Analytica Chimica Acta 1018 (2018) 45–53

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

# The influence of pH on sampler uptake for an improved configuration of the organic-diffusive gradients in thin films passive sampler

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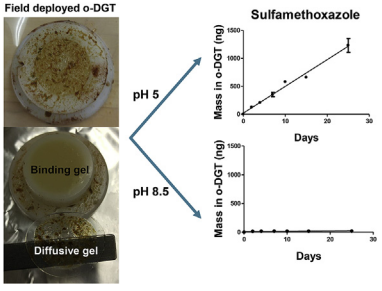
## HIGHLIGHTS

- o-DGT with polyacrylamide gels are more robust than with agarose diffusive gel.
- Sampling rates in this configuration are comparable with previous o-DGT.
- Sepra ZT binding gel appears to perform in a similar manner as OASIS HLB.
- 6 of 31 compounds had changes in sampling rate with varying pH.
- Such discrepancies may be explained by speciation changes affecting sorption.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 10 November 2017
Received in revised form
22 February 2018
Accepted 24 February 2018
Available online 10 March 2018

*Keywords:*
Passive sampling
o-DGT
pH
Pharmaceuticals
Pesticides

## ABSTRACT

Recent literature has demonstrated the utility of the organic-diffusive gradients in thin films (o-DGT) device as an effective passive sampler for polar organics in aquatic environments. Here, a new configuration comprising a polyacrylamide diffusive gel and Sepra™ ZT sorbent was developed and calibrated under multiple pH conditions. Linear uptake ($r^2 > 0.9$) was observed at pH ≈ 5 for a suite of 31 pharmaceuticals and pesticides over 25 days, suitable for typical passive sampler deployments. At pH ≈ 8.5, linear uptake ($r^2 > 0.9$) was observed for many of the same compounds. Comparisons of the uptake rates between the two pH experiments generally agreed (14% average relative error), with only 6 compounds exhibiting marked reduction with pH (e.g. sulfonamide antibiotics). These discrepancies may be explained by changes in analyte-sorbent interaction (H-bonding) due to speciation changes at varying pH. Samplers performed well in field evaluations conducted in an impacted river system, showing close agreement with the previously validated agarose/HLB o-DGT configuration deployed simultaneously. This work illustrates that polyacrylamide diffusive gels are a more robust and resistant outer-membrane material compared to agarose used in earlier o-DGT configurations. Sepra™ ZT binding gels served as an effective binding resin, offering a cost effective and commercially available sorbent.



## 1. Introduction

As awareness and regulations around water contamination increases globally, the need for simple and efficient tools for monitoring aquatic contaminants is more apparent [1]. Polar organic

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https://doi.org/10.1016/j.aca.2018.02.074
0003-2670/

molecules (e.g. pharmaceuticals and pesticides) represent one such class of contaminant that are ubiquitous in impacted surface waters due to many diffuse and point sources, including urban wastewater and agricultural runoff [2–5]. Traditional methods of determining analyte concentrations involve grab sampling at specific time intervals in the field, followed by filtering and concentrating these samples in the lab. This method, while conceptually simple, is inefficient, time consuming, and can miss fluctuations in analyte levels caused by stochastic inputs (e.g., sewage releases, spills, precipitation and runoff events, changing water levels) [2,3,6,7].

Passive sampling devices overcome many of these problems as they continuously monitor freely dissolved analytes in water over typical deployment times of 2–4 weeks. These devices can be used to determine a time-weighted average concentration over a deployment time and are thus able to provide an average contaminant concentration that is more representative of exposure scenarios for organisms in those systems [6,8–10]. Currently, the most widely used device for measuring polar organic contaminants in water is the POCIS (polar organic chemical integrative sampler) [10,11]. The POCIS is an attractive design as it is simple to use, resistant to biofouling, and has been calibrated for a large number of contaminants [11]. However, variations in field-observed sampling rates ($R_S$) compared to those derived in lab result from in-situ environmental factors such as changing temperatures and flow rates [12,13]. These factors can cause major discrepancies in $R_S$ (2–9 fold variation) which can greatly affect reported concentrations [14–16].

To address these concerns, the existing diffusive gradients in thin films (DGT) passive sampler, used widely for measuring metals, was modified by Chen et al. [17–19] to bind polar organic contaminants effectively (o-DGT). This new sampler was initially tested on sulfamethoxazole [17] and was then expanded to a set of 40 antibiotics [18,19]. Since then, this design has been modified and calibrated for many different analytes and has been shown to perform well in both laboratory and field experiments [20–22]. The o-DGT design offers many advantages over current polar passive sampling tools (e.g. POCIS), namely, being largely unaffected by changing water flow and allowing for simple determination of temperature-specific $R_S$. These advantages result from the inclusion of a thick outer diffusive gel layer controlling analyte uptake. The thick diffusive gel ($\Delta g \approx 0.5$–1 mm) ensures that resistance to mass-transfer is sampler controlled as opposed to boundary layer controlled (as in POCIS), an idea well-established in the DGT metals literature [23]. As a result, o-DGT sampling rates can be accurately determined from analyte-specific diffusion coefficients (D) through this gel [20,24], greatly reducing the need for *in situ* or laboratory based calibrations required for other polar passive sampling tools. To date, much of the work around o-DGT has focused on demonstrating and improving the usefulness and effectiveness of this new sampler design. Presently, the o-DGT has been characterized for around 50 different pharmaceuticals, personal care products (PPCPs) and pesticides. However, more work is still needed to fully understand the optimal configuration of o-DGT (gel and sorbent material) and understand the factors that impact sampler performance.

Environmental conditions such as temperature and flow rate have been tested for their possible impacts on o-DGT $R_s$, showing predictable and minimal effects, respectively [20]. One effect yet to be tested comprehensively with a large suite of analytes is pH and how changes in analyte speciation may affect $R_s$. Solution pH is important as many sorbents used for sequestering polar analytes in an environmental context (polar passive samplers, solid phase extraction, etc.) work mainly through neutral and weak ion interactions (van der Waals or π-π interactions, hydrogen bonding, and Coulomb forces) at the surface of the sorbent (e.g., OASIS™ HLB sorbent [25]). Since the speciation of chemicals is a function of solution pH and $pK_a$, changes in pH may change the affinity of certain analytes to the sorbent [13], thus impacting the uptake efficiency in passive samplers. To date, only two studies have investigated pH effects on passive sampler uptake of PPCPs and pesticides known to have speciation changes falling within realistic environmental pH ranges ($4 < pKa < 10$) [13]. Li et al. [13] investigated pH effects on the POCIS sampling rates of 21 model PPCPs and endocrine disputing substances. They showed that sampling rates generally increased with pH for basic compounds, decreased with pH for acidic compounds, and remained relatively constant for phenolic and neutral chemicals [13]. Recently, Jeong et al. [26] studied pH effects on the OASIS™ HLB sorbent independent of a sampler and reported similar results to Li et al. [13], namely that compounds in their neutral form generally exhibit more favorable sorption.

The objective of the present study was to develop and test a new configuration of the o-DGT passive sampler that utilizes a tougher and more resistant diffusive gel and a more affordable and widely available sorbent material compared to earlier designs [20]. Laboratory calibration studies using static-renewal systems were conducted for a suite of pharmaceuticals and pesticides to determine the linear uptake range of this o-DGT configuration and analyte-specific sampling rates. Additionally, we investigated the effects of pH on o-DGT $R_S$, a parameter that is rarely characterized when calibrating passive samplers.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Stock solutions of the 31 target and 27 internal standard (IS) mixtures were prepared in methanol at 10 and 2 ng $\mu L^{-1}$, respectively. Further details on these are found in the Supporting Information (SI). HPLC grade methanol from Fischer Scientific (Ottawa, ON) and 18.2 MΩ-cm Milli-Q water (EMD Milli-Pore Synergy® system, Etobicoke, ON), were used for LC solvents, analytical standards, and sample extractions. Optima LC/MS grade formic acid was purchased from Fischer Scientific as an LC solvent additive. Chemicals for making gels (agarose, acrylamide, *N,N′*-methylenebisacrylamide, ammonium persulfate, *N,N,N′,N′*-tetramethylethylenediamine), buffering pH (sodium tetraborate decahydrate), and adjusting ionic strength (potassium nitrate) were from Sigma-Aldrich (Oakville, ON).

### 2.2. Preparation of diffusive and binding gels

Preparation of agarose diffusive and binding gels followed protocols detailed in Challis et al. [20]. Briefly, a 1.5% agarose mixture was casted (allowed to set for ≈60 min) in sheets using a 0.75 mm Bio-Rad Laboratories (Mississauga, ON) Mini-Protean® casting system. The gel sheets were then cut into disks and rinsed periodically with Milli-Q water over 24 h, before storage at 4 °C in 5 mM $KNO_3$ solution. Binding gels were prepared using the same 1.5% agarose, with the addition of 0.35 g of either OASIS™ HLB powder (Waters Corporation, Milford, MA) or Sepra™ ZT powder (Phenomenex, Torrance, CA). The gel/powder mixture (≈4.5 mL of gel + 0.35 g powder per cast) was vortexed to homogenize the solution, then immediately poured and the whole cast was flipped horizontally to allow for the powder to settle to one side of the gel. This ensured the cut gels contained around 25 mg of powder (nominal) per gel disk, which were set, cut, and washed as above.

Polyacrylamide diffusive gels were prepared using 12.5 mL of 30% AA monomer, 2.5 mL of 1% BAA cross-linker, 9.79 mL of Milli-Q water, 200 μL of 10% APS initiator and 10 μL of TEMED catalyst. This