Analytica Chimica Acta xxx (2018) 1–7

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Assessing sample extraction efficiencies for the analysis of complex unresolved mixtures of organic pollutants: A comprehensive non-target approach

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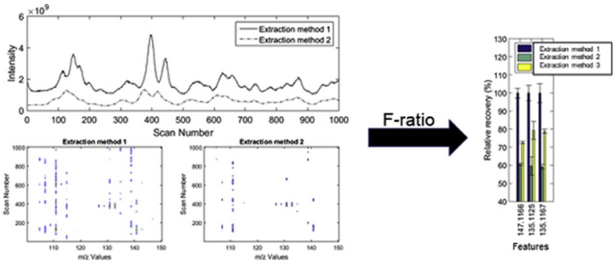
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 December 2017
Received in revised form
10 April 2018
Accepted 14 April 2018
Available online xxx

ABSTRACT

The comprehensive extraction recovery assessment of organic analytes from complex samples such as oil field produced water (PW) is a challenging task. A targeted approach is usually used for recovery and determination of compounds in these types of analysis. Here we suggest a more comprehensive and less biased approach for the extraction recovery assessment of complex samples. This method combines conventional targeted analysis with a non-targeted approach to evaluate the extraction recovery of complex mixtures. Three generic extraction methods: liquid-liquid extraction (Lq), and solid phase extraction using HLB cartridges (HLB), and the combination of ENV+ and C8 (ENV) cartridges, were selected for evaluation. PW was divided into three parts: non-spiked, spiked level 1, and spiked level 2 for analysis. The spiked samples were used for targeted evaluation of extraction recoveries of 65 added target analytes comprising alkanes, phenols, and polycyclic aromatic hydrocarbons, producing absolute recoveries. The non-spiked samples were used for the non-targeted approach, which used a combination of the F-ratio method and apex detection algorithm. Targeted analysis showed that the use of ENV cartridges and the Lq method performed better than use of HLB cartridges, producing absolute recoveries of 53.1 ± 15.2 for ENV and 46.8 ± 13.2 for Lq versus 19.7 ± 6.7 for HLB. These two methods appeared to produce statistically similar results for recoveries of analytes, whereas they were both different from the produced recoveries via the HLB method. The non-targeted approach captured unique features that were specific to each extraction method. This approach generated 26 unique features (mass spectral ions),

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https://doi.org/10.1016/j.aca.2018.04.020

Please cite this article in press as: S. Samanipour, et al., Assessing sample extraction efficiencies for the analysis of complex unresolved mixtures of organic pollutants: A comprehensive non-target approach, Analytica Chimica Acta (2018), https://doi.org/10.1016/j.aca.2018.04.020

which were significantly different between samples and were relevant in differentiating each extract from each method. Using a combination of these targeted and non-targeted methods we evaluated the extraction recoveries of the three extraction methods for analysis of PW.

1. Introduction

Comprehensive extraction recovery assessments of complex mixtures of organic analytes are extremely difficult. This is caused mainly by the complexity of the sample and lack of knowledge regarding the chemical constituents of the sample. Consequently, a generic/wide range extraction method is typically employed for the analysis of complex mixtures such as produced water (PW; reviewed by Oetjen [1]). Often, different extraction methods are tested on a small number of potential target analytes (compared to the number of chemicals in a complex mixture) in order to define an optimized extraction method [1,2]. This approach assumes that the fate and behavior of each chemical constituent in the complex mixture can be linearly extrapolated by the behavior of the target analytes and that there are no interactions between different chemicals. Such an approach is perhaps questionable, for example, when an examination of PW for naphthenic acids is made, since these compounds also behave as surfactants. Another method used for the extraction recovery assessment of complex mixtures is the gravimetric approach [1,3]. This method focuses on the total non-volatile extractable material. In this case if the amount of a certain chemical in the sample is smaller than the experimental error (e.g. ± 10%) then it is impossible to capture any mass loss for that chemical caused by different extraction methods. Therefore, both mentioned methods are not applicable to comprehensively evaluate the recovery of different extraction methods when dealing with complex mixtures such as PW.

PW is one of the largest streams of treated industrial wastewater in the world [4] and its discharge into the marine environment is of ecological relevance. For example from Norwegian off shore activities PW volumes are 140 mil m^3 y^{-1} [5]. PW is a complex mixture containing a diverse range of chemical constituents [1,6–8]. Organic compounds in PW, typically vary from oil droplets to large organic acids [6–8]. Thus, PWs exhibit a wide range of chemical and physical properties, fate and behaviors. As a consequence of this chemical diversity and the fact that not all of its (i.e. PW) chemical constituents are known, extraction of PW typically reveals complex mixtures that are largely unresolved by typically used techniques (e.g. unit mass GC-MS) [9–11].

High resolution mass spectrometry coupled with different chromatographic technologies (gas and/or liquid chromatography) has shown great potential in partially resolving the unresolved complex mixture (UCM) [12–15,37,38]. However, when dealing with UCMs, these analytical techniques are not capable of comprehensively characterize the analyzed samples [14]. Consequently, chemometric tools such as principal component analysis (PCA), F-ratio, and N-way partial least-squares in combination with HRMS are usually employed to tackle the complexity of these UCMs [15–18].

The combination of F-ratio method and the apex detection algorithm has been shown to be a powerful tool when dealing with complex environmental samples, including petroleum related matrix [17,20]. F-ratio is a parametric supervised method, which uses the ratio of the between-groups variability and within each group variability to define the significance of each variable [19,20]. Therefore, it identifies the features in the samples which are statistically significant, while the apex detection algorithm reduces the redundancy in those features by grouping them as unique statistically significant features. PW was selected as the test/validation matrix for the applicability of this approach in comprehensive recovery assessment of complex mixtures due to its complexity.

The aim of the present study was to use the F-ratio method to comprehensively assess the extraction recovery of three generic (i.e. wide range of chemical and physical property) extraction methods for PW. We employed three extraction methods: liquid-liquid extraction (Lq), HLB cartridges (HLB), and the combination of ENV+ and C8 cartridges (ENV) for an applicability proof of concept. These methods have been widely used for recovering complex mixtures of analytes from matrices including PW [21–26]. We employed a combination of the conventional targeted and the alternative non-targeted analysis for a comprehensive recovery assessment. PW was divided into three categories: non-spiked, spiked level 1, and spiked level 2. For the targeted approach we used a spike solution consisting of a mixture of 65 target analytes that were added into the PW at two different concentrations (i.e. spiked level 1 and spiked level 2). The concentration differences between the two spike levels were used to calculate the absolute recoveries of each target analyte. For the non-targeted approach, we used the non-spiked PW. We employed the null-distribution in order to define the threshold of false positive detection. Finally, we calculated the relative recoveries of unique features based on the average intensity of those features. This study was a proof of concept for the applicability of the suggested approach in comprehensive recovery assessment of complex unresolved mixtures of organic analytes.

2. Experimental methods

2.1. Sample preparation and extraction

PW (20L) was obtained from the Heidrun oil platform [27] in the Halten bank off the coast of mid-Norway during February 2017. PW was subdivided into 27 aliquots each of 400 mL. These aliquots were divided into three categories: non-spiked, spiked level 1 and spiked level 2, thus 9 samples in each category (Fig. 1). We added a predefined volume of a standard mixture solution to the spiked samples (i.e. spiked level 1 and spiked level 2) in order to reach a certain concentration for each added component of the mixture. The standard mix solution consisted of a mixture 29 alkanes (Als) from C10-C33 at 8 $\mu g\, mL^{-1}$ each, 19 alkylated phenols (ALPs) at 10 $\mu g\, mL^{-1}$ each, and 16 polycyclic aromatic hydrocarbons (PAHs) at 2 $\mu g\, mL^{-1}$ each. The spiked level 1 samples (i.e. 9 out of 27) were spiked with 50 μL of standard mix solution resulting in addition of 0.4 μg of Als, 0.5 μg of ALPs, and 0.1 μg of PAHs whereas spiked level 2 samples were spiked with 100 μL of standard mix solution resulting in addition of 0.8 μg of Als, 1 μg of ALPs, and 0.2 μg of PAHs. The non-spiked samples were used for non-targeted recovery assessment while the spiked samples were employed for the targeted workflow. Detailed information regarding the standard mixtures and suppliers is provided in the Supporting Information, Section S1.1 and Table S1.

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