



Delta-8: Minimizing or avoiding carry-over?

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Introduction

To minimize carry over the Delta-8 uses a measurement procedure in which the dilutions are measured in order of increasing concentration. Despite this precaution, carry over of surfactant from well to well may result. This occurs in a mechanism where the probe is coated by a surfactant film as it is withdrawn from the sample solution of a well. Then when the probe is inserted into the following well the film desorbs onto the liquid/air surface, lowering the surface tension significantly. The excess surfactant put at the air/water interface will slowly equilibrate with the bulk solution, however, this is a slow mass transfer process, usually governed by diffusion, and may take several minutes. The amount of material carried forward by the probe is very small and consequently the change of the bulk concentration achieved after equilibration is insignificant for most practical purposes.

The Delta-8 Manager software (v. 2.73 and later) has been equipped with an option to clean the probes between every column. In this fashion the adsorbed film is removed by heating and the user can be certain that carry over does not affect the results. The cost is a decrease in throughput from ca 2 minutes to 8 minutes per plate, as well as an decrease in the lifespan of the cleaning unit since it stressed by the additional cleaning cycles.

The purpose of this note is to show the extent of carry over for a small set of compounds.

Experimental

The dilution series of LAS was prepared by the staggered method, where rows A through D had a maxi-

imum concentration of 0.1 times and E through H the four last 0.07 times the stock solution concentration (prepared as described by P&G from the material provided in summer 2003). The dilutions were prepared following standard procedure as described in the Delta-8 manual, using a dilution factor of 0.5. Thus, 1 A.U. corresponds to 0.1 times the stock solution concentration. The used buffer solutions were 0.02 N and 0.1 N Na_2SO_4 (provided by P&G). The detection plates were allowed to equilibrate for 1 h prior to the measurement. Each plate was first measured with an additional cleaning of 5 s between each column and then normally, *i.e.* cleaning was applied only before the plate was measured. The adsorption isotherms were obtained by pairwise combination of rows. The CMC data were calculated by standard procedure excluding data in which the surface tension has decreased less than 30% of the maximum decrease. The surface tension data for the isotherm plots were averaged for each concentration.

The DiC_8PC (dioctylphosphatidylcholine) dilutions were prepared and measured as for LAS in 0.02 N Na_2SO_4 .

Results

The adsorption isotherms using the two measurement procedures, *i.e.* the normal and the cleaning between columns procedures, for LAS measured in 0.02 N and 0.1 N Na_2SO_4 are shown in Figure 1. Figure 2 contains the adsorption isotherm for DiC_8PC in 0.02 N Na_2SO_4 .

In the beginning of the isotherm, where the surface tension matches that of pure water, no significant difference between two corresponding isotherms mea-

sured by the different procedures can be observed, evidencing that carry over is negligible. Obviously, a surfactant monolayer has not been established yet, and consequently carry over is not expected. However, when the surface tension starts decreasing the carry over error can be clearly seen as a systematic decrease in surface tension, approaching ca 3 mN/m in the middle of the decreasing part of the isotherm.

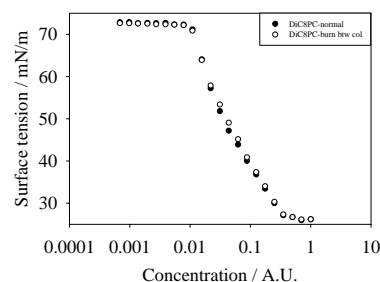
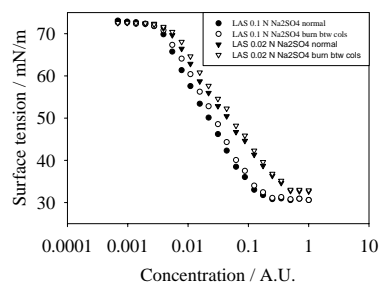
Importantly, when the CMC is approached the error decreases and disappears at the CMC. This is a consequence of the mass transfer conditions that prevail. As the bulk concentration increases mass transfer becomes relatively enhanced, which provides for a faster equilibration of the surfactant excess brought to the surface by the probe. Additionally, micellation provides a sink for surfactant, in which the excess can be stored, and hence the concentration of free surfactant in the near vicinity of the surface and surface tension remain constant.

Table 1 contains the statistical data for the determined CMC values. The standard deviations show that the data is reproducible using the same method. The error due to carry over ranges from ca. 2-13 %. Comparing LAS in the two different buffers shows that the error is larger in the condition where LAS is more surface active and has a lower CMC value. This can be explained by mass transfer that becomes relatively more effective as the surface to bulk concentration ratio decreases. Importantly, cleaning between columns becomes more important with earlier onset of surface activity and lower CMC values.

Since the error in the measured surface tension decreases when the CMC is approached, the CMC should be determined using a small portion of the isotherm in the vicinity of the CMC for best accuracy. However, this is restricted by the number of points on the isotherm.

The consumption of probe cleaning units is roughly doubled for the same number of plates due to the additional burning between columns. Considering only heating time the consumption should be up to 6 times

the normal. However, the stress put on the cleaning unit is also dependent on the temperature of the heating resistor. During the 5 s heating time the heating resistor becomes sufficiently hot to avoid carry over problem, however, short enough to save the furnace.



Conclusions

Carry over is observed as a decrease in surface tension below CMC and above the onset concentration of surface activity. The error disappears gradually as the CMC is approached. Carry over errors seem more severe for compounds that are more surface active and have lower CMC values.

Cleaning between columns effectively avoids carry over, however, roughly doubling the consumption of cleaning units and extending the measurement time from 2 to 8 minutes.

Table 1: Effect of carry-over on the determination of CMC from dilution series prepared by the 22-pt staggered method.

Compound	Method	CMC/A.U.	AVG	STDEV	CV%	Error%
LAS 0.02 N Na₂SO₄	burn	0.415	0.416	0.005	1.213	
	btw cols	0.411				
		0.419				
		0.422				
	normal	0.400	0.406	0.007	1.734	
		0.402				
		0.408				
0.416						
Error			0.010			2.4
LAS 0.1 N Na₂SO₄	burn	0.183	0.159	0.016	10.316	
	btw cols	0.160				
		0.150				
		0.145				
	normal	0.145	0.139	0.009	6.740	
		0.146				
		0.140				
0.126						
Error			0.020			12.5
DiC₈PC 0.02 N Na₂SO₄	burn	0.335	0.329	0.007	2.009	
	btw cols	0.321				
		0.327				
		0.334				
	normal	0.329	0.323	0.004	1.324	
		0.323				
		0.319				
0.321						
Error			0.006			1.8