



Review

Use of diffusive gradient in thin films for *in situ* measurements: A review on the progress in chemical fractionation, speciation and bioavailability of metals in waters



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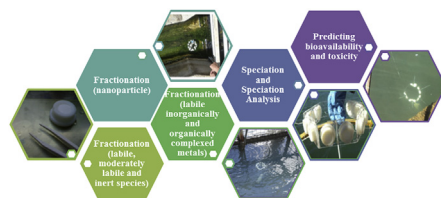
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HIGHLIGHTS

- This review provides an overview of the applications of DGT for speciation.
- Approaches were grouped according to IUPAC guideline definitions for speciation.
- Knowledge gaps and areas for further DGT research on speciation are highlighted.

GRAPHICAL ABSTRACT



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ABSTRACT

Chemical fractionation, speciation analysis and bioavailability of metals and metalloids in waters have received increased attention in recent years. However, this interest is not matched by progress in improving species integrity during standard 'grab' sample collection, processing and storage. Time-averaged, low disturbance sampling, *in situ*, of trace element species, in particular, is a more reliable approach for environmental chemical surveillance and methods based on the diffusive gradients in thin films (DGT) technique stand out as one of the most widely used of the passive sampler classes, and hence will be the primary focus of this review. The DGT technique was initially developed to sample metals and semi-metals in freshwaters, and later was extended to include marine settings as well as the measurement of metal fluxes in sediments/soils. Nowadays, DGT based technologies are used extensively in a variety of geochemical and environmental health research disciplines. This review specifically surveys the application of the DGT measurement for fractionation and speciation analysis (as defined by IUPAC) of metal or metalloids *in aqua*. Use of DGT in fresh, estuarine and marine waters, as well as effluents has improved the knowledge base of *in situ* data related to fractionation processes (e.g. labile and inert species; organic and inorganic species; dissolved and nanoparticles), and speciation analysis. This supports not only the calculations underpinning numerous software speciation models for cation and anion behavior, but also our understanding of the bioavailability and toxicity of these species. The measurement of metals by DGT are easy to obtain, which is core to its popular use, but often the results require sophisticated interpretation and a wide spectrum of chemical knowledge to really explain in full, which is why the method has and continues to capture the interest of researchers.

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1. Introduction and relevance for *in situ* speciation (fractionation, speciation analysis and bioavailability)

Metallic elements and species in natural waters can be *free*, complexed (e.g. by humic substances) or adsorbed by suspended solids. The metals in the *free* or labile form in most cases are more reactive, possess a smaller mass enabling faster diffusive transport, and have a higher toxicity [1]. Some organometallic species, for example, methylmercury (MeHg) or tributyltin (TBT) are considerably more toxic than their inorganic counterparts, Hg(II) and Sn(IV) respectively. These exceptions to the rule, relate to a very specific case of molecular mimicry, which confers upon these species the ability to be transported freely within living systems via pathways that are intended for biologically essential organic compounds [2]. Additionally, metalloid (e.g. Sb, As and Se) toxicity varies in relation to valency characteristics, for example trivalent As(III) and Sb(III) are more harmful than their pentavalent As(V) and Sb(V) counterparts [3]. Therefore, analytical techniques to selectively determine these fractions are essential for the study of hazard risk associated with metals in aquatic environments [4]. Differentiation of organometallic species from their inorganic form or separation based on valence followed by species quantification normally requires the use of a combination of techniques, firstly to separate the target analytes/molecules and then to measure them (e.g. gas chromatography coupled with inductively coupled plasma mass spectrometry, GC-ICP-MS) [5]. Although approaches based on the use of coupled techniques have been increasing in recent years, less attention has been afforded to the preservation of species integrity during sample collection and processing. In this sense, the use of sophisticated and state-of-the-art techniques (e.g. GC-ICP-MS) to selectively determine highly toxic but stable species at low environmental concentrations (e.g. determination of TBT in water or sediments) can be considered indeed an evolution in analytical chemistry. However, determination of labile metal fractions, or selective determination of metalloid redox species in both the laboratory and field settings cannot always replicate the true conditions as accurately as we as a research community would ideally like.

Ensuring that the correct protocols for collection and sample preparation are followed is critical if contamination and transformation (changes in the distribution of species) of a sample during collection, handling, transport and storage, are to be minimised. It is worth noting, that even the most rigorous preservation techniques will only ever slow down the inevitable on-going chemical and biological changes that occur after collection, with the complete preservation of samples being nearly impossible [6]. In this context, passive samplers may be considered an effective alternative compared to traditional grab sampling collection techniques since the analytes are being sampled *in situ*, with low environmental disturbance. In addition to other advantages, passive samplers can integrate multiple levels of speciation data to provide a better overall measurement of metal bioavailability. Particularly for determination of trace element species, methods based on the DGT technique are the most widely used globally [7], and hence form the focus of this review.

The DGT technique was developed in 1994 [8] and was initially applied to sample metals and semimetals in freshwaters *in situ*. In 1998, the range of DGT applications was extended to include the measurement of metal fluxes in sediments and soils [7,9–11]. Since then, DGT based technologies have been used extensively in a variety of geochemical and environmental health research disciplines. In addition to the ability to sample species selectively, DGT provides a time-weighted measure of concentration, acts to stabilise and pre-concentrate target analytes, while providing an effective alternative to multiple repeat single sampling events that not only take-up resources (time and expense) but are risk points for contamination. All these attributes are key for the quantification of metals at ultra-trace concentrations (ppb or ppt) in the environment. When measured with plasma based analytical techniques such as optical emission spectrometry (ICP-OES) or mass spectrometry (ICP-MS) multiple element parameters can be obtained simultaneously [7]. The DGT technique is based on the immersion of a polypropylene device comprising of two pieces, the piston and the cap. The piston works as a support for the gel-layers that are placed inside the devices (firstly a membrane, then diffusive matrix

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