



Letter to the Editor

Comments on “Determination of trihalomethanes in chlorinated sea water samples using a purge-and-trap system coupled to gas chromatography” by Allonier et al.

Dear Editors,

Allonier et al. [1] studied the determination of trihalomethanes (THMs) in chlorinated sea water samples using a purge-and-trap system coupled to a gas chromatographer (PT–GC). The authors performed a series of preliminary tests in order to evaluate the purge efficiency. They calculate the efficiency (E) of two successive purges of the same sample as the amount of the compound recovered during each extraction as compared to the total amount recovered by both purges. Their Fig. 1 shows that an almost complete extraction of all the analytes was achieved during a first purge cycle of two samples containing $2 \mu\text{g L}^{-1}$ and $10 \mu\text{g L}^{-1}$ THMs in distilled water, respectively. Furthermore it can be seen in Fig. 1 that the efficiency of the first purge is greater for substances of higher volatility for both samples. Since the vapour pressure of chloroform, dichlorobromomethane, chlorodibromomethane and bromoform decrease in that order, the purge efficiency should decrease in that order as well (approximately 98%, 95%, 90% and 80% respectively). This reasoning is consistent with the data reported in a recent and extensive study [2] into purge efficiency in the determination of THMs in water by PT–GC.

Allonier et al. also studied the effect of the nature of the sample matrix on the purge-and-trap efficiency for each THM presented in their Fig. 2. The solvents used for the determination represented in their Fig. 2 are: distilled water, sea water and methanol. In the case of methanol the results seem consistent: the authors find that THMs cannot be purged from this solvent due to their high solubility in methanol. Nevertheless in the case of a distilled water or sea water matrix the results presented by the authors in their Fig. 2 are questionable.

Firstly, let us consider formal aspects of Fig. 2 in Allonier et al. [1]:

- In contrast to what their Fig. 1 shows, Fig. 2 does not specify the THM concentration, not even in the figure caption nor the text of the article.
- The ordinate-axis in Fig. 1 is labelled “Purge efficiency (%)”. That same axis has been labelled “Recovery (%)” in Fig. 2 despite the fact that in the figure caption one reads “efficiency”. The reader must guess that “Purge efficiency (%)” and “Recovery (%)” refer to the same value since the authors do not define “Recovery (%)” in their paper.

- There is a typographical error in the legend of Fig. 2 since “Dibromochloromethane” is written twice and “Dichlorobromomethane” does not appear at all.

Secondly, let us consider the content of Fig. 2 in Allonier et al. [1]:

- It is not possible to obtain a “Purge efficiency (%)” = “Recovery (%)” in excess of 100% during a single purge according to the definition expressed in their text: “the amount of the compound recovered during each extraction as compared to the total amount recovered by both purges”. The authors present in Fig. 2 values of around 130% for chloroform, 115% for dichlorobromomethane and 105% for dibromochloromethane for the data with distilled water as matrix. These results contradict first, those shown in their Fig. 1, which have also been performed using distilled water. Therefore, a reader that examines the information corresponding to the part of deionised water shown in their Fig. 2 would expect it to be exactly the same as that in Fig. 1. These numbers contradict second, the principle of mass conservation since in the purge process more mass is obtained than originally in the sample.
- In the case of sea water the percentages are even greater than in the case of deionised water with values for the first recovery of around 157% for chloroform, 130% for dichlorobromomethane, 118% for dibromochloromethane and 158% for bromoform. Again, these numbers contradict the principle of mass conservation.
- Lastly, there is another aspect of their Fig. 2 that is not consistent with Fig. 1 namely, bromoform, the least volatile THM, is purged easier than the other THMs when the matrix used is sea water. The THM purge efficiency (%) decreases since the volatility diminishes from chloroform to bromoform as shown in Fig. 1 and in the part corresponding to deionised water in Fig. 2 (ignoring the absolute values). But when using sea water as matrix the authors find unexpectedly that the tendency is disrupted for bromoform. In spite of these inconsistencies in Fig. 2, the authors conclude that the increase in efficiency is due to a “salting out effect”.

The signing authors of the present letter consider that the influence of the sample matrix and quantification of the foreseen salting-out effect of sea water have not been demonstrated clearly enough.

References

- [1] A.S. Allonier, M. Khalanski, A. Bermond, V. Camel, *Talanta* 51 (2000) 467–477.
[2] F. Ruiz-Bevia, M.J. Fernandez-Torres, M.P. Blasco-Aleman, *Anal. Chim. Acta* 632 (2009) 304–314.

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