate[31].

EXPERIMENTAL

The method used for formaldehyde determination involved the formation of a fluorescent compound, diacetyldihydrolutidine (DDL), from a reaction formaldehyde with ammonium ion and acetylacetone[32]. This method presents the advantage of very low sensitivity for the higher aldehydes. The method is linear in the range 0.4–2000 μg/l, with detection limit 0.4 μg/l and reproducibility better than 3% at concentrations of few μg/l levels[10]. This method was improved by use of a surfactant.

Apparatus

The flow injection manifold used in this work is shown in Fig. 1.

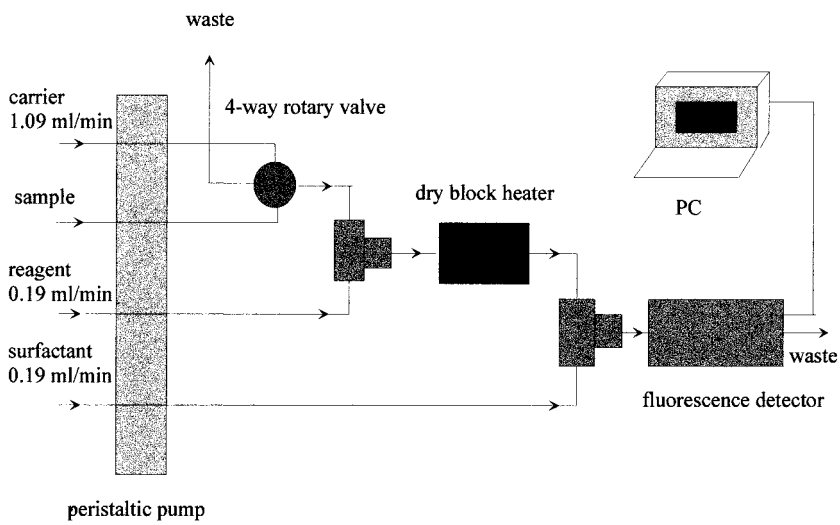

FIGURE 1 Scheme of flow injection manifold used.

The manifold consists of a peristaltic pump (Ismatec IPC), a 4-way Teflon rotary valve (Rheodyne, type 50), a dry block heater (thermobloc Falk 3372, working temperature from room temperature to $99.9^{\circ}C \pm 0.2^{\circ}C$) and a fluorescence detector Shimadzu (RF-551) with a 150 W Xenon lamp.

The excitation and emission wavelengths are set to 410 and 502 nm respectively. Peak detection and quantification of the results presented here were obtained using a PC-based axquisition program (CSW version 1.7 Data Apex Ltd.).

The other optimum conditions are: reaction coil length 0.5 mm i.d. × 200 cm, cooling and mixing coil length 150 cm, sample size 250 µl, flow rate of the carrier solution 1.09 ml/min, flow rate of the reagent 0.19 ml/min and flow rate of the surfactant 0.19 ml/min.

Reagents

Reagent:	Acetic acid	0.177 M
	Acetylacetone	0.145 M
	Ammonium acetate	2 M
Surfactant:	Trition X-100	10% w/w (see further).

All solutions were prepared with UHQ water and reagent grade chemicals.

Surfactants tested are producted by Aldrich Chemical Company Inc. (Span 20, Span 85, Tween 20, Tween 85, Igepal CO-210, Igepal DM-970, Brij 30, Brij 700, Triton X-405) and Merk KgaA (Brij 35 and Triton X-100).

Reagents were prepared every day and stored in glass bottles.

Fresh formaldehyde standards were prepared for each calibration by serial dilution from a stock standard of 1000 ppm prepared by dilution of a commercial solution 37% p.a. and titred as reported in "ACS specifications" of American Chemical Society[33]. This stock standards have been found to be stable for months to years.

RESULTS AND DISCUSSION

The primary goal of this method development was to provide a technique that would be capable of producing analytical determinations within a few seconds of sample introduction and of high sensitivity so that very low formaldehyde concentrations in snow matrices can be easily determined.

In various fluorimetric determinations surfactants were used to increase analyte fluorescence. The increase in the sensitivity of fluorescent reaction of the complexing of aluminium with morin using surfactant agents was investigated by Medina *et al.*[30]. The surfactant agents used were Genapol PF-20, Genapol PF-10 and Tergitol XD. The detection limit was reduced and some of the most notable interferences were also eliminated.

More recently a sensitive modification of the lumogallium fluorescence assay for aluminium is presented that exploits the 5-fold increase in the fluroscence intensity of the lumogallion–aluminium complex in the presence of the non-ionic surfactant Brij-35[34].

In this work the effects of surfactants on fluorescence analysis of formaldehyde were studied. The anionic and cationic surfactants that were examined (anionics: sodium

TABLE I Non-ionic surfactants examined and results obtained

Surfactant (commercial name)	*Type of compound*	*PM*	*Concentration of signal stabilisation*	*Maximum signal increase*	*Notes*
Span 83	Sorbitan sesquioleate	952			opalescence problems
Span 20	Sorbitan monolaurate	346			opalescence problems
Tween 85	Poluoxyethylene sorbitan trioleate	1839			signal decrease
Tween 20	Polyoxyethylene sorbitan monolaurate	1228	0.6% w/w, 1.4% w/w	26%	
Igepal DM-970	$(C_9H_{19})_2C_6H_3$–$(OCH_2CH_2)_{150}OH$	6950	0.75% w/w	16%	
Igepal CO-210	*p*–C_9H_{19}–C_6H_4–$(OCH_2CH_2)_2OH$	308	0.25% w/w	9.5%	
Brij 700	$C_8H_{37}(OCH_2CH_2)_{100}OH$	4670	0.25% w/w	15%	
Brij 35	$C_{12}H_{25}$–$(OCH_2CH_2)_{23}OH$	1198	1.3% w/w	39%	
Brij 30	$C_{12}H_{25}$–$(OCH_2CH_2)_4OH$	362	0.5% w/w	22%	
Triton X-405	*p*–C_8H_{17}–C_6H_4–$(OCH_2CH_2)_{40}OH$	1966	0.7% w/w, 1.25% w/w	34%	
Triton X-100	*p*–C_8H_{17}–C_6H_4–$(OCH_2CH_2)_{10}OH$	652	0.4% w/w, 1.3% w/w	70%	

dodecylsulfate (SDS), sodium hexadecylsulfate (SHS); cationics: *N*,*N*,*N*-trimethylammonium bromide (TAB), dodecyltrimethylammonium bromide (DTAB) did not show any influence on sensitivty of measures and thus were chosen non-ionic surfactants (see Table I).

The surfactants *Span 83* (sorbitan sesquioleate, PM = 952) and *Span 20* (sorbitan monolaurate, PM = 346) showed opalescence problems and produced high background fluorescence, thus they are not considered.

The *Tween 85* (polyoxyethylene sorbitan trioleate, PM = 1839) showed an unexpected signal decrease.

The *Tween 20* (polyoxyethylene sorbitan monolaurate, PM = 1228) evidenced a double plateau correspondingly at a surfactant concentration of 0.6 and 1.4% w/w in the fluorimetric cell with a maximum signal increase of 26%.

The *Igepal DM-970* ($(C_9H_{19})_2C_6H_3(OCH_2CH_2)_{150}OH$, PM $\sim$6950) showed a stabilization of fluorescence increase after a concentration of 0.75% w/w with a maximum increase signal of 26%.

The fluorescence intensity increased with the increasing concentration of *Igepal CO-210* (*p*-C_9H_{19}-C_6H_4-$(OCH_2CH_2)_2OH$, PM = 308) and reached to a constant and maximum intensity by the addition of more that 0.25% w/w of surfactant; the signal increase was of 9.5%.

The *Brij 700* ($C_8H_{37}(OCH_2CH_2)_{100}OH$, PM = 4670) showed a signal increasing of 15% for a surfactant concentration of 0.25% w/w; it was not possible to continue the study for higher concentrations because the noise background strongly increased.

For the *Brij 35* ($C_{12}H_{25}(OCH_2CH_2)_{23}OH$, PM = 1198) the signal reached a stabilization at about 1.3% w/w of surfactant; the maximum signal increase was of 39%.

For the *Brij 30* ($C_{12}H_{25}(OCH_2CH_2)_4OH$, PM = 362) it was analogous, but the maximum signal increase (22%) was minor and it was reached at a surfactant concentration of 0.5% w/w.

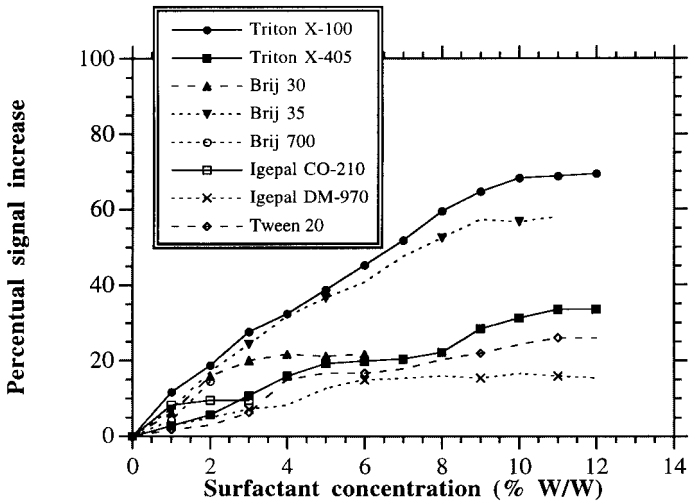

FIGURE 2 Effect of various non-ionic surfactants examined.

The *Triton X-405* (p-C_8H_{17}-$C_6H_4(OCH_2CH_2)_{40}OH$, PM = 1966) showed a double stabilisation, like Tween 20, at a surfactant concentration of 0.7 and 1.25% w/w, with a maximum signal increase of 34%.

Finally, also the *Triton X-100* (p-C_8H_{17}-$C_6H_4(OCH_2CH_2)_{10}OH$, PM = 652) appeared to show a double signal stabilization, even though less evident, reaching the maximum response increase (70%) at a surfactant concentration of 1.3% w/w.

The Fig. 2 summarizes these results. In this figure the percentual signal increase from signal without surfactant *vs.* the surfactant concentration (as % w/w) in the solution in the flow system is reported.

We can think that the signal stabilization is reached at the cmc, but from Fig. 2 we see that often there are two steps. In fact, recent studies have evidenced two cmc for Triton X-100: the first critical micellar concentration is $cmc_1 = 3.1 \times 10^{-4}$ mol/l and the second is $cmc_2 = 1.3 \times 10^{-3}$ mol/l[35]. Surfactant can exist as monomer molecules, premicelles, spherical micelles and rod-like micelles with surfactant concentration increasing to lower their free energy. Probably the cmc_1 is the transition concentration between premicellar assemblies and spherical micelles, whereas the cmc_2 is the transition concentration between spherical micelles and rod-like micelles[36].

Because the cmc is indicated by the point of abrupt increase of fluorescence emission intensity[37], we calculated the Triton X-100 cmc_2 by our measures: $cmc_2 = 1.1 \times 10^{-2}$ M (the cmc_1 is not easily evident). This value is higher than those reported in the literature, but we have to consider that the apparent cmc of a surfactant increase significantly in the presence of various substances, like cyclodextrins and carbohydrates[38, 39].

We calculated also the apparent critical micellar concentrations for Triton X-405 in presence of DDL (more easily evaluated from Fig. 2): $cmc_1 = 1.8 \times 10^{-3}$ M and $cmc_2 = 4.6 \times 10^{-3}$ M. the addition of non-ionic surfactants causes a remarkable enhancement of fluorescence (see Fig. 2). In particular, by use of Triton X-100 the sensitivity of fluorimetric determination of formaldehyde is increased about two-fold over conventional methods. Considering the good results obtained with Triton X-100, the

successive experiences were carried out with this surfactant. The *excitation and emission spectra* with and without the Triton X-100 for evaluation the signal increase were examined (Fig. 3).

As the surfactant concentration increases the fluorescence emission peaks progressively shift toward shorter wavelengths; concomitantly, the fluorescence intensity of these peaks significantly increases.

In Fig. 3b are shown the emission spectra of the DDL in the presence and in the absence of the surfactant at the chosen concentration. With Triton X-100 there was a shift of about 10 nm to a shorter wavelength in the emission maximum and about two-fold increase in the fluorescence intensity at the maximum. The shift of the emission maximum indicates that the interaction of the surfactant with the DDL gave rise to the energy change of the excited state of the fluorescent compound. No detectable

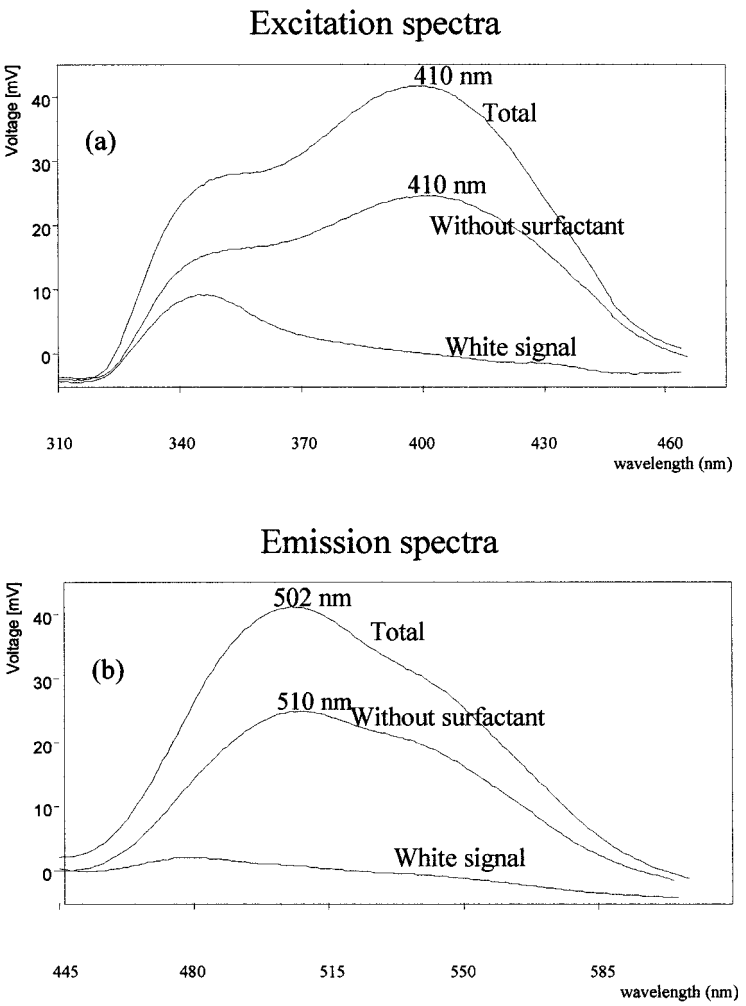

FIGURE 3 Excitation spectra (a) and emission spectra (b) of the DDL in presence and in absence of Triton X-100 and blank signal.

wavelength shift was observed in the fluorescence excitation spectra (Fig. 3a) by the use of surfactant. The following working wavelengths were chosen: $\lambda_{ex} = 410\,nm$ and $\lambda_{em} = 502\,nm$. The effect of varying the *reaction pH* was investigated by varying the ratio of acetic acid and ammonium acetate in the buffer (Figs. 4a and 4b). The response of the system of *acetylacetone concentration* (Fig. 4c) tends to reach a plateau between concentrations of 0.02 ± 0.04 M in the system effluent (the combined sample and reagent

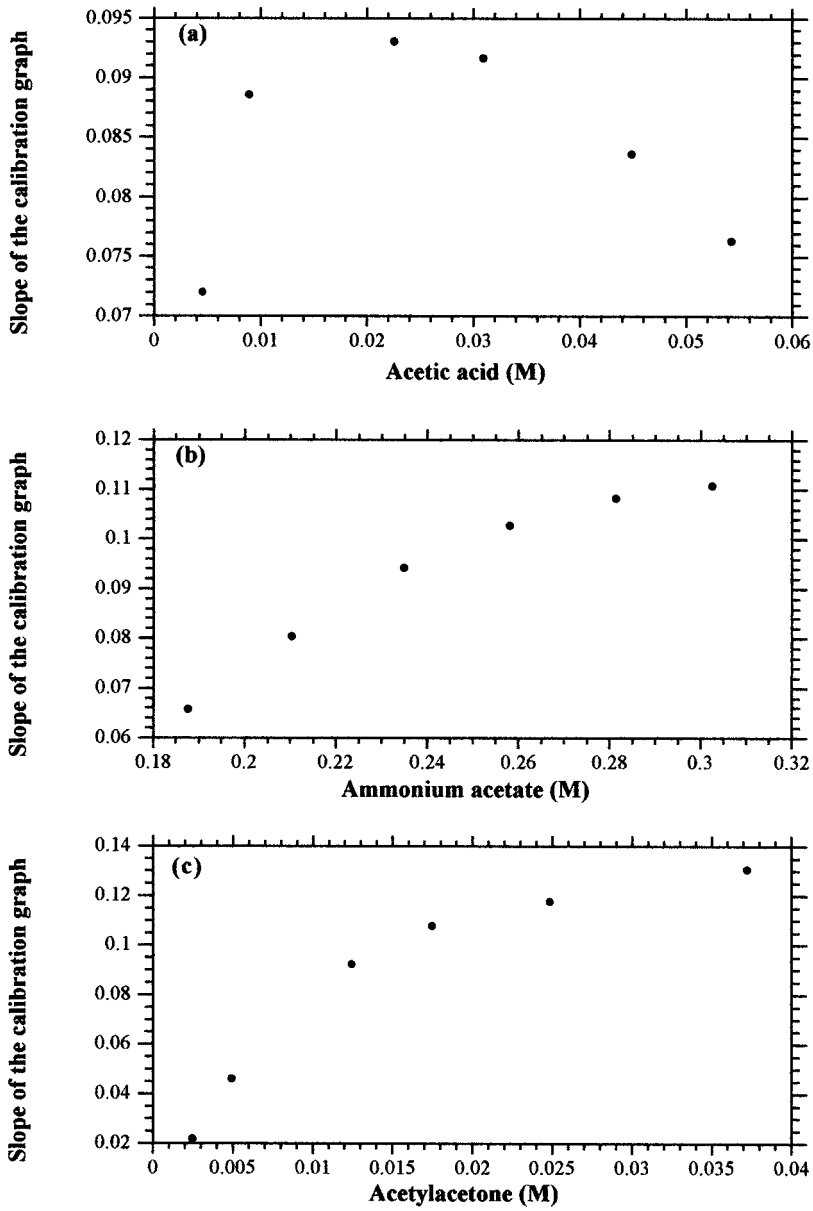

FIGURE 4 Response of the system to variation of acetic acid (a), ammonium acetate (b) and acetylacetone (c) concentration in the reagent.

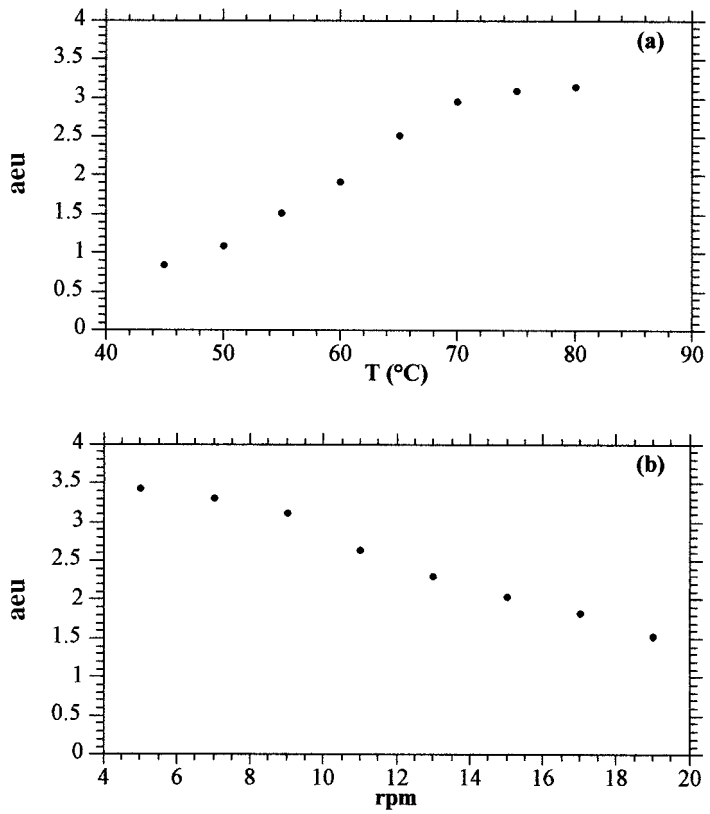

FIGURE 5 Effect of temperature (a) and reaction time (b) on the technique sensitivity. aeu = arbitrary emission units; rpm = revolutions per minute.

mixture leaving the detector). This compares with a concentration of 0.0175 M by Dong and Dasgupta[32]. The slightly higher acetylacetone concentration used here (0.02 M in the system effluent) is chosen by the need to achieve a greater extent of the reaction. No increase in background noise over the entire concentration range of acetylacetone investigated were found. The sensitivity of the technique to *temperature* was investigated (Fig. 5a). It was found that increasing the temperature from 45–75°C increased the response by a factor of −4. At temperatures above 75°C the response stabilizes; thus, for the our FIA method a temperature of 75°C was adopted. The half-time for the reaction between acetylacetone and formaldehyde is 10 min at 60°C and 25 s at 95°C[32]. In order to assess the degree of reaction, the effect that changing pump speed (and thus *reaction time*) had on the sensitivity of the technique was examined (Fig. 5b). As a compromise between sensitivity and response time, a pump speed of 15 rpm was chosen, corresponding to 1.09 ml/min surfactant flow, 0.19 ml/min reagent flow and 0.19 ml/min surfactant flow.

PERFORMANCE OF THE DEVELOPED METHOD

Generally the accuracy, precision and detection limit of procedures in micelles are as good as or better than those in water. In common with all fluorescence methods, the

sensitivity is largely determined by the choice of instrument and operating conditions, and lowest determinable levels by reagent purity and handling conditions.

Sensitivity

In discussing the sensitivity of a fluorescence procedure in analysis, it is convenient to separate the contributions from the properties of the fluorescent molecule itself (absolute sensitivity), the performance of the instrument (instrumental sensitivity) and the chemistry involved in the sample preparation (method sensitivity).

The *instrumental sensitivity* determine the detection limit for a particular compound on a particular instrument and the factors involved are: source intensity, efficiency of the optical systems used to irradiate the sample and to collect the radiation emitted, aperture of the monochromator, efficiency of the detector, noise level in the detector circuit.

A precise standard has recently been adopted by some manufacturers. This is to quote the signal/noise ratio for the Raman band of water observed at maximum sensitivity settings (when a sample of water is irradiated at 350 nm its Raman band appears at 395 nm). For a typical modern dual monochromator spectrofluorimeter this signal/noise ration is greater that 150[40].

Thus, to evaluate our instrumental sensitivity the signal/noise ratio was measured:

$$S/N = A/B = 379$$

where A is the height of the Raman scatter peak of water at 395 nm (excitation wavelength 350 nm) and B is the width of noise from the recorder output data for ten minutes (peak-to-peak noise, eliminating the upper two and the lower two peaks the exceed the straight portion). The S/N value obtained is very good.

The *method sensitivity* takes account of steps in the preparation of the sample and limitations imposed by the fluorescence of the blank.

In the strict sense, the sensitivity of an analytical method is the rate of change of analytical signal with concentration, in other words the slope of the calibration graph[40]. For this method was obtained: $y = 0.196x + 0.071$ (see further).

Reproducibility

The standard deviation, SD, for the analysis of ten replicates of a sample containing 0.5 μg/l of HCHO was equivalent to 0.028 μg/l (relative standard deviation $SD_r = 5.65\%$). With an HCHO content 0.8 μg/l $SD_r = 2.6\%$ and for 25 μg/l $SD_r < 0.5\%$ (Figs. 6a, b and c).

Detection limit

The observed fluorescence enhancement directly led to lower detection limit. It may be calculated as the concentration equivalent to twice the standard deviation of at least ten readings on an analyte sample at a concentration just above the blank level[40].

On 10 readings of a sample of HCHO 0.5 μg/l we have obtained a detection limit of 0.055 μg/l.

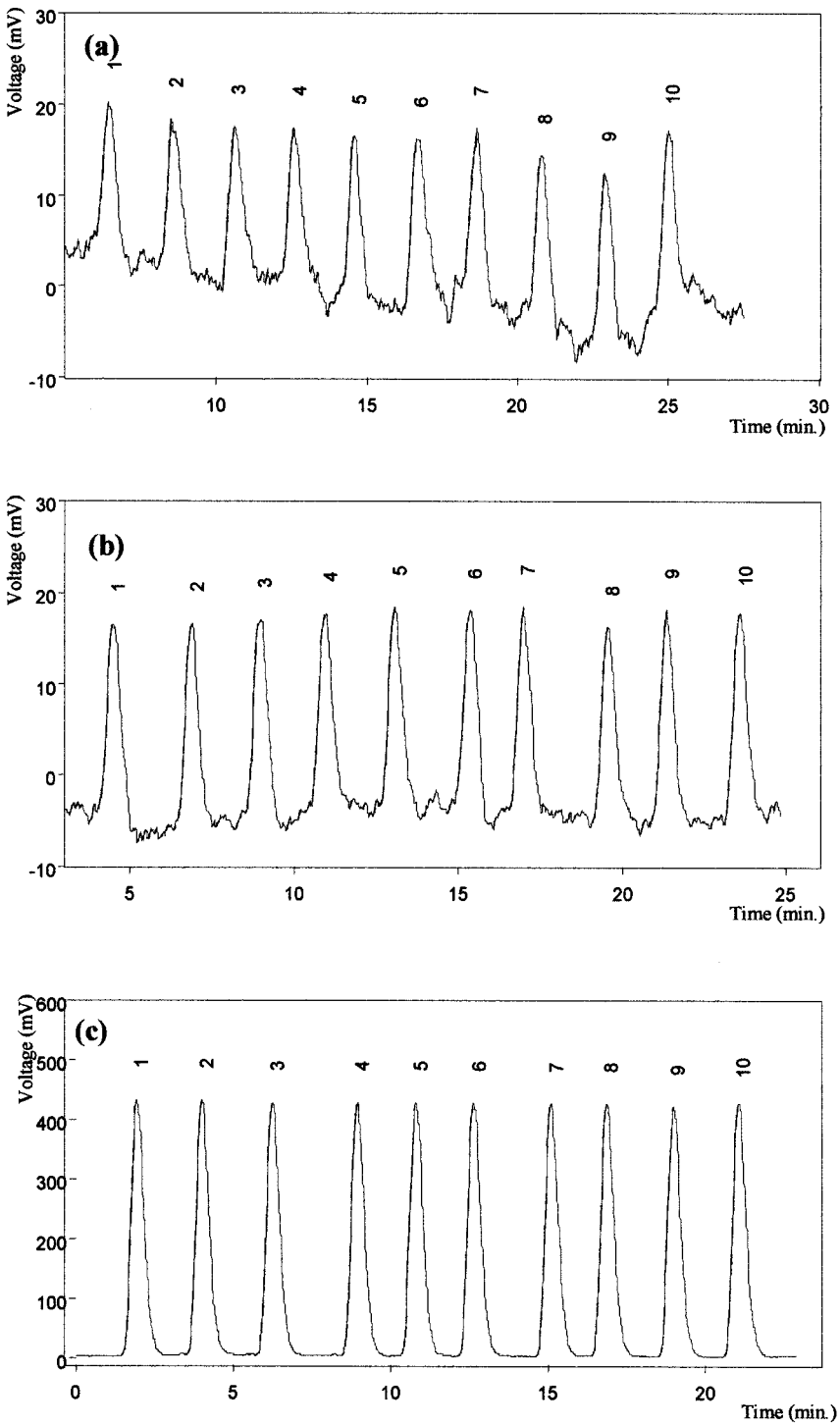

FIGURE 6 Reproducibility on formaldehyde samples of 0.5 (a), 0.8 (b) and 25 (c) μg/l.

Dynamic Range

The range of concentrations in which the recommended procedure can be applied was studied and it was found that the calibration graph was linear from about 0.1 μg/l up to 3000 μg/l of HCHO: $y = 0.196x + 0.200$ with correlation coefficient $R = 0$ 0.99996 (see Fig. 7), while without surfactant the linearity range is 0.4–2000 [10]. In fact the working curves usually exhibit a longer linearity range in micelles as compared to that observed in homogeneous solvents[41].

At very low concentrations only the intercept of the calibration graph varies, while the slope is unchanged: $y = 0.196x + 0.071$.

In Table II we have reported the performances of principal methods for formaldehyde determination. The performances of this method for formaldehyde determination have been decisively improved and this method can be conveniently used for formaldehyde determination in snow and rain samples.

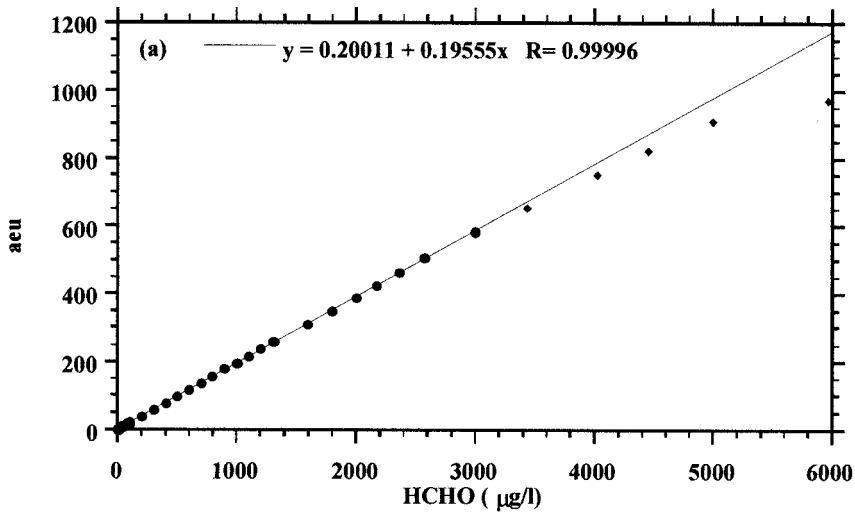

FIGURE 7 Total calibration graph (aeu = arbitrary emission units).

TABLE II Performance characteristics of various formaldehyde determination systems

	Dong and Dasgupta 1987[a] *[32]*	*Nishikawa et al., 1998*[b] *[42]*	*Viskari et al., 2000*[c] *[7]*	*Largiuni et al., in press*[a] *[10]*	*Largiuni et al., this work*[d]
Linear range (μg/l)	3–> 100	10–100		0.4–2000	0.1–3000
Reproducibility (%)	1.50 in the linear range	< 1 at 50 μg/l	4 for 56 standard solutions 11.5 for 5 parallel samples	< 3	5.65 at 0.5 μg/l 2.60 at 0.8 μg/l < 0.5 at 25 μg/l
Detection limit (μg/l)	3		0.2	0.4	0.055
Sample rate (s/h)	45			20	30
Loop sample (μl)	100	150		(Flow Analysis)	250

[a]Determination of HCHO by formation of DDL and analysis with fluorimeter.
[b]Determination of HCHO by use of cyclohexane-1, 3-dion and analysis with fluorimeter.
[c]Determination of HCHO by derivatization with DNPH and analysis with HPLC.
[d]Determination of HCHO by formation of DDL in presence of Triton X-100 and analysis with fluorimeter.

APPLICATIONS

The developed method was applied on analysis of rain samples and snow samples. For example in Fig. 8a formaldehyde concentrations was reported for rain event of July 10 1999. The mean, minimum and maximum values (170, 4.3 and 497 μg/l) are in accordance with concentrations reported in literature.

In Fig. 8b we can see the formaldehyde concentration/profundity profile for the Snowpit Dome C – Antarctica (position 75°07′35.0″ S, 123°16′58.8″ E; altitude 3309 ± 62 m a.s.l.; sampling period 31.12.1997–03.01.1998). The mean, minimum and maximum values are 6.7, < 0.1 and 24.2 μg/l, in accordance with concentration of 0–25 determined in Antarctica[22]. Thus, the performance of the developed method is sufficient to determine formaldehyde concentration in environmental samples.

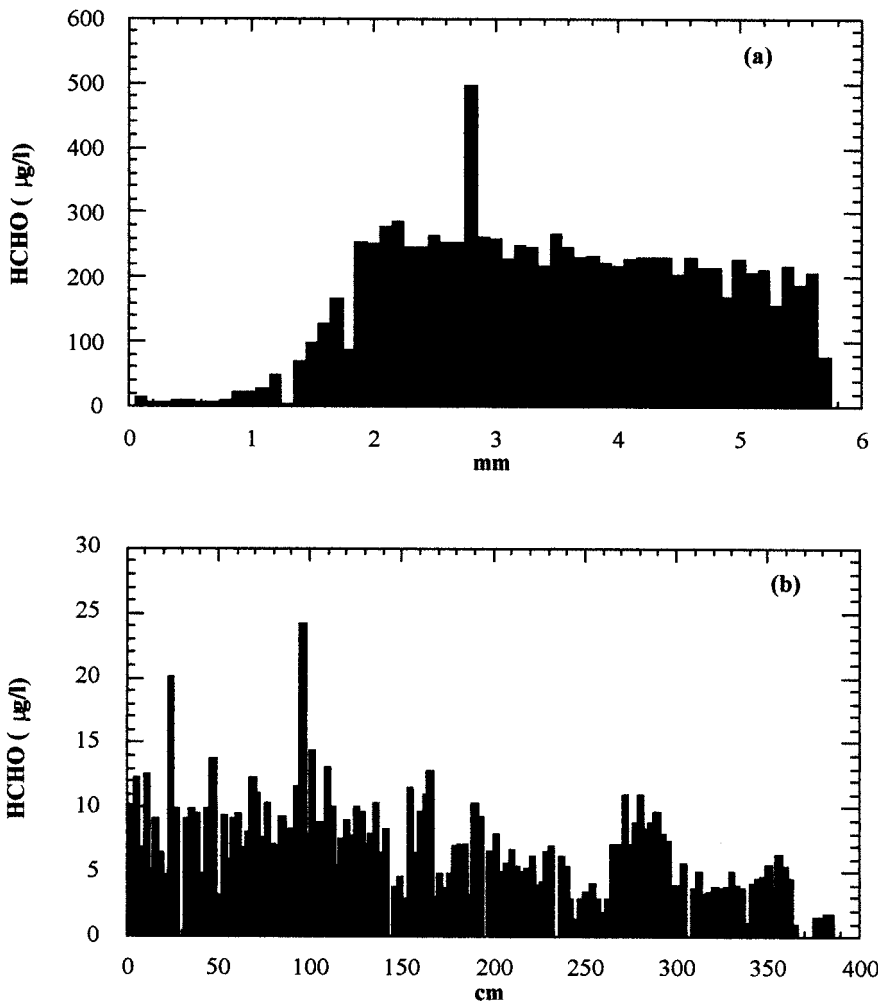

FIGURE 8 Formaldehyde concentration *vs.* total mm of rain for the precipitation of July 10 1999 (a) and formaldehyde concentration *vs.* snow profundity for Snowpit Dome C (b).

CONCLUSION

A fluorimetric procedure for the determination of HCHO has been developed. In this work the effects of surfactants on fluorescence analysis of formaldehyde was studied. The technique described is based upon the use of a micellar system and their unique properties that lead to drastically enhanced fluorescence. The addition of non-ionic surfactant causes a remarkable enhancement of fluorescence, by which means the sensitivity of the formaldehyde fluorimetric determination by the formation of DDL is increased about two-fold over conventional methods.

The approach is simple, convenient, rapid and accurate. The developed method has a very high linearity from very low concentrations to very high concentrations ($> 3000\,\mu g/l$, more that sufficient to determine formaldehyde content in rain samples by polluted areas) and a good reproducibility, even at low concentration. The detection limit is sufficient to determine formaldehyde content in snow sample of remote areas. The enhancement of fluorescence and concomitant reduction of the detection limit by use of micelles should prove to be a very useful technique in chemical analysis.

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