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The challenge of sample-stabilisation in the era of multi-residue analytical methods: A practical guideline for the stabilisation of 46 organic micropollutants in aqueous samples

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HIGHLIGHTS

- Stabilisation strategies for 46 micro-pollutants in water samples are evaluated.
- Influence of temperature, water matrix, two common biocides and SPE is investigated.
- Sodium azide is found to stabilise some, but not all analytes.
- Copper sulphate interferes with caffeine and other azole and imidazole structures.
- Solid phase extraction is determined to be the most promising stabilisation strategy.

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ABSTRACT

Water sample storage and stabilisation may affect data quality, if samples are managed improperly. In this study three stabilising strategies are evaluated for 46 relevant organic micro-pollutants: addition of the biocides (i) copper sulphate and (ii) sodium azide to water samples directly after sampling with subsequent sample storage as liquid phase and (iii) direct solid phase extraction (SPE), stabilising the samples by reducing the activity of water. River water and treated effluent were chosen as commonly investigated matrices with a high potential of biotransformation activity. Analyses were carried out for sample storage temperatures of 4 and 28 °C for water samples stored as liquid phase and for sample storage temperatures of 4, 20 and 40 °C for SPE cartridges. Cooling of water samples alone was not sufficient for longer storage times (>24 h). While copper sulphate caused detrimental interferences with nitrogen containing heterocyclic compounds, sodium azide proved to be a suitable stabilising agent. The best results could be obtained for SPE cartridges stored cool. Recommendations for samples preservation are provided.

1. Introduction

Within the last 20 years, researchers increasingly investigated the occurrence and fate of organic compounds in trace concentrations (μg L^{-1} to ng L^{-1}). These so-called micro-contaminants or micro-pollutants, such as pharmaceuticals and personal care products, endocrine disrupting compounds, pesticides and/or industrial chemicals at low concentrations were detected in virtually all parts of the water cycle (Focazio et al., 2008; Heberer, 2002; Schwarzenbach et al., 2006; Ternes, 2007; Weigel et al., 2001). Due to the diversity of these compounds, analytical methods focussing on only one class of compounds do not meet the requirements of current research undertaken in environmental sciences (Estévez et al., 2012; Nödler et al., 2011; Reh et al., 2013). However, thanks to significant progress in the field of analytical science several multi-residue analytical methods were developed (e.g. Huntscha et al., 2012; Nödler et al., 2010; Nurmi and Pellinen, 2011; Wode et al., 2012).

Although the diversity of compounds can nowadays be handled analytically by multi-residue analysis, the wide spectrum of compounds with various stabilities and reactivities (e.g. Nödler et al., 2010; Wode et al., 2012) results in a challenge for sample preservation. In cases when the immediate sample analysis is difficult or impossible (e.g. remote areas) or the sampling is intended to be realised over longer periods (e.g. weekly-integrated sampling; Kylin, 2013), the storage conditions become highly relevant (Barceló and Alpendurada, 1996; U.S. EPA, 2010; Vanderford et al., 2011). Especially for easily degradable compounds, their reliable determination largely depends on proper sample storage conditions. Various processes such as microbial degradation, chemical reactions, volatilisation or adsorption may occur even during relatively short sample storage times resulting in low analyte recoveries. For example, caffeine, ibuprofen and paracetamol (acetaminophen) are

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Table 1
Investigated analytes and their application/origin.

Application or origin	Compound	Application or origin	Compound
Analgesics/anti-inflammatories	Diclofenac	Lipid regulators	Bezafibrate
	Ibuprofen		Clofibric acid
	Naproxen		Gemfibrozil
	Paracetamol	Antihistamines	Cetirizine
	Phenazone		Loratadine
Stimulants/caffeine metabolites	Caffeine	Anticonvulsants/sedatives	Carbamazepine
	Paraxanthine		Diazepam
	Theobromine		Primidone
	Theophylline		Tetrazepam
	1-Methylxanthine	Selective serotonin reuptake inhibitors	Citalopram
	3-Methylxanthine		Fluoxetine
Antihypertensive agents	Atenolol		Sertraline
	Metoprolol	Herbicides/herbicide metabolites	Atrazine
	Sotalol		Desethylatrazine
Iodinated contrast media	Iohexol		Desisopropylatrazine
	Iomeprol		Diuron
	Iopamidol		Isoproturon
	Iopromide		Mecoprop
Antibiotics	Clarithromycin		Metazachlor
	Erythromycin	Corrosion inhibitors	1H-benzotriazole
	Roxithromycin		Tolyltriazole
	Sulfamethoxazole	Cocaine metabolite	Benzoylecgonine
	Trimethoprim	Gastric acid regulator	Pantoprazole

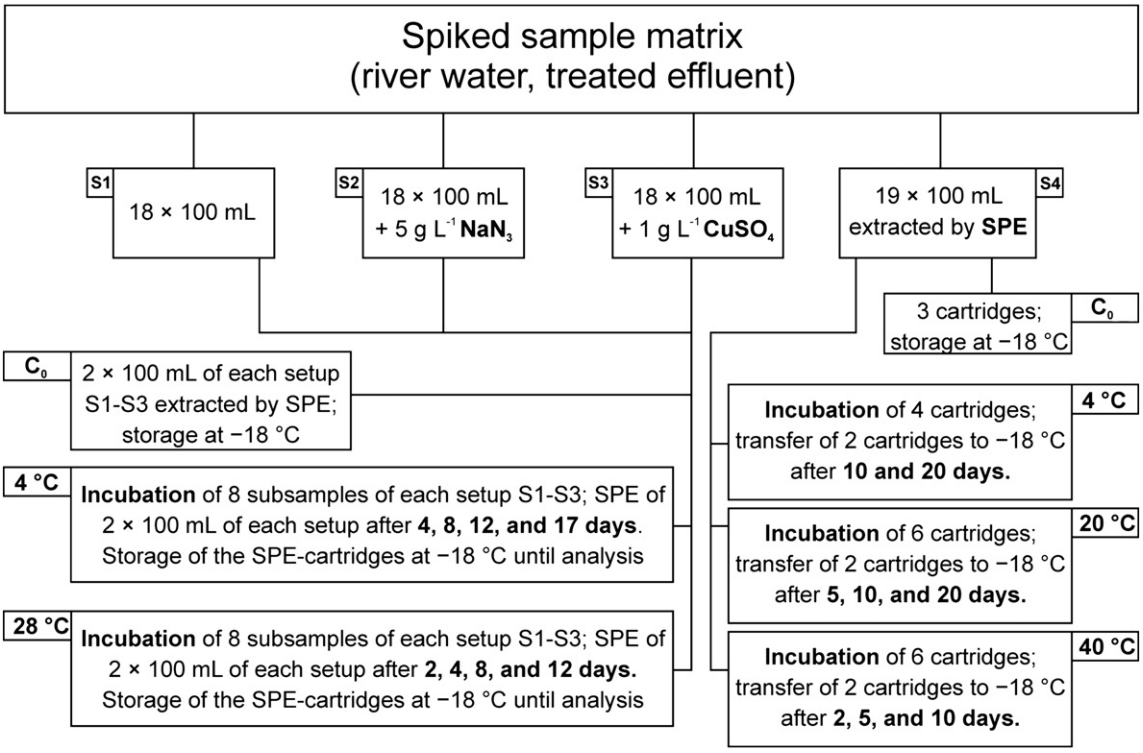

Fig. 1. Schematic overview of the experiments to investigate the influence of different stabilisation techniques (c_0 = initial concentration).

commonly investigated micro-contaminants and known to be easily degradable in wastewater treatment plants (WWTPs) and in the environment (e.g. Halling-Sørensen et al., 1998; Joss et al., 2006) while carbamazepine is known to be a very stable compound (Clara et al., 2004; Gasser et al., 2010). Acknowledging the large range of stability encountered for compounds in multi-residue analysis, it is obvious that a proper sample pre-treatment and storage is essential to obtain reliable results. Thus, sample stabilisation methods should be applied to minimise concentration changes between sampling and analysis. These methods are most common in inorganic analysis and include addition of chemicals, cooling, pH-modifications and choice of storage container.

For micro-contaminants the influence of storage temperatures, the material of the storage container and different quenching agents have been investigated for water samples, stored as liquid phase (U.S. EPA, 2010; Vanderford et al., 2011). As stabilising agents sodium

Fig. 2. Recoveries of selected analytes in WWTP treated effluent with respect to storage time; stored as liquid (WW 28 N = non-stabilised wastewater sample stored at 28 °C; WW 28 A = wastewater sample stored at 28 °C, stabilised with NaN_3; WW 4 N = non-stabilised wastewater sample stored at 4 °C; WW 4 A = wastewater sample stored at 4 °C, stabilised with NaN_3; the dashed grey line at 80% indicates the significance threshold).