Colourimetric Determination of Features of an Air Sampling Technique Optimal for Detection of Surfactants
(Penentuan Keadaan Optimum Teknik Pensampelan Udara bagi Pengesanan Surfaktan Secara Kolorimetri)

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ABSTRACT

Surfactants in the atmosphere may act as cloud condensation nuclei, with a potentially negative impact on the global climate. Therefore, accurate determination of surfactants is crucial in order to investigate the possible effects of surfactants on the atmosphere. The aim of this study was to identify the optimum sampling method for measuring the maximum quantity of surfactants present in ambient air. Air samples were collected using a range of air sampling pumps that were made to vary in terms of flow rate, storage period, type of absorbing solution and the characteristics of the impinger tube. Samples obtained were analysed by colourimetry for anionic and cationic surfactants as methylene blue-active substances (MBAS) and disulphine blue-active substances (DBAS), respectively. Absorbance was measured at 650 nm for MBAS and 628 nm for DBAS using UV-visible spectrophotometer. We found that the optimum sampling method consisted of an absorbent solution (deionised water, buffer solution and methylene blue/disulphine blue solution) with the flow rate of 1.0 L/min. The concentration of surfactants in all sampling methods remained constant regardless of the storage period (1 day and 4 days), indicating that surfactants in the absorbing solution are quite stable. Covering the impinger tube was shown to influence the amount of both anionic and cationic surfactants detected.

Keywords: Ambient air; anionic and cationic surfactants; colourimetry

ABSTRAK

Surfaktan di atmosfera berpotensi untuk bertindak sebagai nukleus kondensasi awan yang berupaya memberi kesan negatif terhadap iklim global. Kaedah yang tepat bagi penentuan surfaktan adalah penting bagi mengkaji pelbagai kesan surfaktan terhadap atmosfera. Kajian ini bertujuan mengkaji dan membangunkan satu kaedah pensampelan optimum yang berpotensi dalam menyerap kandungan maksimum surfaktan yang hadir di udara. Pensampelan udara dijalankan dengan menggunakan pam udara yang berbeza daripada segi kadar aliran, tempoh penyimpanan, jenis larutan penyerap dan keadaan tiub penyerap. Sampel yang diperoleh kemudiaanya dianalisis secara kaedah kolorimetri sebagai sebatian aktif metilena biru (MBAS) bagi surfaktan anionik dan sebagai sebatian aktif disulfina biru (DBAS) bagi surfaktan kationik. Serapan analit seterusnya diukur dengan menggunakan spektrometer ultra lembayung boleh nampak pada panjang gelombang 650 nm bagi MBAS dan 628 nm bagi DBAS. Hasil kajian menunjukkan bahawa keadaan yang optimum bagi pensampelan surfaktan adalah dengan menggunakan campuran larutan penyerap (air nyahion, larutan penimbal dan larutan metilena biru/disulfina biru) pada kadar alir 1.0 L/min. Kepekatan surfaktan didapati malar bagi tempoh penyimpanan 1 hari dan 4 hari, menunjukkan sukfaktan di dalam larutan penyerap adalah agak stabil. Penutupan tiub penyerap didapati mampu mempengaruhi kepekatan kedua-dua surfaktan yang ditentukan.

Kata kunci: Kaedah kolorimetri; surfaktan anionik dan kationik; udara persekitaran

INTRODUCTION

Surfactants present in the atmosphere impact the global climate (Brimblecombe & Latif 2004). Their ability to reduce the surface tension of the aqueous phase indicates that surfactants can act as cloud condensation nuclei, resulting in the enhancement of the cloud albedo effect. This enhancement has been shown in a number of studies identifying the surface tension reduction caused by these atmospheric organic compounds (Facchini et al. 1999, 2000; Hyvärinen et al. 2006; Shulman et al. 1996; Tuckermann & Cammenga 2004; Latif et al. 2005). Accurate determination of surfactants is crucial to the investigation of the possible effects of surfactants on the atmosphere.

Surfactants have usually been determined by spectrophotometric methods using methylene blue for anionic surfactants; this standard method is used, for example, to determine the surface agents in tap-water samples (ISO 7875-1 1996). This standard method has been adopted for the determination of surfactants for

aerosol sampling (Sukhapan & Brimblecombe 2002). Additionally, disulphine blue has been used as a reagent for the determination of cationic surfactants (Latif et al. 2005). Most studies quantifying surfactants are only concerned with the development of a method for analysing surfactants using various techniques; fewer studies deal with effective sampling procedure. Although all the analytical techniques are important, we propose that the sampling techniques should as well be taken into account.

Prior to analysis, particular sampling conditions are required in order to gather the maximum amount of surfactants present in air. Surfactants might be lost due to oxidation by radicals or ozone during the sampling process (Gao et al. 2001). Therefore, degradation taking place during the sampling process may also influence the concentration of surfactants gathered for examination. Consequently, specific sampling conditions should be employed in order to obtain the air sample that represents most accurately the true amount of surfactants present at the time of sampling. Therefore, this study undertook preliminary identification of the particular features of the sampling procedure and equipment that would provide optimum sampling conditions for surfactant studies, particularly studies of surfactants in ambient air. To achieve this objective, an air sampling pump was used to collect ambient air, and the effects of varying each of several sampling parameters (i.e. absorbing solutions, impinger tube conditions, flow rate and storage period) were investigated.

MATERIALS AND METHODS

The method to determine the optimum procedure for surfactants analysis in the atmosphere was divided into two steps. The first step was to determine the most suitable absorbing solutions, and the second step was to determine the optimum conditions for surfactant analysis after the most suitable absorbing solution had been identified. The sampling was conducted near the roadside of the heavily travelled intersection at the entrance of Universiti Kebangsaan Malaysia, Bangi, to ensure that surfactants would be present in the atmosphere due to anthropogenic sources, e.g. from motor vehicles.

The principle underlying the methodology for surfactant determination is that the surfactants in the air sample will be absorbed into the absorbing solution in the air pump's impinger tube, and then the measurement of levels of surfactants will be determined by the reaction of surfactants to the specific dyes in the absorbing solution in the presence of an organic solvent (chloroform).

SELECTION OF ABSORBING SOLUTION

The first step of the experiment was to choose the optimal absorbing solution for determination of surfactants in ambient air. Three types of absorbing solutions were prepared to obtain the optimal reaction of each type of surfactant (anionic and cationic) in the ambient air to the specific analyte in the absorbing solution.

The first absorbing solution for anionic surfactant analysis (Solution 1) consisted of 10 mL of dionised water. The second absorbing solution (Solution 2) was prepared using a mixture of deionised water (8 mL) and alkaline buffer solution (2 mL) prepared by a mixture of 24 g sodium hydrogen carbonate (BDH Chemicals) and 27 g sodium carbonate (BDH Chemicals) in 1 L ultrapure water. The function of the alkaline buffer solution was to maintain the pH of the solution above 7. The third absorbing solution (Solution 3) consisted of the mixture of deionised water (7 mL), alkaline buffer solution (2 mL) and natural methylene blue dye (1 mL), prepared using 0.35 g methylene blue (BDH Chemicals) in 1 L ultrapure water in a volumetric flask.

For cationic surfactant analysis, 10 mL deionised water also was used for the first absorbing solution (Solution 1). The second absorbing solution (Solution 2) was prepared using a mixture of deionised water (8 mL) and 2 mL acetate buffer solution prepared using acetic acid (Aldrich) (0.5 M) with 0.5 M sodium acetate (Sigma). The acetate buffer solution was used to maintain the pH between 3.5 and 5.6. The third absorbing solution (Solution 3) consisted of a mixture of 7 mL deionised water, 2 mL acetate buffer solution and 1 mL natural disulphine blue dye, prepared with 0.35 g disulphine blue (BDH Chemicals) in 1 L ultrapure water in a volumetric flask.

SURFACTANT ANALYSIS

Analysis of anionic surfactants as methylene blue active substances (MBAS) Chloroform (5 mL) was added to each vial containing a sample in one of three absorbing solutions (Solution 1, Solution 2 and Solution 3). The vial was tightly closed using a screw-cap with a Teflon liner before being vigorously shaken for two minutes using a vortex mixer. The screw-cap was then loosened to release the inner pressure, and then the vials were inverted for the separation phase. Once the two phases were separated, a Pasteur pipette was used to transfer the bottom (chloroform) layer into a new vial (vial B) containing ultrapure water (22 mL) and acidic methylene blue solution (1 mL). Vial B was shaken using a vortex mixer for two minutes. The cap was then loosened for few seconds and re-tightened. After the chloroform had completely separated from the water (after two minutes), the chloroform layer was collected using a Pasteur pipette and placed in a 10 mm quartz cell. The absorbance of the chloroform phase was measured by ultra-violet spectrometer at a wavelength of 650 nm. The blank for the MBAS analysis was prepared using 5 mL sodium dodecyl sulphate (SDS) at a concentration of 0.05 mM instead of sample, while the calibration curve was prepared using the same chemical in the range between 5 mM and 20 mM.

Analysis of cationic surfactants as disulphine blue active substances (DBAS) About 5 mL chloroform was added to a vial containing a sample in one of the three absorbing solutions. The vial was then vigorously shaken for a minute using a vortex mixer. The cap was loosened for a

few seconds to release the pressure and then re-tightened. The vial was inverted and left until the two phases were completely separated (about two minutes). The chloroform layer was removed using a Pasteur pipette and placed in a 10 mm quartz cell. The absorbance of the chloroform layer was then measured using an ultra violet spectrometer (Shimadzu Model 1650) at a wavelength of 628 nm. The blank for the DBAS analysis was prepared using 5 mL of zephiramine at a concentration of 0.05 mM, while the calibration curve was prepared using the same chemical in the range between 5mM and 20 mM (Latif & Brimblecombe 2004).

Selection of Optimum Features of Sampling Procedure and Equipment After the optimal absorbing solution had been determined, we proceeded to determine the optimum features of the sampling procedures and equipment, i.e. the effect of flow rate of the sampling pump and of covering the impinger tube or leaving it exposed to sunlight. This part of the study also determined the effects of storage period (within 1 to 4 days) on the amount of surfactants detected in the absorbing solution.

To find the optimum flow rate, the air sampling pump was set at different rates (0.5 L/min, 1.0 L/min and 2.0 L/min) to sample air for 1 hour. To indicate the influence of sunlight on the reaction of absorbing solution and surfactants, the impinger tube was covered with aluminum foil or were left uncovered. To determine the stability of the surfactants in the absorbing solutions, the samples were stored under laboratory conditions between 1 and 4 days. The different conditions of these experiments are summarised in Table 1.

Each absorbing solution for either anionic or cationic surfactants then was put into a vial and taken for surfactant analysis in the laboratory. Three replicates were obtained for each experiment. The surfactants in absorbing solutions from each experiment were analysed by the same method of surfactant analysis used for the determination of surfactants in samples used for the selection of the optimum absorbing solution (above).

RESULTS AND DISCUSSION

SELECTION OF ABSORBING SOLUTIONS

The average concentration of surfactants in different absorbing solutions is shown in Table 2. Of the three conditions, the absorbing solution consisting of deionised water, buffer solution and dyes (Solution 3) recorded the highest concentration both of anionic surfactants as MBAS and of cationic surfactants as DBAS at 0.100 ± 0.012 µmol/m³ and 1.414 ± 0.186 µmol/m³ respectively. Statistical tests showed that the differences between the levels of surfactants measured by the absorbing solutions were significant ($p<0.05$).

Surfactants were determined based on colourimetric measurement of a solvent-extractable ion pair formed between the surfactants and ionic dye (mainly methylene blue for anionic surfactants and disulphine blue for cationic surfactants) (Latif et al. 2004; Latif et al. 2005; Pedraza et al. 2007). All three solutions have the potential to promote a condition where surfactants can be absorbed, increasing the efficiency of the formation of an ionic pair between anionic surfactants and cationic dye (methylene blue) and between cationic surfactant and anionic dye (disulphine blue). Buffer solutions promote good conditions for the reaction to take place. On the other hand, the fact that surfactants were undetected in deionised water alone, as shown in Table 2, indicates that deionised water alone cannot be used to determine the surfactant concentration in air due to its inability to absorb surfactants effectively.

SELECTION OF OPTIMAL FEATURES OF THE SAMPLING EQUIPMENT

Flow rate In this study, different flow rates ranging from 0.5 to 2.0 L/min were tested. Table 2 shows that for DBAS, a flow rate of 1 L/min gave the highest average concentration (0.221 ± 0.024 µmol/m³) of cationic surfactants compared to a rate of 0.5 L/min (0.024 ± 0.011 µmol/m³) and of 2 L/min (0.099 ± 0.060 µmol/m³). Thus, it is suggested that the flow rate of 1 L/min is the most suitable for

TABLE 1. Parameters of sampling equipment and procedures investigated

Factor		Elements
Absorbing solutions	Solution 1	Deionised water (10 mL)
Anionic Surfactants	Solution 2	Deionised water (8 mL) + alkaline buffer (2 mL)
	Solution 3	Deionised water (7 mL) + alkaline buffer (2 mL) + Methylene blue (1mL)
Cationic Surfactants	Solution 1	Deionised water (10 mL)
	Solution 2	Deionised water (8 mL) + acetate buffer (2 mL)
	Solution 3	Deionised water (7 mL) + acetate buffer (2 mL) + Disulphine blue (1mL)
Impinger tube		Aluminium-coated tube
		Non-coated tube
Flow rate		0.5 L/min
		1.0 L/min
		2.0 L/min

detection of DBAS. The flow rate of 1 L/min also resulted in the detection of the highest average concentration of anionic surfactants. Hence, the flow rate of 1.0 L/min is suggested for sampling for the determination of both kinds of surfactants in ambient air.

Influence of exposure to sunlight Previous studies have indicated that the oxidation process triggered by ozone or ultra-violet radiation might lead to an increase of those more hydrophilic compounds that increase the surface-active properties of organic compounds (Decessari et al. 2002). On the other hand, a continuous oxidation process might lead to surfactant degradation (Latif et al. 2005). Thus, each impinger tube was either uncovered or covered with aluminium foil to either expose the absorbing solution to sunlight or to shut out sunlight.

Table 2 shows that the two types of surfactant responded differently to different impinger tube conditions. The average concentration of MBAS was found to be higher when the uncoated tube was used. In contrast, the aluminum-covered tube offered the higher concentration of cationic surfactants as DBAS (Table 2) at 0.160 ± 0.047 μmol/m^3 compared to the concentration (0.079 ± 0.031 μmol/m^3) found using an uncovered impinger tube. Since the concentrations of each type of impinger tube showed insignificant difference ($p > 0.05$), the covered impinger tube was selected as the optimal feature as it offers the highest detection of cationic surfactants. On the other hand, the uncovered impinger tube was found to be more suitable for maximal detection of anionic surfactants as MBAS. The uncovered impinger tube showed the highest average concentration of anionic surfactants at 0.174 ± 0.082 μmol/m^3 compared to that of the covered impinger tube at 0.057 ± 0.012 μmol/m^3, suggesting the importance of exposure to light for analysis of each kind of surfactant.

Stability of Surfactants in Absorbing Solution Results of this analysis showed that for both surfactants, the concentration of surfactant detected 4 days after sampling were higher than the shorter storage period in the lab condition with values of 0.190 ± 0.078 μmol/m^3 for MBAS and 0.258 ± 0.017 μmol/m^3 for DBAS. Both values were slightly higher than the surfactant concentrations detected 1 day after sampling at 0.074 ± 0.040 μmol/m^3 for MBAS and 0.208 ± 0.017 μmol/m^3 for DBAS. However statistical tests showed that the differences were not significant ($p > 0.05$). This result suggests that the surfactants in absorbing solution as both MBAS and DBAS are quite stable, but it is expected that an extended storage time still can influence the amount of surfactants in the stored sample especially for MBAS.

CONCLUSION

This study showed that the suitable absorbing solution for both anionic and cationic surfactants in the atmosphere contains buffer for optimal pH and dyes believed to act as a binding agent between the surfactants and the absorbing solution. A low flow rate was found to reduce the amount of surfactants absorbed, while higher flow rates were found to reduce the amount of surfactants in the absorbing solution due to oxidation processes. Ambient air can be a good agent for oxidizing surfactants into other organic compounds. The sunlight was found to affect the levels of surfactants detected. Surfactants can be generated by the degradation of high molecular weight molecules in the solution due to photo-oxidation processes. The destruction of molecules by photo-oxidation leads to low levels of DBAS. Results from this study also suggest that surfactants in the absorbing solution are quite stable up to four days after sampling.

TABLE 2. Average concentration of cationic and anionic surfactants in air for each factor tested

Bil	Factors	Elements	Average concentration (μmol/m^3)	
			DBAS	MBAS
1	Absorbing solution	Solution 1	ud	ud
		Solution 2	0.060 ± 0.002	0.484 ± 0.093
		Solution 3	0.100 ± 0.012	1.414 ± 0.186
2	Condition of impinger tube	covered	0.160 ± 0.047	0.057 ± 0.012
		uncovered	0.079 ± 0.031	0.174 ± 0.082
3	Flow rate (L/min)	0.5	0.024 ± 0.011	0.060 ± 0.018
		1	0.221 ± 0.024	0.222 ± 0.017
		2	0.099 ± 0.060	0.004 ± 0.003
4	Storage period	1 day	0.208 ± 0.078	0.074 ± 0.040
		4 days	0.258 ± 0.017	0.190 ± 0.078

Note: sampling replicate ,

n=3 ud = undetected

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