COMPARING THREE QUICK AND EASY METHODS FOR SAMPLE PREPARATION OF CWA SIMULANTS IN WATER

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ABSTRACT

Analytical chemistry in CBRNe context requires not only high quality data; quickness, ruggedness and robustness are also mandatory. In this work, we compared three samples preparation methods using as test compounds several organophosphorus pesticides, used as simulants of nerve CWA (Chemical Warfare Agents) to choose the one with best characteristics. Liquid Liquid Extraction, Solid Phase Microextraction and the new Dispersive Liquid-Liquid Micro Extraction (DLLME).

Keywords: NBC deployable laboratory, CBRNe, Chemical warfare agents, Dispersive micro liquid - liquid extraction, Nerve agent simulants

Introduction

Organization for the Prohibition of Chemical Weapons (OPCW) and United States of America Environmental Protection Agency (EPA) developed field methods [1,2] for sample preparation and analysis based on Liquid - Liquid Extraction (LLE), both with dichloromethane as extracting solvent. Further example of sample preparation method is represented by Solid Phase Micro Extraction [3,4] (SPME) this technique developed during the Nineties for environmental application is now well known in CBRN field. A third way is recently available, the Dispersive Liquid - Liquid Micro Extraction (DLLME), this method has already been well referenced [5,6] for environmental pollutants. The aim of this work is to compare these rugged sample preparation methods in terms of sensibility and reproducibility, in order to choose the best extraction protocol. Organophosphorus pesticides have been used as nerve agent simulants [7].

Conclusion

Sample preparation can be more time consuming and more complex than the analysis itself, and it represents a critical step to obtain good analytical results but this aspect is often overlooked respect to the choice of instrumentation. The DMLL extraction compared with others sample preparation techniques offers high sensibility, low uncertainty but also quickness, easiness of use and ruggedness. All these features are very important for NBC deployable laboratory activities.

References

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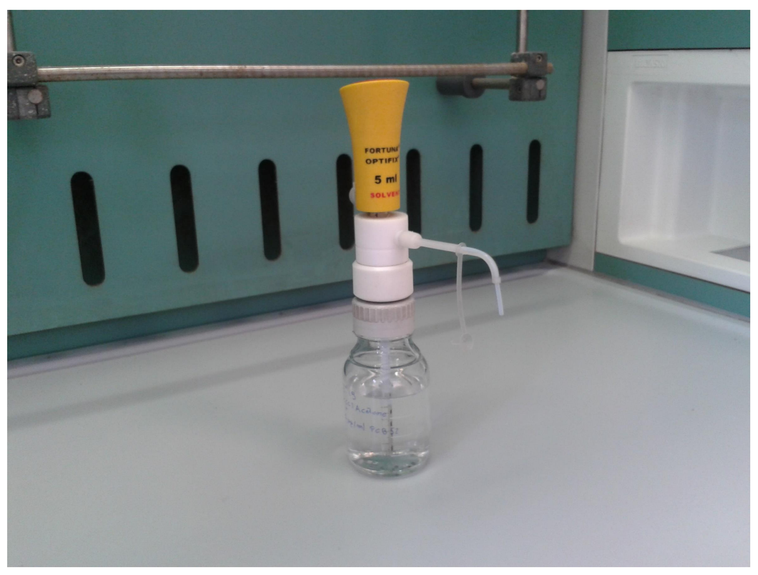
The DLMME technique use two different organic solvents mixed: the first one, defined as dispersant, is water-soluble; the other one, which represents the real extraction solvent, is insoluble in H_2O. This second solvent, defined as extracting, is present in minor amount and it is denser then water, in order to facilitate the subsequent recovery phase. After the mixing of the two solvents in an aqueous phase, they separate instantly: the organic pollutants that could be present in the water sample move to the extracting solvent, which, being hydrophobic and denser than water, precipitates on the bottom of glassware and then is recovered and analyzed.

To compare sample preparation techniques are used 35 ml water spiked sample in 40 ml vials for every techniques. For DLLME 0,350 ml of carbon tetrachloride and 6,650 ml of acetone mixed together are added to the samples vial with the dispenser shown in following figure, the extraction is immediate.



For LLE are used 5 ml of methylene chloride. The sample are stirred with vortex for 2 minutes and the organic phase is left to separate for 1 minute. For SPME a 100 um PDMS fiber is used, soaked in sample for 10 minutes. Uncertainty and limit of detection are listed in table below

Simulant	RSD LL	LOQ (µg/l)	RSD SPME	LOQ (µg/l)	RSD DLLME	LOQ (µg/l)
Dichlorvos	25 %	0.2	25 %	0.05	8 %	0.01
Fenitrothion	27 %	2.5	33 %	0.5	11 %	0.01
Malathion	30 %	0.8	45 %	0.06	10 %	0.03
Parathion ethyl	23 %	0.6	30 %	0.01	15 %	0.01
Ethion	31 %	0.25	50 %	0.03	12 %	0.01
Azinphos ethyl	30 %	2.5	46 %	0.05	11 %	0.08

In following images are reported a chromatogram of a spiked sample obtained with DLMME technique and a plot of area of a single simulant (azinphos ethyl) spiked at different concentration to show the linearity of technique.