On-line sample treatment coupled with atomic spectrometric detection for the determination of trace elements in natural waters

Journal:	*Journal of Analytical Atomic Spectrometry*
Manuscript ID	JA-CRV-11-2019-000403.R1
Article Type:	Critical Review
Date Submitted by the Author:	10-Mar-2020
Complete List of Authors:	Fischer, Lisa; University of Natural Resources and Life Sciences Vienna, Department of Chemistry, Institute of Analytical Chemistry Hann, Stephan; University of Natural Resources and Life Sciences Vienna, Department of Chemistry, Institute of Analytical Chemistry Worsfold, Paul; University of Plymouth, SoGEES Miro, Manuel; University of the Balearic Islands, Department of Chemistry

ROYAL SOCIETY OF **CHEMISTRY**

JAAS

Journal of Analytical Atomic Spectrometry

Guidelines for Referees

Thank you very much for agreeing to review this manuscript for *Journal of Analytical Atomic Spectrometry* (*JAAS*)

JAAS is the central journal for publishing innovative research on fundamentals, instrumentation, and methods in the determination, speciation and isotopic analysis of (trace) elements within all fields of application. This includes, but is not restricted to, the most recent progress, developments and achievements in all forms of atomic and elemental detection, isotope ratio determination, molecular analysis, plasma-based analysis and X-ray techniques.

JAAS' Impact Factor is **3.646** (2018 Journal Citation Reports®)

The following manuscript has been submitted for consideration as a

CRITICAL REVIEW

Critical reviews should be definitive, evaluative reviews and must provide a critical overview of the chosen topic area. Authors should be selective in the choice of material, offering personal opinions where appropriate, whilst still covering all the important topics in the field, and indicating possible future developments. Potential writers should contact the editorial office before embarking on their work.

Please consider these standards when making your recommendation for publication in *JAAS*:

- Use the **journal scope and expectations** to assess the manuscript's suitability for publication in *JAAS*.
- **Comment on** the originality, importance, impact and reliability of the science. English language and grammatical errors do not need to be discussed in detail, except where it impedes scientific understanding.
- **Note that routine or incremental** work should not be recommended for publication.
- Check for an accompanying '**Significance to *JAAS***' statement
- **Contact the Editorial Office** if there is any conflict of interest, if the work has been previously published or if there is a significant part of the work which you are not able to referee with confidence.

Best regards,

Professor Martin Resano
Chair, *JAAS*

Dr Jeanne Andres
Executive Editor, *JAAS*

Contact us

Please visit our reviewer hub for further details of our processes, policies and reviewer responsibilities as well as guidance on how to review, or click the links below.

What to do when you review

Reviewer responsibilities

Process & policies

Dear Professor Resano,

Based on your previous invitation, we are pleased to submit the manuscript entitled “On-line sample treatment coupled with atomic spectrometric detection for the determination of trace elements in natural waters” which critically reviews fully automatic on-line strategies for matrix separation and/or preconcentration and speciation of metals in natural waters including marine waters, fresh waters, groundwater and precipitation prior to atomic spectrometric detection.

All articles concerning this topic and published within the last 10 years were carefully evaluated with respect to their applicability to accurately quantify metals/metalloids or metal species at natural concentration levels in the aquatic environment. We have taken into consideration on-line sample preparation techniques based on solid phase extraction, cold vapour and hydride generation techniques (in combination with solid phase extraction), liquid phase extraction and cloud point extraction. The focus is not only on metals/metal species regulated by e.g. the EC Water Framework Directive, but also on less prominent elements such as rare earth elements, precious metals and actinides. Method validation using appropriate (certified) reference materials was another key factor for the selection of articles discussed in this review.

With best regards,
Dr. Lisa Fischer
Professor Manuel Miró

Highlights

On-line strategies for sample treatment prior to atomic spectrometric detection discussed.

Emphasis on flow injection and related flow-based approaches.

Focus on real world natural water samples.

Comprehensive method details tabulated.

On-line sample treatment coupled with atomic spectrometric detection for the determination of trace elements in natural waters

Lisa Fischer[a], Stephan Hann[a], Paul J. Worsfold[b] and Manuel Miró[c]

[a] Department of Chemistry, University of Natural Resources and Life Sciences, Vienna (BOKU), Muthgasse 18, 1190 Vienna, Austria

[b] Biogeochemistry Research Centre, SoGEES, University of Plymouth, Plymouth PL48AA, Devon, UK.

[c] FI-TRACE group, Department of Chemistry, University of the Balearic Islands, Carretera de Valldemossa km 7.5, E-07122 Palma de Mallorca, Spain

Keywords. Natural waters, trace elements, atomic spectrometry, flow injection, sequential injection, solid phase extraction, cold vapour generation, hydride generation, liquid membrane extraction, speciation.

Abstract

This review discusses the application of on-line strategies for sample treatment prior to atomic spectrometric detection. These strategies are based on flow injection and related flow-based approaches and focus on publications that have been published in the last ten years and have been explicitly applied to real world natural water samples (open ocean, coastal and estuarine water, river water, lake water and groundwater) and matrix relevant certified reference materials. The focus is on the use of solid phase extraction for matrix removal and analyte preconcentration. For convenience of searching, methods are grouped by element type, i.e. transition metals (plus zinc, cadmium, lead and arsenic), rare earth elements (the 15 lanthanides plus scandium and yttrium), precious metals (platinum group elements plus silver and gold) and actinide elements (the transuranic elements plus actinium, thorium, polonium and uranium). There is a separate section on methods for elemental speciation. Other on-line treatment strategies covered are cold vapour and hydride generation, and liquid phase microextraction. Comprehensive method details and analytical figures of merit are provided for key selected papers covering each of these strategies in associated tables.

1 Introduction

Natural waters include marine waters (e.g. open ocean, shelf sea, coastal and estuarine), fresh waters (e.g. river, stream, lake), groundwater and precipitation (e.g. rain, snow, ice). Each of these reservoirs has a different chemical composition, including their trace element profile (see e.g. [1, 2]), that varies spatially and temporally but all are interconnected via the global water cycle. Biogeochemical processes[3] impact on the fluxes of trace elements between these compartments and their physico-chemical speciation[4] within each compartment.

The need to quantify trace elements in natural waters is driven by several factors. Some elements or elemental species are toxic[5], even at low concentrations, whilst others are essential micronutrients[6]. Others can be used to elucidate transport processes or act as specific markers for aquatic processes or events[7]. The low concentrations of many elements or their compounds in natural waters requires sensitive detection techniques such as ICP-MS, often hyphenated with some form of separation[8] or preconcentration/matrix removal[9]. This review focusses on the use of flow injection (FI) manifolds and advanced flow setups for on-line sample treatment, coupled mainly with ICP-OES/MS detection, for the determination of trace elements and their compounds in natural waters published since 2008 (for previous reviews on the role of flow analysis in sample preparation see e.g. [10,11]).

2 Flow-through approaches and interfaces

The three main cornerstones of FI, i.e. controllable dispersion, reproducible timing and controlled sample injection, have been fully exploited in combination with atomic spectrometric detection, for which the transport of aerosols into the atomizer is regarded as the 'Achilles heel' of atomic spectrometric techniques. Flow injection approaches were conceived for sample introduction of a metered aqueous sample volume to a detection system (FAAS in the case of elemental analysis), capitalizing on the high (carrier) wash to sample ratio. Hereto, the nebulizer and burner are continuously cleaned by a carrier solution, thus alleviating problems of clogging, even in high salt matrix samples. In fact, FI setups hyphenated to ICP-(qQq)/(SF)MS, based on the continuous operating nature of both the flow setup and detection technique, are now regarded as the second dawn for high-throughput elemental and molecular automatic analysis. The advances in sample injectors (e.g. nano-valves) and improved designs of nebulizers and spray chambers that enable continuous injection of, e.g. organic eluates and alcoholic solvents, have helped to overcome the limitations of FI-ICP couplings in terms of the nature of the sample to be injected[12,13], in as much as high carbon content matrices have been traditionally excluded from ICP analysis. Nowadays the utilization of organic solvents in ICP-MS is performed on a routine basis with robust interfaces allowing the controlled addition of oxygen in order to eliminate carbon deposition on cones and other parts of the ICP-MS introduction system[12,13]. In quadrupole MS based systems, the implementation of reaction/collision cell technology has enabled the development of strategies for the reduction or elimination of almost all polyatomic interferences that would otherwise hamper the accurate determination of the elements amenable to this technique. Tandem QMS systems are now state-of-the-art and regarded as equivalent with ICP-SFMS systems in terms of selectivity and limits of detection.

With regard to system configuration, on-line hyphenation of FI with ICP involving the use of a mechanically movable element, namely a rotary valve, has been the interface of choice for practitioners to integrate sample handling seamlessly with analysis. Nonetheless, at-line automatic interfacing, achieved by exploiting advanced robotic arms or autosamplers, is a simple means of conditioning the sample/extract prior to analysis [14]. However, coupling of flow approaches to discontinuously operating detectors such as electrothermal atomic absorption spectrometry (ETAAS) is not straightforward. The second generation of FI, so-called Sequential Injection (SI), has however paved the way for automatic sample handling across a multi-position selection valve as a core element of the flow system and a bi-directional syringe pump as a liquid driver with on-line sample injection of minute volumes (< 50 µL) into the graphite tube[15]. This is accomplished by integrating a flow line (usually PTFE tubing) in the ETAAS autosampler arm, which connects the selection valve with the graphite tube at pre-set injection times. Advantage is taken of the fact that the ensuing sample might be processed in the SI manifold while running the ETAAS program of the previous sample. A conceptual diagram of the combination of on-line FI/SI sample preparation with atomic spectrometric detectors is shown in Fig. 1.

FI, SI and related techniques can also be used as automatic platforms for accommodating appropriate pre-treatment schemes prior to the actual detection when handling troublesome samples for which matrix clean-up and/or analyte preconcentration to attain suitable detectability are required.

3 On-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the determination of metal concentrations in natural waters.

3.1 Transition metals, zinc, cadmium, lead and mercury

This section focusses on the use of on-line solid phase preconcentration for the determination of transition metals (V, Mn, Fe, Co, Ni and Cu) and includes group 12 elements (Zn, Cd (and Hg)), along with other metals (Pb) and metalloids (As). These elements can be classified in different ways depending on the context in which they are being determined. Their interaction with biota is a particularly important classification and these elements can be described as micronutrients (e.g. Fe, Co), toxic elements (e.g. Pb, Cd) or both (depending on the concentration, e.g. Cu).

The major analytical challenge is the potential for contamination during sampling, storage and analysis as concentrations in natural waters (particularly seawater) are typically very low (≤ nM). In this regard flow manifolds incorporating on-line solid phase extraction (SPE) are attractive due to the confined and controlled nature of the sample handling step, the ability to preconcentrate the analyte(s) and the removal of major sea salt ions that would otherwise interfere with the detection step (see e.g. [11] and [15]). Filtration of samples and refrigeration immediately after collection are essential for obtaining high quality data. The application of flow manifolds, coupled with the use of high purity reagents and a meticulous approach to cleaning of all laboratory ware, are essential prerequisites for minimising the blank signal and hence achieving the desired limit of detection (LOD).

Transition metals can often be determined simultaneously using e.g. ICP-MS or ICP-OES detection and the key analytical performance data for selected papers are summarised in Table 1. It is also possible to determine individual elements using e.g. flame atomic absorption spectrometry (FAAS) or ETAAS and performance data for selected papers are similarly summarised in Table 2. Particularly noteworthy features from these papers are considered in more detail below.

The most important component of the flow manifold for these methods is the on-line SPE micro/mini-column. The chemistry of the SPE phase used for on-line preconcentration and matrix removal, i.e. the nature of the support material and the attached chelating ligand or sorptive material, and the design of the column, e.g. column dimensions, shape and fabrication material, and the elution mode (e.g., the use of back-flushing elution) are important considerations. The most common ligands are iminoacetate based chelates (IDA, NTA, EDTA), quinolinol based chelates (8HQ) and dithiocarbamate based chelates. Nobias-chelate PA1 is a chelating resin that has ethylenediaminetriacetic acid and iminodiacetic acid chelating groups immobilized on a hydrophilic methacrylate polymer. It is popular because it is commercially available, functions over a relatively wide pH range and has a high affinity for several transition metals[9]. This paper reported an enrichment factor (also called a preconcentration factor) of ~200 for Co, Cu, Fe, Mn, Ni and Zn with a 9 mL sample volume, which allowed excellent detection limits to be achieved. As a general comment it is recommended that all papers using on-line SPE state the method used to calculate the enrichment factor and the experimental details used to obtain the data. Toyopearl AF-Chelate 650 is another popular polymeric resin incorporating iminodiacetate chelating groups that has been used to estimate the uncertainties associated with on-line preconcentration and ICP-MS detection of trace metals in seawater[16]. A schematic diagram of the FI manifold used for this work is shown in Fig. 2.

It is also possible to react the transition metal with the ligand on-line and then use a reversed-phase material such as octadecyl-chemically modified silica for trapping the neutral chelate. In an interesting example, Giakasikli and Anthemidis[17] formed a cadmium complex with diethyldithiocarbamate on-line and then pre-concentrated the complex on octadecylsilane functionalized maghemite magnetic particles. The complex was then eluted with isobutyl methyl ketone.

Proprietary resins include 1,5-bis (2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide which was immobilized on aminopropyl-controlled pore glass and incorporated within the injection valve of a simple flow manifold[18]. However, enrichment factors were relatively low, ranging from 2.2 – 6.8 for a range of transition metals. Another proprietary resin utilised a natural product (chitosan) as the support material and ethylenediamine-N,N,N'-triacetate as the immobilised chelating ligand[19], achieving enrichment factors of 14 – 35 for a range of transition (and rare earth) metals. A conventional mini-column (4 cm length x 2 mm i.d.) was incorporated within a 6-port switching valve as part of a fully automated system.

Unconventional advanced sorbents exploiting nanotechnology, based on the large surface area of nanomaterials, have also been adapted for metal assays in natural waters. For example, multi-walled carbon nanotubes (MWCNTs) have been used for preconcentration, with ligands such as *L*-tyrosine immobilised on the walls of the tubes to enhance interaction with transition metals via cation-π interactions (e.g. [20]). An enrichment factor of 180 was reported for Co using FAAS detection.

Recent developments in microchip fabrication have been used to design compact, on-line miniaturized preconcentration devices. One example is the use of dipole–ion interactions between the highly electronegative C–Cl moieties of 2,2'-azobisisobutyronitrile, which was cross-linked to the channel interior of a poly(methyl methacrylate) fabricated chip, and the positive charges on the transition metal ions in the sample[21]. Using this approach, detection limits ranging from 1.6 – 42 ng L^{-1} were achieved for Co, Cu, Mn, Ni and Pb in river water[22].

It is essential that robust quality assurance procedures are used to ensure that the results are fit for purpose. For water quality management it is important that results are sufficiently accurate to monitor environmental threshold levels such as the EU maximum admissible concentration values. This requires the use of appropriate (matrix matched) certified reference materials (CRMs) or waters with consensus values such as those produced by the GEOTRACES programme[23]. All publications should report at least one (preferably more) CRM/consensus value for each element, including appropriate statistical assessment of the results.

Unfortunately, this is not the case in many reports compiled in Tables 1 and 2 (indicated by °) for which CRMs of matrices other than waters, including biological matrices (e.g., urine or seafood tissues) or environmental solids (e.g. sediments and soils) have been inappropriately selected. For elucidating environmental processes, a key requirement is to be able to statistically distinguish changes in recorded data from analytical uncertainty. Thus, a rigorous assessment of all uncertainties in the sampling and analysis steps should be undertaken[16].

3.2 Rare earth elements

In this section, on-line matrix separation and preconcentration methods based on solid phase extraction for the quantification of rare earth elements (REEs) are discussed. The group of REEs comprises the 15 lanthanoids as well as Sc and Y. They can be further divided into light REEs (Sc, La, Ce, Pr, Nd, Sm, Eu) and heavy REEs (Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). They are not regulated with respect to threshold levels and maximum admissible concentrations in water but there is a growing interest in knowing their concentrations in the aquatic environment. They have been confirmed as critical raw materials by the European Commission in 2014[24] due to their significant economic importance as they are widely used in numerous applications such as the automotive industry and nuclear, oil and green technologies[25]. This, however, increases the emission of REEs into the aquatic environment, resulting in anthropogenic anomalies, e.g. Gd due to its intense use in Gd-based magnetic resonance imaging contrast agents. The assessment of anthropogenic contamination requires a knowledge of naturally occurring concentrations of REEs, which are generally in the low ng L^{-1} range in seawater and fresh water and are found in varying concentrations, depending on the surrounding bedrock geochemistry, in groundwater. Hence, direct measurement with state-of-the-art atomic spectrometry techniques is not sensitive enough, particularly if the sample has to be diluted to decrease the total dissolved solid concentration, as required when ICP-MS is applied, to obtain accurate data. Only a handful of methods dealing with the determination of REEs using an on-line approach have been published in the last decade. It is important to stress (again) that the use of an automated flow-manifold is advantageous due to the increased efficiency and the lower risk of contamination and other accidental errors. Table 3 summarizes key analytical performance data of selected publications reporting the determination of REEs in lake water, river water, coastal water and open ocean seawater by ICP-OES and ICP-(SF)MS. All of these methods use on-line SPE mini- or micro-columns incorporating in-house fabricated chelating resins based on the natural polymer chitosan and functionalized with either ethylenediamine-N,N,N-triacetate (EDTriA-type chitosan)[26] or N-(2-hydroxyethyl)glycine[19] as chelating moieties. These resins were used in a fully automated manifold coupled to ICP-OES for the extraction of REEs including Sc and Y from river waters at a pH of 5 with recoveries, assessed from spike experiments, in the range of 90 – 110%[19, 26]. Preconcentration factors were estimated by comparison of peak heights obtained by processing a standard solution with the preconcentration system and conventional nebulization. High preconcentration factors, in the range of 83 – 120 (EDTriA-type chitosan) and 83 – 102 (N-(2-hydroxyethyl)glycine-type chitosan) were obtained, except for Y and Sc which were ≤ 30, by processing a sample volume of 20 mL. Due to the operation of the manifold in a “multi-mode” with three synchronized collection systems, up to 12 samples h^{-1} could be analysed for a suite of metals. However, LODs of ≥ 0.002 ng mL^{-1} are relatively high compared with other methods surveyed in this review (see Table 3), which might be attributed to the use of ICP-OES as the detection system.

Resins with IDA and ED_3A chelating groups (also referred to as polyaminopolycarboxylic acid groups – PAPC) packed in a chelating column and sold as Nobias PB1M were used by Zhu *et al.* for the determination of REEs in coastal seawater[27], lake water[28] and seawater[29] in an on-line SI manifold directly coupled to ICP-(SF)MS. Initially, 10 mL of seawater were processed within 6 min and a preconcentration factor of 9.6 was obtained, leading to LODs in the range of 0.005 – 0.09 pg mL^{-1}. Recoveries were determined based on spiked sample solutions and the trueness of the method was estimated by comparing published and measured values obtained by the repetitive analysis of CRM NASS-5[27].

Even faster analysis could be performed with an automatic column changing system as reported by the same authors[28]. Elution and measurement of one sample, including the time required for column changing, was performed in 3 min but sample loading was carried out off-line. They compared Nobias PB1M with InterSep ME1, a chelating resin with only IDA moieties. For both resins, a pH of 5.0 was optimal for adsorption and similar recoveries, ranging from 97 – 103%, and precision (RSDs of the peak areas) were obtained with identical elution conditions.

Far lower LODs, ranging from 0.0008 – 0.004 pg mL^{-1}, could be obtained using an automatic pH-adjustment system for SPE of REEs on Nobias-PB1M from seawater by preconcentrating 50 mL of sample[29]. As sample pH is crucial for the sorption efficiency of the target metals and each sample manipulation step (i.e. a manual pH adjustment) increases the risk of contamination, the main focus of this work[29] was the development of a device for automated and contactless pH-adjustment and monitoring, involving the addition of a quantity of aqueous ammonia solution into the sample via a nebuliser, which was controlled by an electromagnetic valve while the transmitted light at 550 nm (the pH indicator was methyl red) was spectrophotometrically monitored. The system has been used to pH adjust sample volumes of 20 to 100 mL within < 5 min per sample prior to REEs determination using the automatic column changing system described above[28]. Blank values measured were significantly lower compared with those obtained by applying "conventional" pH-adjustment with glass- or all-plastic pH electrodes, leading to improved LODs. Spike recovery experiments with two concentration levels were performed to validate the method but CRMs were not analysed.

The use of the commercially available seaFAST^{TM} system (Elemental Scientific Inc.), coupled to ICP-QMS, has been reported by Hathorne *et al.*[30] LODs in the range of 2 – 302 ppq, determined from a 2% HNO_3 solution, were reported by pre-concentrating 7 mL of seawater on the commercially available chelating resin Nobias PA1, which has similar chelating moieties to Nobias PB1M. The system allows automated in-line buffering of the sample and is equipped with trace metal clean-up columns in the up-take capillaries, which deliver buffer solution and carrier. This resulted in extremely low background signals and hence low signal/noise ratios for most REEs. By adjusting the pH value of the samples loaded onto the column to pH 6.0, yields in the range of 94 – 102% were obtained. Yields were estimated by comparing time resolved peaks of a matrix matched (NaCl) standard solution containing 5 ng L^{-1} of REEs after preconcentration with signals obtained from standards diluted in the eluent by bypassing the column. The authors state the susceptibility to errors during the determination of column yields (absolute recoveries) if there is any inconsistency in the acid strengths of eluted and directly analysed standards, which leads to the conclusion that the accurate determination of column recovery is not easy. Trueness of the reported method was appropriately assessed by standard additions of deep Atlantic seawater samples, isotope dilution analysis (for Nd) and by measuring reference samples such as NASS-5 as well as 1:10 diluted VIDAC18 reference mine waste water and SCREE and PPREE reference acid mine waters produced by the USGS, and diluted in different matrices with an appropriate content of NaCl to mimic seawater matrixes.

In addition to commercially available chelating resins, a graphene oxide-TiO_2 composite was synthesized as a novel and inexpensive type of carbon-based nanomaterial and packed into a micro-column for the online preconcentration and ICP-OES detection of La, Ce, Eu, Dy and Yb (additionally Cu and Pb)[31]. High adsorption capacity, fast sorption kinetics, and stability over a wide pH range have been reported due to the unique characteristics of the material, e.g. the large surface area and various oxygen containing groups which offer binding sites for metal ions such as heavy metals and REEs. Adsorption kinetics have been well studied in this work and the adsorption capacity obtained was indicated to be comparable with related SPE materials. Preconcentration factors of 10 could be obtained, yielding LODs in the range of 0.13 – 2.64 ng mL^{-1}. They are, however, orders of magnitude higher compared with those obtained using the chelating resins described above, in particular those obtained using ED_3A/IDA functionalized resins, and significantly higher than those obtained with chitosan based chelating resins[19, 26], even though the detection system in this case was also ICP-OES, and thus the graphene oxide-TiO_2 composite is not a viable low-cost alternative for the preconcentration of REEs from natural water samples.

3.3 Precious metals

In this section, on-line matrix separation and preconcentration methods based on solid phase extraction for the quantification of precious metals are discussed (see Table 3 for details of selected methods). The determination of precious metals, including the platinum group elements (PGEs) Ru, Rh, Pd, Os, Ir and Pt, as well as Ag and Au, in natural waters is still in its infancy. Naturally occurring concentrations are in the sub-ng L^{-1} - pg L^{-1} range, thus requiring powerful extraction and preconcentration methods. However, the interest in the determination of, in particular, PGE concentrations in the aquatic environment is steadily increasing because of anthropogenic emissions resulting from their use in industrial, chemical, electrical and pharmaceutical applications and in catalytic converters for cars[32, 30]. Silver has also been used in a wide variety of chemistry, electronics, medicine and other industrial fields and is highly toxic to marine organisms due to bio-accumulation[33]. Time consuming as well as potentially harmful methods based on liquid-liquid extraction using ammonium 1-pyrrolidinedithio-carbamate/diethylammonium diethyldithiocarbamate (APDC/DDDC) and co-precipitation and flotation techniques are being replaced by methods based on SPE using chelating sorbents, prior to detection by atomic spectrometry. Due to the characteristic of these metals to mainly occur as anionic chloro-complexes in the aqueous phase, as facilitated by the chloride content in seawater[34,35], (strong) anion exchangers have traditionally been used. However, few publications report the automation and online separation/preconcentration of precious metals from natural waters. More than 10 years ago, a method was published for the determination of Pt using a chelating ion exchange resin (silica gel modified with 1,5-bis(di-2-pyridyl)methylene thiocarbohydrazide - DPTH-gel) in an on-line flow system coupled to ETAAS[36]. Since this publication is not within the timeframe for references, it will not be discussed further; nevertheless, it is worth mentioning that the LOD obtained by this method is not sufficiently low for monitoring naturally occurring concentrations of these metals, clearly indicating that the sample volume processed by the on-line flow system does not provide adequate preconcentration factors for the determination of PGEs in natural waters.

As a viable alternative to commercial strong anion exchangers, polyaniline (PANI) has been evaluated for the on-line preconcentration of Pd from natural waters including ground water, lake water and seawater as a low cost and easy to synthesize alternative to other sorbents[37].

The extraction mechanism is based on anion exchange and preconcentration factors of 125 have been reported by applying a sample volume of 250 mL, thus resulting in LODs of 0.0004 – 0-003 ng mL^{-1} (LODs given for individual Pd isotopes) with ICP-MS detection. These however are still not sufficiently low for monitoring natural Pd concentrations.

Several methods were published for the automatic on-line preconcentration and matrix separation of Ag from seawater more than 10 years ago e.g.[38, 39] using the strong anion exchanger Dowex®1x8 with trimethylbenzylammonium functional groups immobilized on a styrene-divinylbenzene gel but only one method has been published recently for the analysis of estuarine samples[40] using the same sorbent. This resin is very popular for the extraction of Ag chloro-complexes as it has a high adsorption capacity. With a sample consumption of only 7.5 mL, a LOD of 0.06 ng kg^{-1} was obtained. This LOD is comparable with those obtained by the two previous methods[38, 39]. The advantage of the latter method, however, is the lower sample volume required (7.5 mL vs 12 mL) and the low column volume of only 18 µL. Validation was performed with SLEW-3 and CASS-4 certified reference materials. These are not certified for Ag but the authors demonstrated the trueness and good precision of the method by comparing these values with previously reported concentrations.

3.4 Actinides

In this section, on-line matrix separation and preconcentration methods based on solid phase extraction for the quantification of actinides (Th, U) are discussed (see Table 3 for details of selected methods). The actinide elements encompass Ac, Th, Pa, U and the transuranic elements, whereas U and Th are the most abundant actinides naturally occurring in all environmental compartments[41]. Additionally, anthropogenic sources of these radionuclides and their synthetic isotopes (^{232}U, ^{233}U, ^{236}U and ^{229}Th) include technological applications (metallurgy, ceramic and nuclear industries), phosphorous mineral fertilizers and pesticides, uranium mining and milling, coal combustion, fuel processing, nuclear power plants and nuclear tests[42,43]. Due to the high chemical and radiological toxicity of their soluble compounds, permissible limits of U in drinking water are regulated by the Word Health Organisation (WHO; 30 µg L^{-1}) [44], Environmental protection Agency (EPA; 30 µg L^{-1}) [45] and the Atomic Energy Regulatory Board (AERB; 60 µg L^{-1}) [46]. In the last revision of the Drinking Water Directive of the European Commission[47], U was included in the list of parameters of naturally occurring but harmful substances to be monitored. In addition, environmental quality standards for freshwater have been elaborated by some member states, ranging from 0.015-25 µg L^{-1} [48] within the EU Water Framework Directive. The WHO also set guidance levels for radionuclides in drinking water, i.e.

10 Bq L^{-1} for ^{238}U (81 µg L^{-1}) and 1 Bq for ^{232}Th (246 µg L^{-1}) [44]. Thus, concentrations in the (aquatic) environment need to be monitored. Various methods, mostly employing SPE on actinide specific resins such as TEVA, UTEVA, TRU and DGA resins, based on flow analysis in combination with atomic spectrometric detection, have been reported for the determination of actinides in natural waters e.g. [49, 50 ,51 ,52]. They were, however, operated with off-line detection, mostly by applying two or more different resins to cover a wider range of analytes and perform in-line extraction chromatographic separation and hence are not within the scope of this manuscript.

One method has been published for the simultaneous determination of U and Th at environmentally relevant concentrations in various water matrices based on a fully automated lab-on-valve FI system coupled to ICP-QMS[53]. The performance characteristics are outlined in Table 3. Extraction and simultaneous elution, i.e. no separation involved, was based on SPE using the UTEVA chromatographic resin functionalised with dipentyl pentylphosphate (DP[PP]) moieties (also called diamyl amylphosphate (DAAP). The authors estimated a resin durability of 150 injections (up to 8 mL sample volume) and reported recoveries of >95%, determined by analyte-spike recovery experiments, and clearly pointed out the low cost of the method as only 30 mg of resin were packed on-line in the column. They also reported the suppressive effect of high concentrations of phosphate due to the formation of a non-extractable charge neutral complex with Th^{4+} cations. Addition of Al^{3+} counteracts this due to the formation of Al^{3+}-phosphate complexes which inhibits Th-phosphate complexation.

3.5 Metal speciation

There are many publications on the use of ICP-MS and ICP-OES, as well as AAS, combining on-line sample preparation with elemental speciation analysis of metal(loid)s in natural waters. Arsenic is the most commonly studied metal, followed by Cr and, to a lesser extent, Hg, Sb, Fe, Se and V. In general, elemental speciation involves the differentiation between oxidation states or organic/inorganic elemental fractions. Historically, research and development on elemental speciation analysis was mainly curiosity driven, whereas nowadays legal institutions and governmental bodies such as WHO, US EPA and EC (e.g. via the Water Framework Directive) define limits not only on total elemental concentrations but also on elemental species (oxidation states) or organic molecules containing certain elements, which is a major driver for research on elemental speciation analysis. On-line SPE is mainly used for separation of elemental species or fractions of interest in combination with atomic spectrometric detection and only very few studies deal with the on-line combination of SPE with liquid chromatographic separation. The key analytical performance data for selected papers using on-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the speciation of metals in natural waters are summarised in Table 4.

Chromium speciation with SPE was performed on-line in several studies using either ETAAS[54, 55, 56] or ICP-MS[57, 58, 59, 60] as the detection technique. In general, these studies achieved LODs in the low ng L^{-1} range and trueness was, in most cases, demonstrated using CRMs. In 2008, Hu *et al.*[59] reported a useful method for the simultaneous speciation of inorganic As(III)/As(V) and Cr(III)/Cr(VI) in natural waters. They used mesoporous Al_2O_3, which was prepared by sol-gel technology, as a capillary micro-extraction coating material. The column retained AsO_4^{3-} and $Cr_2O_7^{2-}/CrO_4^{-}$ under acidic condition while cationic As(III) and Cr(III) were not retained. Elution of the retained species was performed under alkaline conditions. They reported LODs of 0.7 and 18 ng L^{-1} for As(V) and Cr(VI), and 3.4 and 74 ng L^{-1} for As(III) and Cr(III), respectively. Evidently, such differential approaches can also be performed on-line with ETAAS. Zou *et al.*[56] combined a *C. vulgaris* cell (green microalgae) mini-column in sequential combination with an anion exchange resin mini-column for the retention of Cr(III) and Cr(VI), respectively. Utilizing a SI system, Cr(III) and Cr(VI) were eluted by 0.04 mol L^{-1} and 1.0 mol L^{-1} nitric acid, respectively, and quantified on-line with ETAAS. LODs were 0.02 µg L^{-1} for Cr(III) and 0.03 µg L^{-1} for Cr(VI), which unfortunately does not meet the California Public Health Goal set to 0.02 µg L^{-1} for Cr(VI).

Selenium speciation is of great interest as the toxicity, bioavailability, and essential nature of this element is highly depend on its chemical form. Huang *et al.*[61] published a double column method combining nanometre-sized Al_2O_3 and mesoporous TiO_2 which was chemically modified by dimercaptosuccinic acid. A schematic diagram of the flow manifold used for this work is shown in Fig. 3. The inorganic selenium species Se(IV) and Se(VI) were selectively adsorbed by Al_2O_3 while the organic Se species, i.e. the seleno-amino acids selenocysteine and selenomethionine, which were not retained on the first column, were retained on the chemically modified, mesoporous TiO_2. Sequential elution enabled the selective and sensitive determination of the four species (LODs were in the range of 45 - 210 ng L^{-1}) in lake water.

Vanadium, like Se, is one of the major essential elements, but also has toxic properties depending on both the concentration and oxidation state. Xiong *et al.* [62] speciated V(IV) and V(V) on a conical micro-column packed with cetyltrimethylammonium bromide-modified alkyl silica. The species showed different pH dependent retention behaviour: V(V) was quantitatively retained in the pH range 2.0 – 7.0, while V(IV) was not retained at pH 2.0 - 3.5 but quantitatively retained at pH 5.0 - 7.0. V(IV) was quantified by subtracting V(V) from total V. The LOD for V(V) was 0.03 µg L^{-1}.

It can be concluded that FI in combination with elemental speciation analysis is mature in terms of the technical developments, which have been achieved over many decades. The situation regarding CRMs certified for elemental species is still not well developed, as for many matrices no reliable materials are available. Regarding validation, the authors of this work wish to emphasise that in order to assure comparability of different studies in terms of LODs and LOQs and in terms of their applicability to control legal limits, improvements towards setting a harmonized procedure are much needed. Evidently there are several ways to calculate these values for transient signals, but most of the time the procedures are not fully described or completely missing. Accordingly, we propose adoption of the well elaborated procedure outlined in the EURACHEM guide "The Fitness for Purpose of Analytical Methods"[63] for calculating LODs and LOQs for methods which use peak areas for calibration and quantification purposes.

4 On-line sample preparation techniques based on cold vapour- and hydride generation techniques for matrix separation and preconcentration of metals and metal species in natural waters.

Cold vapour generation (CVG) and hydride generation (HG) techniques have been used in on-line flow systems to separate the analyte from the matrix, in some instances in combination with sorptive preconcentration using chelating sorbents. A pre-condition, however, is the formation of volatile species upon reaction with reducing agents such as sodium borohydride in an acidic environment. The classical elements determined by HG are Ge, Sn, As, Bi, Sb, Se and Te after chemical transformation into their gaseous hydrides, whereas e.g. Hg and Cd are determined by CVG after volatile species are generated. Through gas/liquid phase separation by an argon gas carrier stream, the volatile hydrides/elements are transported into the plasma or graphite furnace. Matrix separation is based on the fact that non-volatile interfering elements such as major ions do not form hydrides, and thus remain in the liquid phase and are drained off to waste. Hydride analyte transport efficiencies up to 100%, leading to higher signal/noise ratios, and hence lower LODs, in comparison with conventional liquid sample introduction, are reported[64]. HG/CVG is an important sample introduction technique when coupled on-line to atomic spectrometric detectors[64] but careful optimization of the hydride generation process is required, e.g. the concentration of the reducing agent because too high a concentration of $NaBH_4$ may lead to foaming and the production of droplets as well as the generation of excessive hydrogen gas. These factors result in plasma instability[65], especially when coupled to ICP-based detectors.

Methods employing CV and HG techniques for the matrix separation and preconcentration of metals in natural waters are summarized in Table 5.

Only a limited number of papers have been published within the last decade reporting the determination of As[66], Cd[67] and Hg[68] in natural waters after HG and CV generation with $NaBH_4$ without preconcentration on chelating sorbents. For example, for the quantification of Hg, the CV technique, even without preconcentration, LODs are reported to improve by a factor of 24 when CV-ICP-QMS is used compared with solution nebulization based ICP-QMS due to reduced signal suppression from matrix effects[68].

Nevertheless, also in combination with CV and HG techniques, matrix effects with a negative effect on the accuracy and sensitivity of these methods have been observed. To overcome matrix interferences arising from e. g. Ca, Mg, K and Na, as well as various transition metals (Cu, Fe, Ni, Co) present in natural waters at high(er) concentrations, SPE based on ion-exchange has been applied prior to HG/CV generation in various applications (see Table 5). The challenge here is to find the optimum acid concentration for both the elution of the retained metal species from the preconcentration column (stronger acids usually enhance recovery) and efficient hydride generation as this process is strongly dependent on the pH and acid strength. For example, Sb, Bi and Sn were pre-concentrated from seawater on 1,5-bis(di-2-pyridyl)methylene thiocarbonohydrazide bonded to silica gel (DPTH-gel) packed in a mini-column prior to HG-ICP-QMS analysis[65]. As hydride generation efficiency depends on the oxidation state of the elements, *L*-cysteine was used as a pre-reducing and masking agent. Increased signal intensities could be obtained for Sn, whereas those for Sb and Bi were not affected by *L*-cysteine addition. Enrichment factors of 2.5 – 8.6 were achieved with a sample volume of 4.8 mL. Limits of detection were in the sub µg L^{-1} range and sufficiently low for the determination of these elements in diluted CRMs and real seawater samples.

A similar approach has been applied for the determination of these elements and, in addition, for Hg from seawater and river water[69]. DPTH was functionalized on mesoporous silica, packed in a mini-column and the elution was performed with HCl (plus thiourea for Hg) while in the former paper[65] HNO_3 alone was used instead. A comparison between these two methods showed similar performance for Sb, Bi and Sn with respect to trueness (estimated from TMDA 54.4 and TM 24.3 fortified lake water CRMs), precision, relative recovery and the detection capability of ICP-QMS vs ETAAS.

Sánchez-Trujillo *et al.*[70] addressed a problem associated with simultaneous multi-element determinations for Pb, Cd and Hg using CVG-ICP-QMS, i.e., different optimal conditions are required for individual elements. Catalysts such as thiourea and Co were used for more efficient reaction of Cd, and hexacyanoferrate (III) was proposed as an oxidizing reagent for the conversion of Pb(II) to Pb(IV) ([70] and therein cited publications). The elimination of interferences on the determination of other elements requires the use of appropriate sorbent materials, oxidizing agents and catalysers. In fact, two mini-columns packed with DPTH-gel were incorporated in the flow manifold in parallel, *viz*., in the injection loop of two rotary valves, and loaded with sample adjusted to pH 5.0. Elution with thiourea in HNO_3 was performed, and whereas the eluted metals from the first column were mixed with a reducing agent consisting of $NaBH_4$ and $K_3Fe(CN)_6$ for the generation of PbH_4 (and Hg^0 vapour), those eluted from the second column were mixed solely with $NaBH_4$ for Cd^0 and Hg^0 vapour generation. Hence, the most efficient vapour generation conditions for each element were obtained. Enrichment factors in the range of 14.4 – 27.3 were obtained and LODs were in in the low ng L^{-1} range. However, these are at least 3 times higher than those obtained by HG/CVG methods developed for the single element determination of e.g. Hg[68], Cd[67] and Pb[71] (see Table 5), probably due to the addition of reagents for pH adjustment, oxidation and improved elution efficiency contributing to the blank signal.

Noble metals are not traditionally analysed by CVG due to the unknown identity and formation efficiency of their hydrides and volatile species but a recent study has shown its suitability for Au, Ag, Pd, Pt, Ir, Rh and Os determinations using $NaBH_4$ as the reducing agent[72]. After preconcentration of these metals onto DPTH immobilized on iron oxide magnetic nanoparticles, which were retained in a knotted reactor by an external magnetic field, and elution with thiourea/HCl, the eluate was directed into a multi-mode sample introduction (MMSI) system for CVG and liquid nebulization. This MMSI also served as the gas/liquid phase separator. *In situ* CVG was a pre-requisite for the applicability of this approach as noble metal hydrides are unstable and require rapid separation from the liquid phase. It was shown that hydride formation in the presence of $NaBH_4$ was appropriate for Ag, Pt, Pd and Os whilst Au, Ir and Th signals did not improve compared with non-CVG results, hence requiring the use of compromise conditions. Enrichment factors were in the range of ≤20 for Pd, Os, Au, Ir and Rh, 144 for Pt and 206 for Ag. The LODs were in the range of 0.03 µg L^{-1} (Ag) and 100 µg L^{-1} (Rh), i.e. not sufficiently low for the determination of ambient noble metal concentrations in natural waters.

Sample introduction techniques based on cold vapour and hydride generation have also been used in this context with elemental speciation analysis. Two studies have addressed the separation of inorganic mercury and methyl mercury. Krishna *et al.* [73] developed a speciation approach for the two fractions employing efficient preconcentration of natural water samples (pH 7) on a polyaniline microcolumn and subsequent selective elution of MeHg and iHg using 2% HCl and a mixture of HCl–thiourea (2% HCl + 0.02% thiourea) respectively. This successful combination of preconcentration, speciation and CVG-ICP-MS (all on-line) enabled quantification of the two species in the high ng L^{-1} range. Sánchez-Trujillo *et al.* [74] published a similar concept using on-line CVG-ICP-MS after on-line enrichment/speciation of the two Hg-fractions on mesoporous silica functionalized with 1,5-bis(2-pyridyl) methylene thiocarbohydrazide. Selective elution of CH_3Hg^+ and Hg^{2+} was obtained with 0.2% HCl and 0.1% thiourea in 0.5% HCl, respectively. Total mercury (calculated as the sum of the two fractions) was determined in LGC 6016 (Estuarine Water) and was in good agreement with the results obtained by the same group in an earlier study[70]. The LODs in this work were lower than those obtained in the earlier study using the polyaniline material, which can be explained mainly by the use of a next generation ICP-MS detection system. In a similar approach to that used in many other studies, method LODs in the two above mentioned studies were calculated from background noise, its standard deviation and the height of a measured standard solution. It is noteworthy that this method allows relative inter-comparison of different methods but is not capable to give reliable LODs or LOQs, as quantification is routinely performed via peak integration (peak area), whereas in these cases LODs/LOQs are calculated via peak height.

Hydride generation was used in two further studies on the speciation of different oxidation states of arsenic[75] and antimony[65]. The work concerning arsenic used a differential approach by passing natural water sample through a strong anion exchanger cartridge, on which As(V) was selectively retained, whereas As(III) passed through the column and was detected via HG AAS. The concentration of As(V) was then determined by subtracting the As(III) concentration from the total As concentration of the sample. LODs were of the order of 0.5 µg L^{-1}. The authors discussed the limitations of their work regarding organic As species (which would also pass through the column and lead to false positive As(III) results) and present a method that is fast and reliable and suitable for the analysis of low salinity natural waters for As(III). For the speciation of inorganic antimony, selective sorption materials were used in a FI approach with sequential elution and on-line HG-ICP-MS detection[65]. Accuracy was demonstrated for the sum of the quantified Sb species by the analysis of the CRMs SLRS-5 River Water and TMDA-54.4 Fortified Lake Water. It should be mentioned that, due to the lack of species-specific CRMs, it is difficult to assess method accuracy with regard to the target species. In such cases inter-comparison with independent methods available in-house, or inter-comparison with other competent laboratories is mandatory for method validation/verification in terms of trueness.

5 On-line sample preparation techniques based on liquid-liquid-micro extraction and cloud point extraction techniques for matrix separation and preconcentration of metals in natural waters.

There are a limited number of published papers dealing with liquid-phase extraction (LPE) in flow systems for trace element analysis in surface waters as compared with those using SPE[76]. This is attributed to operational difficulties in achieving (i) reliable dispersion of the aqueous and organic phases across the conduits of flow platforms, (ii) quantitative separation under the flow regime of the analyte-containing organic phase after extraction and (iii) high enrichment factors on account of the limited organic to liquid-phase ratios in miniaturized systems. Moreover, metal species usually need to be derivatized prior to liquid-phase extraction[77] or reacted with an appropriate surfactant for cloud-point extraction[78], in contrast to SPE for which there is a plethora of commercially available sorbents with a wide range of chelating moieties for direct extraction and preconcentration at the appropriate pH. The key analytical performance data for selected papers using liquid-liquid micro-extraction and cloud point extraction techniques for the matrix separation and preconcentration of metals in natural waters are summarised in Table 7.

Some of the FI-based papers on LPE for trace metal determinations merely report semi-automatic methods. The flow platform is used for automation of the detection step after batch LPE[79], or phase separation by modification of the ionic strength or temperature and retrieval of the metal-containing phase for detection[80].

Computer-controlled flow methodologies using programmable flow, such as sequential injection analysis and its variants[81, 82, 83], have been designed for the miniaturization of liquid-phase extraction schemes, endowing these methods with green chemical credentials whilst also ameliorating extraction efficiencies and enrichment factors. For example, Anthemidis and co-workers have developed a number of intriguing liquid-phase microextraction (LPME) variants, such as dynamic single-drop LPME[82, 83], countercurrent LPME[77] and dispersive LPME (DLPME)[84, 85, 86, 87] that were fully automated as a front-end to flame or electrothermal AAS for direct on-line injection of the metal-enriched organic phase. In those articles dealing with DLPME[84, 85, 86, 87], the aqueous sample, organic solvent containing the chelating reagent and dispersing solvent were merged on-line to generate droplets of the organic phase for efficient extraction of the neutral chelates followed by on-line trapping of the metal containing organic droplets into reversed-phase materials packed in flow-through micro-columns. A schematic diagram of a flow manifold integrating in-line DLPME as a front end to ETAAS is shown in Fig. 4.

The main issue observed by a number of FI/SI systems incorporating LPE/LPME is that method validation is performed with overly simplistic CRMs (e.g. lyophilised solutions[81]) or entirely different matrices (e.g., sediments and mussel tissues) that do not properly simulate the composition of the target matrices (river water, seawater) analysed in those papers[87, 77, 83].

6 Conclusions and perspectives

Flow injection has become a mature approach for metal determination and non-chromatographic speciation analysis, but still constitutes a viable platform and vehicle for on-line implementation of in-house and commercially available sorptive (nano)materials prior to atomic spectrometric detection systems for trace and ultra-trace analysis. The analytical detection techniques have not greatly evolved in terms of sensitivity and instrumental detection limits over the last 10 years and thus efficient sorbent phases and ligands for element preconcentration and clean-up analysis of natural waters are still required. It should however be noted that some of the analytical methods reported in the literature that include enrichment protocols are not sensitive enough for the analysis of natural waters and thus spike concentration levels that are not environmentally relevant of natural waters are used for method validation instead. Likewise, inappropriate reference materials, such as biological materials, sediments and wastewaters, have been selected for evaluation of the trueness of methods applied to natural waters. It is therefore recommended that QC/QA tools and uncertainty measurements should be adopted in fully validated protocols using FI approaches.

The last two decades have also witnessed the advent of novel miniaturized and portable devices based on mesofluidic Lab-on-Valve and microfluidic Lab-on-chip platforms, yet application to continuous on-line monitoring is still in its infancy.

Acknowledgement

Manuel Miró acknowledges financial support from the Spanish State Research Agency (AEI) and Ministry of Science, Innovation and Universities (MCIU) through projects CTM2017-84763-C3-3-R (MCIU/AEI/FEDER, EU) and CTM2017-90890-REDT (MCIU/AEI/FEDER, EU).

Table 1: Multi-element on-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the determination of the total metal concentration of transition metals and metalloids in natural waters. (All units as in the original publication)

Analyte	**Matrix**	**Solid phase**	**Detection technique**	**Sample treatment /Elution**	**Figures of merit**				**Validation**	**Sample volume**	**Enrichment factor**	**Sample throughput**	**Ref**
					DL	**Linear range**	**Precision**	**Relative Recovery**					
Mn, Co, Ni, Cu, Pb	River water	PMMA microchip (treated with saturated NaOH)	ICP-MS	pH 6 (NH_4Ac)/ 0.5% HNO_3	Mn: 2.62 ng L^{-1} Co: 1.69 ng L^{-1} Ni: 42.54 ng L^{-1} Cu: 13.85 ng L^{-1} Pb: 1.64 ng L^{-1}	Up to 5 µg L^{-1}	2.9-3.6% (n=3)	83-110%	NIST 1640a trace elements in natural water	20 µL	≥2	19.35 h^{-1}	22
Zn, Cu, Cd, Cr, V, As	River water, lake water (*well water)	MWCNTs-silica	ICP-OES	pH 8.5/ 2 M HCl	Zn: 0.27 µg L^{-1} Cu: 0.11 µg L^{-1} Cd: 0.45 µg L^{-1} Cr: 0.91 µg L^{-1} V: 0.55 µg L^{-1} As: 0.67 µg L^{-1}	LOD–100 µg L^{-1}	3.1-8.6% at 10 µg L^{-1} (n=7)	82-115%	GSBZ50009-88, GSBZ 50029-94 environmental waters	6 mL	10	n.a.	88
Co, Fe, Pb, V	Seawater	Toyopearl AF-Chelate-650	ICP-MS	pH 5 (NH_4Ac)/ 1 M HNO_3	0.021-0.34 nmol L^{-1}	n.a.	4-23%	76.111%	NASS-5 seawater, GEOTRACES reference samples	7.5 mL	10-15	8.25 min/ sample	16
Mn, Co, Ni, Cu, Cd, Pb	River water	PMMA	ICP-MS	pH 8 (maleate buffer)/ 0.5% HNO_3	Mn: 20.6 ng L^{-1} Co: 5.44 ng L^{-1} Ni: 11.86 ng L^{-1} Cu: 4.90 ng L^{-1} Cd: 16.11 ng L^{-1} Pb: 3.48 ng L^{-1}	0.05-100 µg L^{-1}	< 9% CV (long term)	82-118%	NIST 1643a artificial saline water	50 µL	n.a.	13.33 h^{-1}	21
Mn, Fe, Co, Ni, Cu, Zn	Seawater	Nobias PA 1	ICP-SFMS	pH 5.7, pH 7.0 ($AcNH_4$)/ 1.6 M HNO_3	Mn: 0.002 Co: 0.00029 Fe: 0.014 Ni: 0.013 Cu: 0.003 Zn: 0.016 nmol kg^{-1}	n.a.	1-3% for Ross seawater (long term)	96-107%	GEOTRACES reference samples	9 mL	200	8.75 min/ sample	9

Cd, Co, Cu, Ni, Pb, Zn	Oceanic waters	IDA	ICP-MS	pH 6.0 (AcNH$_4$)/ 0.8 M HNO$_3$	Co: 3.2 pM Ni: 23 pM Cu: 46 pM Zn: 71 pM Cd: 2.7 pM Pb: 1.5 pM	up to: Co: 0.89 nM Ni: 24 nM Cu: 9.6 nM Zn: 20 nM Cd: 2.8 nM Pb: 0.59 nM	3.4-8.6% for SAFe D2	92-102%	NASS-5 seawater, GEOTRACES reference sample (SAFe)	7 mL	10	6 min/ sample	[89]
Co, Cr, Ni, Cd, Mn, Zn, Cu, Pb	Seawater	PTSH-cpg resin	ICP-MS	pH 8.0±0.5 (borate/ boric acid buffer)/ 5% (m/m) HNO$_3$	Co: 0.002 µg L^{-1} Cr: 0.057 µg L^{-1} Ni: 0.117 µg L^{-1} Cd: 0.004 µg L^{-1} Mn: 0.21 µg L^{-1} Zn: 0.260 µg L^{-1} Cu: 0.030 µg L^{-1} Pb: 0.020 µg L^{-1}	DL-60 µg L^{-1}	< 5% (at twice the DL, n=10)	82-111%	SLEW 3 and LGC6016 estuarine water, CASS-5 coastal seawater, SLRS-5 river water, TMDA-54.4 fortified lake water	2.1 mL	2.2-6.8	8.6 h^{-1}	[18]
Cd, Pb, Cu	River water, lake water, (*urine)	SCX Bond Elut® Plexa™ PCX	FAAS	pH 2 (HNO$_3$)/ 1 mol L^{-1} HCl	Cd: 0.1 µg L^{-1} Pb: 1.8 µg L^{-1} Cu: 0.5 µg L^{-1}	Cd: 0.4-20 µg L^{-1} Pb: 7.5-450 µg L^{-1} Cu: 1.8-100 µg L^{-1}	Cd: 2.9% at 2 µg L^{-1} Pb: 3.1% at 30 µg L^{-1} Cu: 2.7% at 10 µg L^{-1} (n=10)	95-99%	NIST CRM 1643e trace elements in water, (°BCR 278-R trace elements in mussel tissue)	2 mL	90-95	30 h^{-1}	[90]
V, Cr, Cu, As, Pb	River water and tap water (*amongst others)	S-CS-MWCNTs	ICP-MS	pH 7 (HNO$_3$, NH$_3$ H$_2$O)/ 0.5 mol L^{-1} HNO$_3$	V: 0.002 µg L^{-1}, Cr: 0.0038 µg L^{-1} Cu: 0.0035 µg L^{-1} As: 0.0013 µg L^{-1} Pb: 0.0036 µg L^{-1}	0.005-10 µg L^{-1}	V: 3.8%, Cr: 1.4%, Cu: 3.1%, As: 4.6%, Pb: 1.6% at 1 µg L^{-1} (n=11)	91-105%	GBW08607 riverine water, (°GBW10024 scallop)	20 mL	V. 111 Cr: 95 Cu: 60 As: 52 Pb: 128	n.a.	[91]
Cd, Co, Ni	Seawater	8-HQ	ICP-MS	AcNH$_4$ buffer/ 1 M HNO$_3$	Cd: 0.008 ng mL^{-1} Co: 0.006 ng mL^{-1} Ni: 0.009 ng mL^{-1}	Cd and Co: 0-0.5 ng mL^{-1} Ni: 0.1-1.0 ng mL^{-1}	Cd: 2.47% Co: 2.09% Ni: 3.03% at 0.25 ng mL^{-1} (n=3)	99-110%	CASS-2 coastal seawater, SLEW-1 estuarine water	40 µL	n.a.	n.a.	[92]

Cd, Pb	Coastal seawater, river water, (*tap water)	OASIS HLB	FAAS	on-line complex formation with DDTP/ Methanol	Cd: 0.09 µg L^{-1} Pb: 0.9 µg L^{-1}	Cd: 0.3-12.0 µg L^{-1} Pb: 3.1-200 µg L^{-1}	Cd: 2.9% at 4 µg L^{-1} Pb: 2.6% at 20 µg L^{-1}	95-99%	NIST CRM 1643e trace elements in water	12 mL	Cd: 155 Pb: 180	24 h^{-1}	[93]
Cu, Mn, Ni	River- and lake water	Alumina hollow fibre	ICP-OES	pH 8.5 (NH_4NO_3)/ 2.5 mol L^{-1} HCl	Cu: 0.88 ng mL^{-1} Mn: 0.61 ng mL^{-1} Ni: 0.38 ng mL^{-1}	Up to 200 ng mL^{-1}	6.2-7.9% at 10 ng mL^{-1} (n=7)	87-110%	GSBZ50009-88 environmental water	3 mL	10	5 h^{-1}	[94]
V, Cu, Pb, Cr	River- and lake water	modified mesoporous TiO_2	ICP-OES	pH 6.5 (NH_4Cl/ NH_3 H_2O)/ 1 M HNO_3	V: 0.09 µg L^{-1} Cu: 0.23 µg L^{-1} Pb: 50 µg L^{-1} Cr: 0.15µg L^{-1}	0.3-50 µg L-1	V: 1.7% Cu: 3.9% Pb: 4.6% Cr: 2.9% at 5 µg L^{-1} (n=7)	89-107%	GSBZ50009-88 environmental water	6 mL	20	10 h^{-1}	[95]
Co, Cr, Cd, Mn, Zn, Ni	Seawater, river water	DPTH-gel	ICP-MS	pH 8.6 (boric acid/Na tetraborate)/ 2% (m/m) HNO_3	0.004-0.530 µg L^{-1}	DL-60 µg L^{-1}	0.3-4% at double the conc. used for Dl of the analytes (n=5)	93-110%	SLEW-3 estuarine water, NASS-5 seawater, SLRS-4 river water, TMDA-54.4 fortified water	5 mL	2.3-32.9	10 h^{-1}	[96]
V, Cu, Pb, Cd, Hg	Lake- and river water	Chitosan modified ordered mesoporous silica	ICP-OES	pH 6.5 (NH_4Cl/NH_3 H_2O)/ 1 M HCl	V: 0.33 ng mL^{-1} Cu: 0.30 ng mL^{-1} Pb: 0.96 ng mL^{-1} Cd: 0.05 ng mL^{-1} Hg: 0.93 ng mL^{-1}	n.a.	V: 2.8% Cu: 6.7% Pb: 1.8% Cd: 4.0% Hg: 5.3% at 10 ng mL^{-1} (n=7)	>90%	GSBZ50009-88 environmental water sample	6 mL	20	10 h^{-1}	[97]
Cd, Co, Cu, Mn, Ni, Pb, V, Zn	River water	EDTriA-type chitosan	ICP-OES	pH 5 ($AcNH_4$)/ 1.5 M HNO_3	0.002-0.15 ng mL^{-1}	n.a.	< 10%	90-110%	SRLS-4 river water	5 mL	14-35	28 h^{-1}	[26]
Cd, Co, Cu, Mn, Ni, Pb, V, Zn	River water	Glycine-type chitosan	ICP-OES	pH 5 ($AcNH_4$)/ 1.5 M HNO_3	0.004-0.17 ng mL^{-1}	n.a.	< 10%	90-110%	SRLS-4 river water	5 mL	14-106	27 h^{-1}	[19]

Mn, Co, Cu, Zn, Pb	(*CRMs)	Fe-based MNPs-PAA	ICP-MS	pH 9 (AcNH$_4$)/ 1% HNO$_3$	0.04-0.06 µg L^{-1} Cu and Zn: 0.6 µg L^{-1}	0.5-50 µg L^{-1}	4% at 5 µg L^{-1} (n=3)	96-109%	CASS-2 nearshore seawater, (°RSM 2670a trace elements in urine)	20 µL	n.a.	5 min/sample	98
Sb, Hg	Seawater, mineral water (*spiked tap water)	Functionalized magnetic graphene oxide	ICP-OES	pH 3.0 (glycin-HCl)/2% (wt/vol) thiourea in 4% (wt/wt) HNO$_3$	Sb: 1.5 µg L^{-1} Hg: 0.05 µg L^{-1}	Sb: 9.0-5000 µg L^{-1} Hg: 0.2-1000 µg L^{-1}	Sb: 4.5 Hg: 1.6 at 25 µg L^{-1} (n=11)	Sb: 93-117 Hg: 93-105	TMDA 54.4 fortified lake water	16.8 mL	Sb: 9 Hg: 3	13 h^{-1}	99

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Abbreviations:
8-HQ: 8-hydroxyquinoline (8-quinolinol)
cpg: controlled pore glass
DPTH gel: 1-(di-2-pyridyl)methylene thiocarbonohydrazide bonded to silica gel
EDTriA-type chitosan: ethylenediamine N,N,N'-triacetate-type chitosan
IDA: iminodiacetate
MNPs-PAA: magnetic nanoparticles with polyacrylic acid
MWCNTs: multi-walled carbon nanotubes
OASIS HLB: poly(divinylbenzene-N-vinylpyrrolidone) co-polymeric beads
PCX: polymeric cation exchanger
PMMA: poly(methyl methacrylate)
S-CS-MWCNTs: Schiff base-chitosan grafted multiwalled carbon nanotubes
SCX: strong cation exchanger

Table 2: Single-element on-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the determination of the total metal concentration of transition metals and metalloids in natural waters. (All units as in the original publication)

Analyte	**Matrix**	**Solid phase**	**Detection technique**	**Sample treatment/Elution**	**Figures of merit**				**Validation**	**Sample volume**	**Enrichment factor**	**Sample throughput**	**Ref**
					DL	**Linear range**	**Precision**	**Relative Recovery**					
Co	Underground water, (*tap water)	Fe_3O_4 nanoparticles	ETAAS	None/ Ethanol	6 ng L^{-1}	0.01-5µg L^{-1}	2.8% at 0.5 µg L^{-1} (n=11)	96-99%	(°GBW 07303 stream sediment, GBW10017 powdered milk)	2 mL	30	18 h^{-1}	100
Co	(*Only CRM)	*L*-tyrosine functionalized WCNTs	FAAS	pH 7.0 ($AcNH_4$)/ 10% (v/v) HNO_3	50 ng L^{-1}	DL-250 µg L^{-1}	2.7-3.4% at 10 µg L^{-1} (n=10)	102%	QC METAL LL2 metals in natural waters	10 mL	180	>600 s/sample	101
Cu	Coastal and estuarine water	TMA	ICP-OES	pH 5.5 ($AcNH_4$)/ 2% (v/v) HNO_3	0.4 µg L^{-1}	0-50 µg L^{-1}	3.2% at 5.0 µg L^{-1}	91-103%	(°CRM22 fish otoliths, SRM 1400 bone ash)	10 mL	5	n.a.	102
As	(*Cave water, tap water)	Live HeLa cells immobilized on Sephadex G-50 beads	GFAAS	pH 3.0 (phosphate buffer)/ 2 M HNO_3	0.05 µg L^{-1}	0.15-2.5 µg L^{-1}	1.7% at 1.25 µg L^{-1} and 3.4% 0.5 µg L^{-1} (n=9)	97-98%	SRLS-4 river water	450 µL	11	13 h^{-1}	103
Cd	Ground-, river- and coastal seawater	SiMAG-Octadecyl	ETAAS	pH 2.0±0.2 (HNO_3); on-line addition of DDTC/ IBMK	3 ng L^{-1}	9-350 ng L^{-1}	3.9% at 50 ng L^{-1} (n=11)	94-98%	NIST CRM 1643e trace elements in water	5 mL	19	8 h^{-1}	17
Cd	Mineral water, (*tap water, synthetic seawater)	3-MPTMS-MWCNTs	FAAS	pH 7.5 (phosphate buffer)/ 1 M HCl	0.15 µg L^{-1}	1-60 µg L^{-1}	4.04% at 1 µg L^{-1} and 2.34% at 55.0 µg L^{-1} (n=10)	92-110%	NIST SRM 1643e trace elements in natural waters, (°NIST SRM 1573a tomato leaves)	20 mL	31.5	14 h^{-1}	104

Cd	Spring water, rain water, snow water	Fe-based MWNTs	ETAAS	pH 6.0 (NaOH)/ 0.002 mol L^{-1} H_3PO_4 and 0.1 mol L^{-1} HN_4NO_3	1.3 ng L^{-1}	0.003-0.2 µg L^{-1}	2.2% at 0.1 µg L^{-1} (n=11)	97-105%	GBW08608 trace elements in water, (°GBW07404 soil)	1000 µL	31.2	12 h^{-1}	105
Cd	Spring water, rain water, seawater, (*tap water)	*S. cerevisiae* cell-loaded cytopore® beads	GFAAS	pH 6-7 (0.1 mol L^{-1} NaOH)/ 0.8 mol L^{-1} HNO_3	1.1 ng L^{-1}	5-100 ng L^{-1}	3.3% at 50 ng L^{-1} (n=11)	69-102%	(°GBW 07404 soil)	1 mL	30	20 h^{-1}	106
Cd	Mineral water, lake water, (*tap water)	Histidine functionalized MWCNTs	FAAS	pH 8.50 (ammoniacal buffer)/ 0.8 M HNO_3	0.20 µg L^{-1}	2-140 µg L^{-1}	3.11% at 40 µg L^{-1} (n=10)	96-104%	(°Tort 2 Lobster Hepato-pancreas)	15 mL	17.7	16 h^{-1}	107
Cd	River water, spring water, ground water, (*tap water)	Salen/Cd(II) complex imprinted polymer	FAAS	pH 6.8 (Britton-Robinson buffer)/ 1% HNO_3	0.11 µg L^{-1}	1-10 µg L^{-1}	6.3% at 1 µg L^{-1} (n=5)	92-107%	ES-H-2 ground water, (°EU-H-3 waste water)	16 mL	117	20 h^{-1}	108
Pb	Mineral water, (*tap water, synthetic seawater amongst other samples)	IIHC	TS-FFAAS	pH 6.46 (phosphate buffer)/ 0.5 mol L^{-1} HNO_3	0.75 µg L^{-1}	2.5-65.0 µg L^{-1}	5% at 10.0 µg L^{-1} and 3.6% at 60.0 µg L^{-1} (n=10)	93-110%	(°DORM-3 fish protein, MESS-3 and PACS-2 marine sediments)	20 mL	128	n.a.	109
Pb	Ground water, river water, coastal seawater	PEEK	FAAS	On-line complex formation with 0.5% (m/v) DDPA in water/ IBMK	0.32 µg L^{-1}	3.6-300 µg L^{-1}	2.2% at 50 µg L^{-1} (n=11)	95-97%	NIST CRM 1643e trace elements in water, (°IAEA-433 marine sediment, BCR 278-R trace elements in mussel tissue)	22 mL	110	20 h^{-1}	110
Pb	Seawater, (*tap water)	Filamentous fungal biomass-loaded TiO_2 NPs	FAAS	pH 4.0 (HNO_3)/ 1 M HCl	0.78 µg L^{-1}	2.5-10 µg L^{-1}	9.1-1.8% at 2.5-100 µg L^{-1} (n=5)	96-104%	NASS-5 seawater	250 mL	868	n.a.	111

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Abbreviations:

IIHC: ion imprinted polyvinylimidazole-silica hybrid copolymer
MPTMS: mercaptopropyltrimethoxysilane
MWCNTs: multi-walled carbon nanotubes
NP: nanoparticle
PEEK: polyether ether ketone
SiMAG: silica maghemite
TMA: 2-thiozylmethycrylamide
WCNT: wall coated nanotubes

Table 3: On-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the determination of the total metal concentration of rare earth elements, precious metals and actinides in natural waters. (All units as in the original publication)

Analyte	Matrix	Solid phase	Detection technique	Sample treatment /Elution	Figures of merit				Validation	Sample volume	Enrichment factor	Sample throughput	Ref
					DL	Linear range	Precision	Relative Recovery					
Rare earth elements													
REEs (incl. Y)	Seawater	Toyopearl AF Chelate 650M®	ICP-MS	pH 5.5±0.2 ($AcNH_4$)/ 0.8 M HNO_3	0.002 ng kg^{-1} (Tm)-0.078 ng kg^{-1} (Ce)	Up to 200 ng kg^{-1}; Tm: 100 ng kg^{-1}	Y6% (n=5)	93-106%	CASS-4, SLEW-3 coastal seawaters	6 mL	n.a.	11 h^{-1}	[112]
La, Ce, Eu, Dy, Yb	Lake water, river water, seawater	GO-TiO_2	ICP-OES	pH 5 / 1 M HNO_3	0.13-2.64 ng mL^{-1}	0.5-1000 ng mL^{-1}	3.2-8.6% at 10 ng mL^{-1} (n=7)	> 90%	(°GBW07301a stream sediment)	7 mL	10	12 h^{-1}	[31]
REEs	Seawater	SDCC (Nobias PB 1 M)	ICP-MS	pH 6 ($AcNH_4$)/ 2 M HNO_3	0.00008-0.04 pg mL^{-1}	n.a.	< 3.3% for seawater (n=4)	97-100%	Previous results	50 mL	n.a.	n.a.	[29]
REEs (incl. Y)	Seawater	Nobias PA 1	ICP-MS	pH 6 ($AcNH_4$)/ 1.5 M HNO_3 + 0.4% acetic acid	1-36 ppq	0.1-10 ppt	< 15-23% for 2000 m seawater sample (n=50)	94-102%	NASS-5 seawater, (°VIDAC18 Portuguese mineral water (1:10 diluted))	7 mL	15	15 min/sample	[30]
REEs	Lake water	SDCC (Nobias PB 1 M) and InterSEP ME1	ICP-SFMS	pH 5 ($AcNH_4$)/ 2 M HNO_3	0.013-0.15 pg mL^{-1}	n.a.	1.03%	96-104%	NMIJ 7201-1 river water	10 mL	n.a.	3 min/sample	[28]
REEs (incl. Sc and Y)	River water	EDTriA-type chitosan	ICP-OES	pH 5 ($AcNH_4$)/ 2 M HNO_3	0.002-0.095 ng mL^{-1}	n.a.	< 10% at 1 ng mL^{-1}	> 95%	SRLS-4 river water	20 mL	83-120	12 h^{-1}	[26]
REEs (incl. Sc and Y)	River water	Chitosan based chelating resin	ICP-OES	pH 5 ($AcNH_4$)/ 1.5 M HNO_3	0.002-0.25 ng mL^{-1}	n.a.	< 10%	90-110%	SRLS-4 river water	20 mL	21-102	11 h^{-1}	[19]
REEs	Coastal seawater	SDCC (PAPC)	ICP-SFMS	pH 5 ($AcNH_4$)/ 2 M HNO_3	0.005 -0.09 pg mL^{-1}	n.a.	<10%	93-99%	NASS-5 seawater	10 mL	9.6	6 min/sample	[27]

Precious metals													
Ag, Au, Ir, Os, Pd, Pt	Seawater, mineral water (*spiked tap water)	Functionalized magnetic graphene oxide	ICP-OES	pH 3.0 (glycin-HCl)/2% (wt/vol) thiourea in 4% (wt/wt) HNO_3	Ag: 0.5 µg L^{-1} Au: 0.6 µg L^{-1} Ir: 0.2 µg L^{-1} Os: 1.2 µg L^{-1} Pd: 2.6 µg L^{-1} Pt: 0.4 µg L^{-1}	Ag: 3.0-5000 µg L^{-1} Au: 4.8-3500 µg L^{-1} Ir: 6.5-400 µg L^{-1} Os: 7.7-400 µg L^{-1} Pd: 8.3-5000 µg L^{-1} Pt:2.8-5000 µg L^{-1}	Ag: 3.2% Au: 2.6% Ir: 3.1% Os: 3.8% Pd: 4.0% Pt: 3.8% at 25 µg L^{-1} (n=11)	Ag: 90-106% Au: 90-104% Ir: 93-113% Os: 90-104% Pd: 95-106% Pt: 86-106%	TMDA 54.4 fortified lake water	16.8 mL	Ag: 22 Au: 29 Ir: 9 Os: 33 Pd: 6 Pt: 28	13 h^{-1}	99
Ag	Estuarine - and seawater	Dowex AG1X	ICP-MS	None/ 2.5 M HNO_3	0.06 ng kg^{-1}	LD-1000 ng kg^{-1}	< 3% (n=5)	99-102%	SLEW-3 estuarine water, CASS-4 coastal seawater	7.5 mL	n.a.	7 h^{-1}	[40]
Pd	Groundwater, lake water, seawater	Polyaniline	ICP-OES, ICP-MS	No acidification/ 3% HCl + 0.06% thiourea	0.0004 ng mL^{-1}	100 (ICP-OES)/0.22 (ICP-MS) ng mL^{-1}	< 3%	> 99%	Standard additions	250 mL	125	n.a.	[37]
Actinides													
Th, U	Seawater, well water, mineral water, fresh water, (*tap water)	UTEVA	ICP-MS	Acidified to 3M HNO_3/ 0.05 M $H_2C_2O_4$/0.01 M HNO_3	0.4 ng L^{-1}, 2.8 ng L^{-1}	0-200 µg L^{-1}	1.7% at 2.5 ng L^{-1} (n=5)	> 90%	(°BCR-320R channel sediment)	8 mL	13	9 h^{-1}	[53]

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Note: Only additional sample treatment other than filtration and preservation with acid is mentioned here.
Abbreviations:
3-MPTMS: 3-mercaptopropyltrimethoxysilane
AC-TBAH: tetrabutylammonium hydroxide-modified activated carbon
AF-MMPs: amine-functionalized magnetite microspheres
APS: 3-aminopropyltriethoxysilane

Bromo-PADAP: 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol
CNTs: carbon nanotubes
CTAB: cetyltrimethylammonium bromide
DDTC: diethyldithiocarbamate
DPTH gel: 1-(di-2-pyridyl)methylene thiocarbonohydrazide bonded to silica gel
EDTriA-type chitosan: ethylenediamine N,N,N'-triacetate-type chitosan
GO-TiO_2: graphene oxide titanium dioxide
IIHC: ion imprinted polyvinylimidazol-silica hybrid copolymer
MNPs-PAA: magnetic nanoparticles with polyacrylic acid
MWCNTs: multi-walled carbon nanotubes
OASIS HLB: poly(divinylbenzene-N-vinylpyrrolidone) co-polymeric beads
PAPC: divinylbenzene-methacrylate copolymeric resin containing polyaminopolycarboxylic acid groups = ethylendiaminetriacetic acid and iminodiacetic acid groups
PDDA: poly(diallyldimethylammonium chloride
PMMA: poly(methyl methacrylate)
PSTH-cpg: 1.5-bis(2-pyridyl)3-sulphophenyl methylene thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass
Salen/Cd(II) complex: (cadmium(II) 2,2'-{ethane-1,2-diylbis[nitrilo(E)methylylidene]} diphenolate)
S-CS-MWCNTs: Schiff base-chitosan grafted multiwalled carbon nanotubes

Table 4: On-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the speciation of metals in natural waters. (All units as in the original publication)

Analyte	Matrix	Solid phase	Sample treatment/ Elution	Detection technique	Figures of merit				Validation	Sample volume	Enrichment factor	Sample throughput	Ref
					DL	**Linear range**	**Precision**	**Relative Recovery**					
Fe(II)/ Fe(III)	Ground water, River water, seawater (*tap water)	Non-functionalized acrylate resin	Fe(II): pH 5 (evacuation by air); Fe(III): pH 4 (evacuation by water)	ICP-MS	Fe(II): 1 ng L^{-1} Fe(III): 1-2 ng L^{-1}	5-5000 ng L^{-1}	n.a.	Total Fe: 97-115% Fe(III): 89-110% Fe(II): 89-108%	SLEW-3, 1640a, 1643e trace metals in natural waters	1 mL	Fe(III) pH 4: 10.1 Fe (II)pH 5: 13.3 Fe(III) pH 5: 20.9	7.5 h^{-1}	[113]
V(V)/ V(IV)	Seawater, fresh water	CTAB-modified alkyl silica	pH 2.5 and 6.0/ 1 M HNO$_3$	ICP-OES	V(V): 0.03 µg L^{-1}	0.1-500 µg L^{-1}	V(V): 4.3% total V: 4.0% at 5 µg L^{-1} (n=9)	>90%	GSBZ50029-94 environmental water	3 mL	27.9	24 h^{-1}	[62]
Cr(III)/ Cr(VI)	Seawater (surface coastal)	Amberlite IRA 910, DPTH-gel	pH 5.5 (NaAc)/ 2 M HNO$_3$	ICP-MS	0.03 µg L^{-1}/ 0.009 µg L^{-1}	DL-60 µg L^{-1}	2.6%/ 3.2% at 0.3 µg L^{-1} (n=10)	98-113%	SLEW-3, LGC6016 estuarine waters, TMDA-54.4 fortified lake water (1:100)	4 mL	2.4/3.7	7.5 h^{-1}	[114]
Cr(VI)	Snow water, spring water, river water	PDDA-MWNTs	pH 6/ 0.1 M ammonium nitrate	ETAAS	0.016 µg L^{-1}	0.05-1.5 µg L^{-1}	3.9% at 0.5 µg L^{-1} (n=11)	100%	GBW08608 trace elements in water	1000 µL	8.6	9 h^{-1}	[55]
Cr(III)/ Cr(VI)	Mineral water, lake water, (*waste water)	SWCNTs	pH 3 (HNO$_3$, CH$_3$COONa)/ 1.2 M HNO$_3$	ICP-MS	0.01 ng mL^{-1}/ 0.024 ng mL^{-1}	0.1-100 ng mL^{-1}	<2.1%/ 4.0% at 1 ng mL^{-1} (n=9)	>90%	spiking experiments	20 mL	63	n.a.	[115]

Cr(VI)	Mineral water, river water (*effluent water)	Functionalized meso-porous silica (APS)	pH 2 (HCl)/ 0.1 M $NH_2OH{\cdot}HCl$ in 1 M HCl	ETAAS	1.2 ng L^{-1}	n.a.	2.5 % at 0.50 µg L^{-1} (n=10)	100%	Recovery studies; total conc.: SRM 1643e trace elements in water	2 mL	27	21 h^{-1}	54
Cr(III)/ Cr(VI)	Lake water, mineral water (*tap water)	Mesoporous Al_2O_3	pH 4.0 (NH_3 H_2O/HNO_3)/ 0.01 M NaOH	ICP-MS	3.4 ng L^{-1}/ 74 ng L^{-1}	n.a.	2.8%/ 3.9% at 1 ng mL^{-1} (n=7)	>90%	GSBZ50027-94, GSBZ50004-88 environmental waters	0.5 mL	5	8 h^{-1}	59
Cr(III)/ Cr(VI)	River water (* tap water)	*C. Vulgaris*/ 717 anion exchanger	pH 6/ 0.04 M/1.0 M HNO_3	ETAAS	0.02 µg L^{-1}/ 0.03 µg L^{-1}	0.1-2.5 µg L^{-1}/ 0.12-2.0 µg L^{-1}	1.9%/ 2.5% at 1.0 µg L^{-1} (n=11)	100%/99 %	GBW08608 trace elements in water	600 µL	10.5/ 11.6	n.a.	56
As(III)/ As(V)	Lake water, mineral water, (*tap water)	Mesoporous Al_2O_3	pH 4.0 (NH_3 H_2O/HNO_3)/ 0.01 M NaOH	ICP-MS	0.7 ng L^{-1}/ 18 ng L^{-1}	n.a.	3.1%/ 4.0% at 1 ng mL^{-1} (n=7)	>90%	GSBZ50027-94, GSBZ50004-88 environmental waters	0.5 mL	5	8 h^{-1}	59
As(III)/ As(V)	River water, lake water, well water, rain water	(CTAB)-modified alkyl silica sorbent	None/ 1 M HNO_3	ICP-OES	As(V): 0.15 µg L^{-1}	0.5-1000 µg L^{-1}	As(V): 4.0% at 5.0 µg L^{-1} (n=9)	n.a.	BW3209 (0602), BW3210 (0602), GSBZ 50031-94 (203706) environmental waters	3 mL	26.7	24 h^{-1}	116
Se(IV)/ Se(VI)	River water, lake water, well water, rain water	(CTAB)-modified alkyl silica sorbent	None/1 M HNO_3	ICP-OES	Se(VI): 0.10 µg L^{-1}	0.5-1000 µg L^{-1}	Se(VI): 3.6% at 5 µg L^{-1} (n=9)	n.a.	BW3209 (0602), BW3210 (0602), GSBZ 50031-94 (203706) environmental waters	3 mL	27.6	24 h^{-1}	116
Se(IV)/ Se(VI), SeCys/ Se-Met	Lake water, (*biological samples)	Nanometre sized Al_2O_3/ mesoporous TiO_2	pH 3.5/pH 6/ 0.2 M NaOH	ICP-MS	45-210 ng L^{-1}	n.a.	7.0-9.7% at 0.8 ng mL^{-1} (n=7), 3.6-5.8% at 5 ng mL^{-1} (n=7)	n.a.		4 mL	1-5	5 h^{-1}	61

*Matrices in brackets indicated with a * are not within the scope of this review.*
n.a.: not available.

Note: Only additional sample treatment other than filtration and preservation with acid is mentioned here.
Abbreviations:
3-MPTMS: 3-mercaptopropyltrimethoxysilane
AC-TBAH: tetrabutylammonium hydroxide-modified activated carbon

AF-MMPs: Amine-functionalized magnetite microspheres
APS: 3-aminopropyltriethoxy silane
CTAB: cetyltrimethylammonium bromide
DDTC: diethyldithiocarbamate
DPTH-gel: 1-(di-2-pyridyl)methylene thiocarbonohydrazide bonded to silica gel
EDTriA-type chitosan: ethylenediamine N,N,N'-triacetate-type chitosan
GO-TiO_2: Graphene-oxide-titanium dioxide
MWCNTs: multi-walled carbon nanotubes
PAPC: divinylbenzene-methacrylate copolymeric resin containing polyaminopolycarboxylic acid groups = ethylendiaminetriacetic acid and iminodiacetic acid groups
PDDA: poly(diallyldimethylammonium) chloride
PMMA: poly(methyl)-methacrylate
PSTH-cpg: 1.5-bis(2-pyridyl)3-sulphophenyl methylene thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass
S-CS-MWCNTs: Schiff base-chitosan-grafted multiwalled carbon nanotubes
SSDC: syringe driven chelating column (packed with divinylbenzene-methacrylate co-polymeric resin containing polyaminopolycarboxylic acid groups (PAPC) = ethylendiaminetriacetic acid and iminodiacetic acid groups
SWCNTs: micro-column packed single-walled carbon nanotubes
TAR: 4-(2-thiazolylazo)resorcinol
TMA: 2-thiozylmethycrylamide
UTEVA: Uranium and TEtraValent Actinides - diamyl amylphosphonate (DAAP) functionalized

Table 5: Methods employing cold vapour generation (CVG) and hydride generation (HG) techniques for the matrix separation and preconcentration of metals in natural waters. (All units as in the original publication)

Analyte	**Matrix**	**Solid phase**	**Detection technique**	**Sample treatment/ Elution/Reduction**	**Figures of merit**				**Validation**	**Sample volume**	**Enrichment factor**	**Sample through-put**	**Ref**
					DL	**Linear range**	**Precision**	**Relative Recovery**					
Hg	Natural water samples	Dithizone chelate	AFS	Sample pH: 4.0; Reduction: 1.5% (m/v) $NaBH_4$ in 0.5% (w/v) NaOH; Elution: 1.5 mol L^{-1} HCl	0.02 µg L^{-1}	0.06-3.0 µg L^{-1}	5.2% (n=7) at 0.5 µg L^{-1}	90-105%	Standard addition/ recovery experiments	50 mL	29	5 h^{-1}	[117]
Pt, Pd, Os, Ir, Rh, Ag, Au	Spiked seawater (*tap water, environmental samples)	DPTH-MNPs	ICP-OES	Water samples: pH 1 (HCl); (*acid digests: pH 0.9 (NaOH)/ 2.5% thiourea (w/v) in 6% (w/w) HCl/ 2.1% (w/v) $NaBH_4$ in 0.1% (w/v) NaOH)	Pd: 1.5 µg L^{-1} Ag: 0.03 µg L^{-1} Os:0.65 µg L^{-1} Au: 0.62 µg L-1 Ir: 0.57 µg L^{-1} Pt: 0.63 µg L^{-1} Rh: 100 µg L^{-1}	n.a.	2.6-8.5% at 0.74-14.7 µg L^{-1}	92-108%	TMDA 54.4 fortified lake water, SRM 1643e trace elements in fresh water (°NIST 2557 autocatalyst)	12 mL	Pd: 20 Ag: 206 Os: 9 Au: 18 Ir: 17 Pt: 144 Rh: 3	17 h^{-1}	[72]
Sb, Bi, Sn, Hg	Seawater, river water	DPTH-silica gel	ETAAS	pH 2.2 (glycine/HCl)/ Sb, Bi, Sn: 3.1% HCl, Hg: 4.6% thiourea/ 0.6% (w/v) $NaBH_4$ in 0.1% (w/v) NaOH	Sb: 0.009 µg L^{-1} Bi: 0.001 µg L^{-1} Sn: 0.18 µg L^{-1} Hg: 0.17 µg L^{-1}	0.025-2.5 µg L^{-1}	1.9-2.4% at 1 µg L^{-1} (n=11)	91-103%	TM 24.3, TMDA 54.4 fortified lake waters	3 mL	Sb: 4 Bi: 18 Sn: 7 Hg: 9	7.5 h^{-1}	[69]
Pb, Cd, Hg	Natural waters including seawater	DPTH-silica gel	ICP-MS	pH 5.0 (acetic acid/sodium acetate)/ 1.5% (w/w) thiourea in 1.5% (w/w) HNO_3/ Pb: 1.25% (w/v) $NaBH_4$ + 3% (w/v) $K_3Fe(CN)_6$; Cd and Hg: 1.25% (w/v) $NaBH_4$ in 0.1% (w/v) NaOH	Pb: 9 ng L^{-1} Cd: 17 ng L^{-1} Hg: 12 ng L^{-1}	DL-30.0 µg L^{-1}	2.5-2.9% at 0.5 µg L^{-1} (n=9)	985-105%	TMDA-54.4 fortified lake water, LGC6016 estuary water, CASS-5 seawater	5.4 mL	Pb: 16.4 Cd: 25.1 Hg:27.3	10.4 h^{-1}	[70]
Sb, Bi, Sn	Seawater	DPTH-silica gel	ICP-MS	pH 3.5 (0.75% cysteine added)/ 4% HNO_3/ 0.5% $NaBH_4$ in 0.1% NaOH	Sb: 0.01 µg L^{-1} Bi: 0.002 µg L^{-1} Sn: 0.142 µg L^{-1}	DL-60.0 µg L^{-1}	1.1-1.5% (n=10)	97-108%	Diluted TMDA-54.5, TM-24.3 natural waters	4.8 mL	Sb: 7.0 Bi: 8.6 Sn: 2.5	12 h^{-1}	[118]

As	River water, tap water, mineral water, (*waste water)	none	AAS	0.01 mol L^{-1} HCl/ 4.0 mol L^{-1} HCl/ 1.0% (m/v)NaBH4 in 0.1% (m/v) NaOH	0.05 µg L^{-1}	0.15-6.0 µg L^{-1}	3.2% at 2.0 µg L^{-1} (n=10)	96-102%	Reference method based on on-line FI-HG-AAS (FIAS 400)	3 mL	n.a.	9 h^{-1}	[66]
Sb	River- and seawater	DPTH-silica gel	ETAAS	pH 5.0 (acetic acid/ sodium acetate)/ 2.0% thiourea in 4.0% HNO_3/ 0.5% (w/v) $NaBH_4$ in 0.1% (w/v) NaOH	1 ng L^{-1}	0.025-2.5 µg L^{-1}	0.9% at 1 µg L^{-1} (n=11)	98-108%	TMDA 54.4 fortified lake water, SLRS-5 estuarine water	5 mL	22	20 h^{-1}	[119]
Cd	Seawater, ground water	none	AAS	2 mol L^{-1} HCl/ 0.75% (m/v) thiourea in 0.05 mol L^{-1} HCl/ 6% (w/v) $NaBH_4$ in 0.5% (m/v) NaOH	5.8 ng L^{-1}	19.3 ng L^{-1}-5 µg L^{-1}	1.4-2.9% at 0.25 and 2.5 µg L-1	94-101%	CASS-4 seawater	2 mL	n.a.	87 h^{-1}	[67]
Pb	Seawater, river water	PSTH-cpg	ETAAS	pH 6.0 (NaH_2PO_4/Na_2HPO_4)/ 1% (v/v) HCl/ 2.6% (m/v) $NaBH_4$ + 3% (m/v) ($K_3Fe(CN)_6$) in 0.5% (m/v) NaOH	3.0 ng L^{-1}	n.a.	2.5% at 50 ng L^{-1} (n=10)	97-105%	TMDA 54.4 fortified lake water, LG6016 estuarine water	6.4 mL	20	18 h^{-1}	[71]
Hg	River water	none	ICP-MS, MC-ICP-MS	stabilization ($K_2Cr_2O_7$), isotope dilution/ 0.2% (w/w) $NaBH_4$ in 0.05% (w/w) NaOH	0.25 ng L^{-1}	n.a.	0.6-2.9% for ERM-CA615 (n=3)	n.a.	ERM-CA615 ground water	500 µL	10-50	40 h^{-1}	[68]

*Matrices in brackets indicated with a * are not within the scope of this review.*

Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.

n.a.: not available.

Abbreviations:

cpg: controlled pore glass

DPTH: 1-(di-2-pyridyl)methylene thiocarbonohydrazide

MNP: magnetic nanoparticle

PSTH: 1.5-bis(2-pyridyl)3-sulphophenyl methylene thiocarbonohydrazide

Table 6: Methods employing cold vapour- and hydride generation techniques for the speciation of metals in natural waters. (All units as in the original publication)

Analyte	Matrix	Solid phase	Detection technique	Sample treatment/ elution/reduction	Figures of merit				Validation	Sample volume	Enrichment factor	Sample throughput	Ref
					LOD	Linear range	Precision	Relative Recovery					
As(III)/ As(V)/ total iAs	Groundwater	Cl-SAX	AAS	None - neutral sample/ As(III): 3.5 mol L^{-1} HCl/ 0.35% (m/v) NaBH$_4$ in 0.025% NaOH	As(III): 0.5 µg L^{-1} iAs: 0.6 µg L^{-1}	1.7-25 g L^{-1}	<2% at 5 µg L^{-1} (n=3)	98-106%	NIST 1643e trace elements in water	500 µL	n.a.	60 h^{-1}	[75]
iHg/ MeHg	Lake water, ground water, seawater, (*tap water, fish tissue)	PANI	ICP-MS	None - neutral sample/ MeHg: 0.5% HCl, iHg: 2% HCl + 0.02% thiourea/ 1% NaBH$_4$	25.2 pg mL^{-1}/ 32.4 pg mL^{-1}	0.1-10 ng mL^{-1}	2%/2.5% at 1 ng mL^{-1} (n=10)	96-102%	(°ERM-CE463, ERM-CE464, IAEA 350 fish tissues)	100 µL	iHg:240; MeHg:120	10 h^{-1}	[73]
iHg/ MeHg	Seawater	DPTH-silica gel	ICP-MS	pH 5.0 (acetic acid/sodium acetate)/ MeHg: 0.2% HCl, iHg: 0.5% HCl + 0.1% thiourea/ 0.25% (w/v) NaBH$_4$ in 0.5% (w/v) NaOH	MeHg: 0.011 µg L^{-1} iHg: 0.024 µg L^{-1}	DL-70 µg L^{-1}	MeHg: 2.8% iHg: 2.6% at 2 µg L^{-1} (n=10)	92-107%	LGC 6016 estuarine water, (°SRM 2976 mussel tissue)	4.6 mL	MeHg: 4.7 iHg: 11	7.1 h^{-1}	[74]
Sb(III)/ Sb(V)	Seawater, river water, lake water	PSTH-cpg/ Amberlite IRA-910	ICP-MS	pH 8.4 (boric acid/borax)/ 0.04% thiourea in 5% HNO$_3$/ 0.2% (m/v) NaBH$_4$ in 0.05% NaOH	Sb(III): 0.05-80 µg L^{-1} Sb(V): 0.05-80 µg L^{-1}	Sb(III): 0.013 µg L^{-1} Sb(V): 0.021 µg L^{-1}	Sb(III): 4.6% Sb(V): 3.0% (n=10)	97-105%	SLRS-5 river water, TMDA-54.4 lake water	2.2 mL	Sb(III): 5.5 Sb(V): 3.9	9 h^{-1}	[65]

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Note: Only additional sample treatment other than filtration and preservation with acid is mentioned here.
Abbreviations:
DMA: dimethylarsinic acid
PANI: polyaniline
DPTH-silica gel: 1,5-bis(di-2-pyridyl)methylene thiocarbonohydrazide bonded to silica gel
MNPs: magnetic nanoparticles
PSTH-cpg: [1,5-bis(2-pyridyl)-3-sulfonphenyl methylene]thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass

Table 7: Methods employing liquid-liquid-micro-extraction for the matrix separation and preconcentration of metals in natural waters. (All units as in the original publication)

Analyte	**Matrix**	**Detection technique**	**Sample treatment**	**Disperser/complexing solution**	**Figures of merit**				**Validation**	**Sample volume**	**Enrichment factor**	**Sample throughput**	**Ref**
					DL	**Linear range**	**Precision**	**Relative Recovery**					
LLME													
Pb	Coastal water, ditch water	FAAS	pH 2 (HNO_3)	DDPA/chloroform	1.5 µg L^{-1}	5.0-280 µg L^{-1}	2.7% at 40.0 µg L^{-1} (n=9)	95-102%	CRM 1643e trace elements in natural water, (°BCR 278-R mussel tissue)	6 mL	130	13 h^{-1}	77
Pb	Lake water, coastal water	FAAS	pH 2 (HNO_3)	APDC/chloroform	1.8 µg L^{-1}	6.0-300 µg L^{-1}	2.9% at 50 µg L^{-1} (n=10)	94-98%	CRM 1643e trace elements in natural water, (°BCR 278-R mussel tissue)	10 mL	125	7 h^{-1}	83
Tl	River water, lake water, coastal seawater (*tap water)	FAAS	pH 2.0 (HNO_3)	Methanol containing 0.6% (v/v) ([Hmim][PF_6]; Elution: MIBK; Support: PUF micro column	0.86 µg L^{-1}	2.8-120 µg L^{-1}	2.7% at 20 µg L^{-1}	94-98%	SRM 1643e trace elements in natural water, (°SRM 2704 river sediment)	15 mL	290	16 h^{-1}	87
U	Ground water, seawater	ICP-OES, ICP-MS	pH 1	APDC/CTAB; extraction into chloroform, back extraction into HNO_3	ICP-OES: 2.0 µg L^{-1} ICP-MS: 30 ng L^{-1}	ICP-OES: 5-200 µg L^{-1}; ICP-MS: 50-5000 ng L^{-1}	ICP-OES: 5% ICP-MS: 4% (n=6)	90-105% at 10 and 5 µg L^{-1}	BCR 403 North Seawater, laser fluorimetry	10 mL	11-25	n.a.	79
Ag	River water, seawater, (*waste water)	FAAS	0.1 mol L^{-1} HNO_3	DDTC in 0.3% (m/v) methanol; Elution: MIBK; Support: PEEK-microcolumn	0.15 µg L^{-1}	0.40-20 µg L^{-1}	2.9% at 5 µg L^{-1} (n=10)	96-99%	NIST CRM 1643e trace elements in natural water	16.2	186	12 h^{-1}	86
Pb, Cd	Natural waters (river water, coastal seawater)	ETAAS	None	Methanol containing 2% (v/v) xylene a + 0.2% (m/v) APDC; Elution: MIBK;	Pb: 10 ng L^{-1} Cd: 2 ng L^{-1}	Pb: 0.04-1.5 µg L^{-1} Cd: 0.006-0.150 µg L^{-1}	Pb: 3.8% at 0.5 µg L^{-1} Cd: 4.1% at 0.03 µg L^{-1}	94-98% (n=3)	NIST CRM 1643e trace elements in natural water	8.1 mL	Pb: 80 Cd: 34	10 h^{-1}	85

				Support: PTFE-tubing									
V	River water, (*tap water)	ETAAS	pH 4.0 (acetic acid/ acetate)	(5-Br-PADAP) + ([C4mim][PF6])RTIL; Elution: 10% (v/v) HNO_3 (in acetone); Support: Florisil	4.8 ng L^{-1}	DL-15 µg L^{-1}	4.1% at 5 µg L^{-1} (n=10)	96-103% (n=6)	NIST CRM 1643e trace elements in natural water	5 mL	n.a.	6 h^{-1}	80
Cd	Seawater, river water	ETAAS	pH 2.0±0.2 (HNO_3)	DDPA/DIBK	0.01 µg L^{-1}	0.03-0.6 µg L^{-1}	3.9% at 0.1 µg L^{-1} (n=9)	94-98%	NIST CRM 1643e trace elements in natural water	15 mL	10	6 h^{-1}	82
Cu, Pb	River water, coastal water	FAAS	pH 1.4 (HNO_3)	Methanol containing 2% (v/v) xylene a + 0.3% (m/v) DDPA; Elution: MIBK; Support: PTFE-micro column	Cu: 0.04 µg L^{-1} Pb: 0.54 µg L^{-1}	0.16-12.0 µg L^{-1}	Cu: 2.1% at 2.0 µg L^{-1} Pb: 1.9% at 30 µg L^{-1} (n=10)	96-100%	NIST CRM 1643e trace elements in natural water	12 mL	Cu: 560 Pb: 265	12 h^{-1}	84
Cr	Spring water, river water, seawater	ETAAS	pH 3.5 (phthalate buffer)	APDC	0.02 µg L^{-1}	0.5-6 µg L^{-1}	7% (n=6)	90-103%	(°CRM 544 lyophilized solution (no real matrix))	2.5 mL	20	n.a.	81

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Note: Only additional sample treatment other than filtration and preservation with acid is mentioned here.
Abbreviations:
APDC: ammonium pyrrolidine dithiocarbamate
([C4mim][PF6])RTIL: 1-butyl-3-methylimidazolium hexafluorosphosphate room temperature ionic liquid
([Hmim][PF6]): 1-hexyl-3-methylimidazolium hexafluorophosphate ionic liquid
(5-Br-PADAP): 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol
CTAB: cetyltrimethyl ammonium bromide
DDPA: ammonium diethyldithiophosphate
DDTC: sodium diethyldithiocarbamate
DIBK: di-isobutyl ketone
MIBK: methyl isobutyl ketone
PUF: polyurethane foam

Figure captions

Figure 1: A conceptual diagram of the combination of on-line FI/SI sample preparation with atomic spectrometric detectors.

Figure 2: A conceptual diagram of the combination of on-line FI/SI sample preparation with atomic spectrometric detectors. Reproduced from [16] (Talanta 133 (2015) 164, authored by Robert Clough, Hagit Sela, Angela Milne, Maeve C. Lohan, Serife Tokalioglu and Paul J. Worsfold), with permission from Elsevier.

Figure 3: FI microcolumn preconcentration/separation system for simultaneous speciation of Se(IV) and Se(VI), selenocysteine and selenomethionine, prior to ICP detection.

Figure 4: Schematic illustration of a sequential injection system for automatic DLPME of trace elements as a front end to ETAAS. Abbreviations: S, sample; MeOH (APDC, xylene), extracting solvent composed of 2.0% (v/v) xylene and 0.2% (m/v) APDC in methanol which acts as dispersant; P, peristaltic pump; SP, syringe pump; MV, multi-position valve; V, head valve; HC, holding coil; C, micro-column containing sorbent; CC, confluence connector; DT, delivery tube; GF, graphite furnace of ETAAS. Reprinted from [85] (A.N. Anthemidis, K.-I.G. Ioannou / Analytica Chimica Acta 668 (2010) 35–40, Copyright (2010)), with permission from Elsevier.

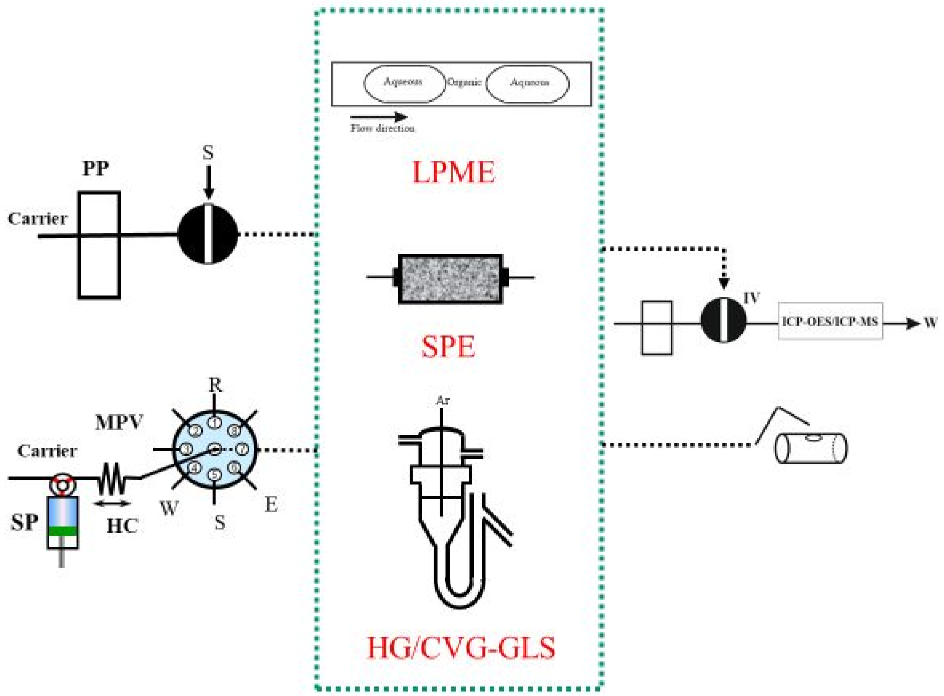
Aqueous
Organic
Aqueous
Flow direction
LPME
SPE
Ar
HG/CVG-GLS
S
PP
Carrier
R
MPV
Carrier
①
②
③
④
⑤
⑥
⑦
⑧
SP
HC
W
S
E
IV
ICP-OES/ICP-MS
W

Fig. 1

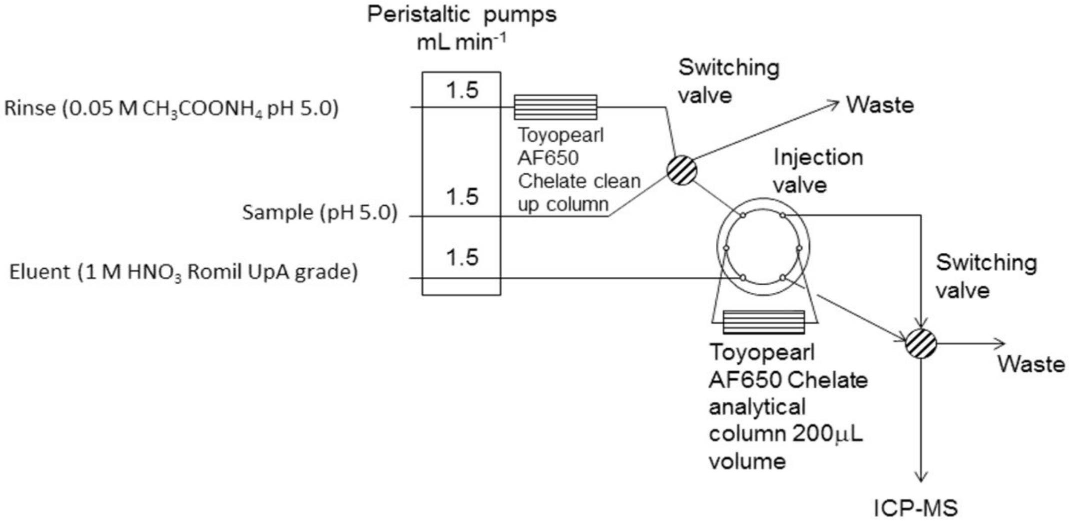
Peristaltic pumps
mL min-1
1.5
1.5
1.5
Rinse (0.05 M CH3COONH4 pH 5.0)
Sample (pH 5.0)
Eluent (1 M HNO3 Romil UpA grade)
Toyopearl AF650 Chelate clean up column
Switching valve
Waste
Injection valve
Switching valve
Waste
Toyopearl AF650 Chelate analytical column 200µL volume
ICP-MS

Fig. 2

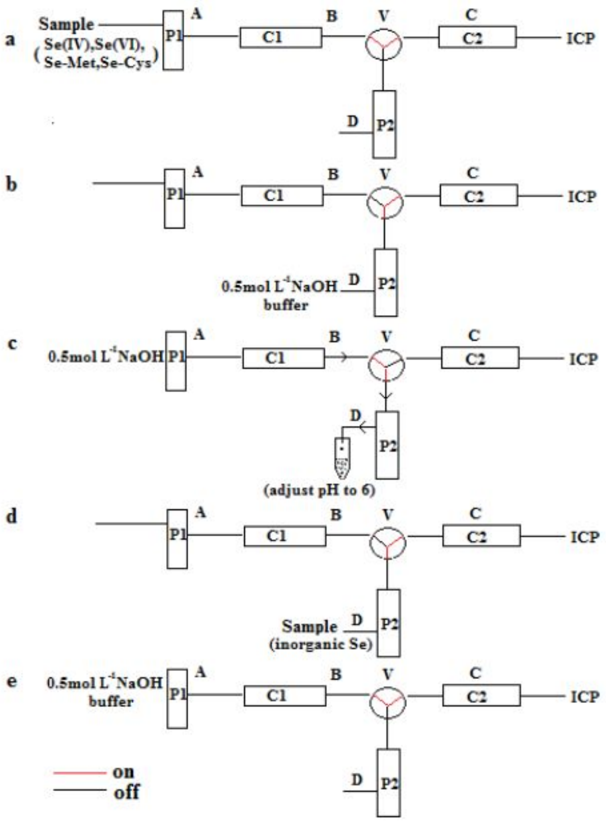
a
Sample
(Se(IV),Se(VI), Se-Met,Se-Cys)
P1
A
C1
B
V
C
C2
ICP
D
P2
b
0.5mol L⁻¹NaOH buffer
c
0.5mol L⁻¹NaOH
(adjust pH to 6)
d
Sample (inorganic Se)
e
0.5mol L⁻¹NaOH buffer
on
off

Fig. 3

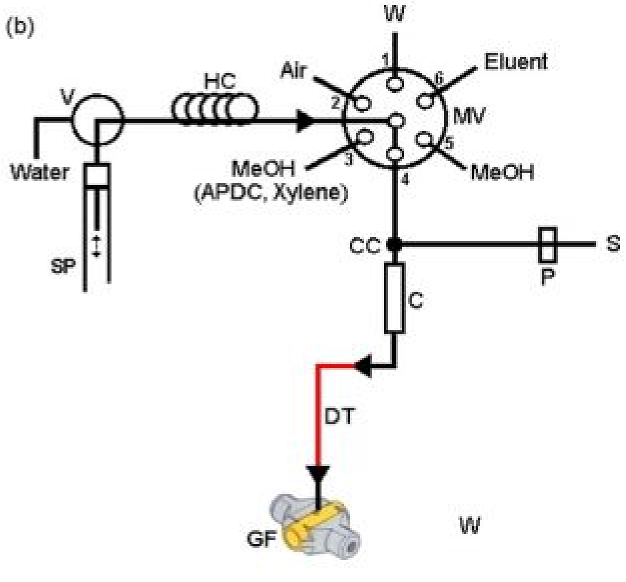
(b)
W
1
Air
Eluent
6
HC
V
2
MV
Water
MeOH
(APDC, Xylene)
3
4
5
MeOH
CC
S
SP
P
C
DT
GF
W

Fig. 4

References

---

[1] J. Gaillardet, J. Viers and B. Dupré, *Treatise on Geochemistry: Second Edition*, Elsevier Inc. 2013, pp. 195-235.

[2] Y. Sohrin and K.W. Bruland, *Trends Anal. Chem.,* 2011, **30**, 1291-1307.

[3] W. H. Schlesinger and E. S. Bernhardt*, Biogeochemistry: An analysis of global change.* Third Edition, Elsevier Inc. 2013.

[4] R. Clough, C. F. Harrington, S. J. Hill, Y. Madrid and J. F. Tyson, *J. Anal. At. Spectrom.,* 2018, **33**, 1103-1149.

[5] B. Buszewksi, W. Piekoszewsky, P. Pomastowski, K. Rafinska, M. Sugajski and T. Kowalkowski, *Recent Advances in Trace Elements*, Wiley Blackwell 2017, pp: 33-60.

[6] S. J. Ussher, E. P. Achterberg and P. J. Worsfold, *Environ. Chem.,* 2004, **1**, 67-80.

[7] P. Lindahl, S. H. Lee, P. Worsfold and M. Keith-Roach, *Mar. Environ. Res.*, 2010, **69**, 73-84.

[8] M. Marcinkowska and D. Baralkiewicz, *Talanta*, 2016, **161**, 177-204.

[9] M. E. Lagerström, M. P. Field, M. Séguret, L. Fischer, S. Hann and R. M. Sherrell, *Mar. Chem.,* 2013, **155**, 71-80.

[10] M. Miró and E. H. Hansen*, Anal. Chim. Acta*, 2013, **782**, 1-11.

[11] P. J. Worsfold, R. Clough, M. C. Lohan, P. Monbet, P. S. Ellis, C. R. Quétel, G. H. Floor and I. D. Mc Kelvie., *Anal. Chim. Acta*, 2013, **803**, 15-40.

[12] A. Leclercq, A. Nonell, J. L. Todolí Torró, C. Bresson, L. Vio, T. Vercouter and F. Chartier, *Anal. Chim. Acta*, 2015, **885**, 33-56.

[13] A. Leclercq, A. Nonell, J. L. Todolí Torró, C. Bresson, L. Vio, T. Vercouter and F. Chartier, *Anal. Chim. Acta*, 2015, **885**, 57-91.

[14] G. R. D. Prabhu and P. L. Urban, *Trends Anal. Chem.,* 2017, **88**, 41–52.

[15] E. H. Hansen and M. Miró, *Flow Injection Analysis-Comprehensive Analytical Chemistry* (S. D. Kolev and I. McKelvie, Eds), Chap. 14, pp. 375-405, Elsevier, The Netherlands, 2008.

[16] R. Clough, H. Sela, A. Milne, M. C. Lohan, S. Tokalioglu and P.J. Worsfold, *Talanta*, 2015, **133**, 162-169.

[17] G. Giakisikli and A. N. Anthemidis, *Talanta*, 2013, **110**, 229-235.

[18] I. Sánchez-Trujillo, E. Vereda-Alonso, A. García de Torres and J.M. Cano-Pavón, *Microchem. J.,* 2012, **101**, 87-94.

[19] R.K. Katarina, M. Oshima and S. Motomizu*, Talanta*, 2009, **79**, 1252-1259.

[20] P. H. Pacheco, P. Smichowski, G. Polla and L. D. Martinez, *Talanta,* 2009, **79**, 249-253.

[21] T. T. Shih, I. H. Hsu, S. N. Chen, P. H. Chen, M. J. Deng, Y. Chen, Y. W. Lin and Y. C. Sun, Analyst, 2015, 140, 600-608.

---

[22] T. T. Shih, C. C. Hsieh, Y. T. Luo, Y. A. Su, P. H. Chen, Y. C. Chuang, Y. C. Sun, *Anal. Chim. Acta*, 2016, **916**, 24-32.

[23] R. Schlitzer, R. F. Anderson, E. M. Dodas, M. Lohan, W. Geibert, A. Tagliabue, A. Bowie, C. Jeandel, M. T. Maldonado, W. M. Landing, D. Cockwell, C. Abadie, W. Abouchami, E. P. Achterberg, A. Agather, A. Aguliar-Islas, H. M. van Aken, M. Andersen, C. Archer, M. Auro, H. J. de Baar, O. Baars, A. R. Baker, K. Bakker, C. Basak, M. Baskaran, N. R. Bates, D. Bauch, P. van Beek, M. K. Behrens, E. Black, K. Bluhm, L. Bopp, H. Bouman, K. Bowman, J. Bown, P. Boyd, M. Boye, E. A. Boyle, P. Branellec, L. Bridgestock, G. Brissebrat, T. Browning, K. W. Bruland, H. J. Brumsack, M. Brzezinski, C. S. Buck, K. N. Buck, K. Buesseler, A. Bull, E. Butler, P. Cai, P. C. Mor, D. Cardinal, C. Carlson, G. Carrasco, N. Casacuberta, K .L. Casciotti, M. Castrillejo, E. Chamizo, R. Chance, M. A. Charette, J. E. Chaves, H. Cheng, F. Chever, M. Christl, T. M. Church, I. Closset, A. Colman, T. M. Conway, D. Cossa, P. Croot, J. T. Cullen, G. A. Cutter, C. Daniels, F. Dehairs, F. Deng, H. T. Dieu, B. Duggan, G. Dulaquais, C. Dumousseaud, Y. Echegoyen-Sanz, R. L. Edwards, M. Ellwood, E. Fahrbach, J. N. Fitzsimmons, A. Russell Flegal, M. Q. Fleisher, T. van de Flierdt, M. Frank, J. Friedrich, F. Fripiat, H. Fröllje, S. J. G. Galer, T. Gamo, R. S. Ganeshram, J. Garcia-Orellana, E. Garcia-Solsona, M. Gault-Ringold, E. George, L. J. A. Gerringa, M. Gilbert, J. M. Godoy, S. L. Goldstein, S. R. Gonzalez, K. Grissom, C. Hammerschmidt, A. Hartman, C. S. Hassler, E. C. Hathorne, M. Hatta, N. Hawco, C. T. Hayes, L. E. Heimbürger, J. Helgoe, M. Heller, G. M. Henderson, P. B. Henderson, S. van Heuven, P. Ho, T. J. Horner, Y. T. Hsieh, K. F. Huang, M. P. Humphreys, K. Isshiki, J. E. Jacquot, D. J. Janssen, W. J. Jenkins, S. John, E. M. Jones, J. L. Jones, D. C. Kadko, R. Kayser, T. C. Kenna, R. Khondoker, T. Kim, L. Kipp, J. K. Klar, M. Klunder, S. Kretschmer, Y. Kumamoto, P. Laan, M. Labatut, F. Lacan, P. J. Lam, M. Lambelet, C. H. Lamborg, F. A. C. Le Moigne, E. Le Roy, O. J. Lechtenfeld, J. M. Lee, P. Lherminier, S. Little, M. López-Lora, Y. Lu, P. Masque, E. Mawji, C. R. McClain, C. Measures, S. Mehic, J. L. M. Barraqueta, P. van der Merwe, R. Middag, S. Mieruch, A. Milne, T. Minami, J. W. Moffett, G. Moncoiffe, W.S. Moore, P. J. Morris, P. L. Morton, Y. Nakaguchi, N. Nakayama, J. Niedermiller, J. Nishioka, A. Nishiuchi, A. Noble, H. Obata, S. Ober, D.C. Ohnemus, J. van Ooijen, J. O'Sullivan, S. Owens, K. Pahnke, M. Paul, F. Pavia, L. D. Pena, B. Peters, F. Planchon, H. Planquette, C. Pradoux, V. Puigcorbé, P. Quay, F. Queroue, A. Radic, S. Rauschenberg, M. Rehkämper, R. Rember, T. Remenyi, J. A. Resing, J. Rickli, S. Rigaud, M. J. A. Rijkenberg, S. Rintoul, L. F. Robinson, M. Roca-Martí, V. Rodellas, T. Roeske, J. M. Rolison, M. Rosenberg, S. Roshan, M. M. Rutgers van der Loeff, E. Ryabenko, M. A. Saito, L. A. Salt, V. Sanial, G. Sarthou, C. Schallenberg, U. Schauer, H. Scher, C. Schlosser, B. Schnetger, P. Scott, P. N. Sedwick, I. Semiletov, R. Shelley, R. M. Sherrell, A. M. Shiller, D. M. Sigman, S. K. Singh, H. A. Slagter, E. Slater, W. M. Smethie, H. Snaith, Y. Sohrin, B. Sohst, J. E.

Sonke, S. Speich, R. Steinfeldt, G. Stewart, T. Stichel, C. H. Stirling, J. Stutsman, G. J. Swarr, J. H. Swift, A. Thomas, K. Thorne, C. P. Till, R. Till, A. T. Townsend, E. Townsend, R. Tuerena, B. S. Twining, D. Vance, S. Velazquez, C. Venchiarutti, M. Villa-Alfageme, S. M. Vivancos, A. H. L. Voelker, B. Wake, M. J. Warner, R. Watson, E. van Weerlee, M. Alexandra Weigand, Y. Weinstein, D. Weiss, A. Wisotzki, E. M. S. Woodward, J. Wu, Y. Wu, K. Wuttig, N. Wyatt, Y. Xiang, R.C. Xie, Z. Xue, H. Yoshikawa, J. Zhang, P. Zhang, Y. Zhao, L. Zheng, X. Y. Zheng, M. Zieringer, L. A. Zimmer, P. Ziveri, P. Zunino and C. Zurbrick, *Chem. Geol.*,2018, **493**, 210-223.

[24] European Commission. *Critical Raw Materials for the EU. Report of the Ad-hoc Working Group on Defining Critical Raw Materials*. 2014. Ref. Ares (2015)1819503 - 29/04/2015, Brussels.

[25] S. Massari and M. Ruberti*, Resour. Policy*, 2013, **38**, 36-43.

[26] R. K. Katarina, M. Oshima and S. Motomizu, *Talanta*, 2009, **78**, 1043-1050.

[27] Y. Zhu, T. Umemura, H. Haraguchi, K. Inagaki and K. Chiba, *Talanta*, 2009, **78**, 891-895.

[28] Y. Zhu, A. Itoh, T. Umemura, H. Haraguchi, K. Inagaki and K. Chiba, *J. Anal. At. Spectrom*., 2010, **25**, 1253-1258.

[29] Y. Zhu, A. Hioki and K. Chiba, *J. Anal. At. Spectrom*., 2013, **28**, 883-889.

[30] E. C. Hathorne, B. Haley, T. Stichel, P. Grasse, M. Zieringer, M. Frank, *Geochem. Geophys. Geosyst.*, 2012, **13**, 1-12.

[31] Y. Zhang, C. Zhong, Q. Zhang, B. Chen, M. He and B. Hu, *RSC Adv*., 2015, **5**, 5996-6005.

[32] M. M. González-García, F. Sánchez-Rojas, C. Bosch-Ojeda, A. García de Torres and J. M. Cano-Pavón, *Anal. Bioanal. Chem.*, 2003, **375**, 1229-1233.

[33] Ratte H. T, *Environ. Toxicol. Chem.*, 1999, **18**, 89–108.

[34] R. H. Byrne, *Geochem. Trans*., 2002, **3**(2), 11-16.

[35] F. L. Bernardis, R. A. Grant and D. C. Sherrington, *Reac. Funct. Polym*., 2005, **65**, 205-2017.

[36] C. B. Ojeda, F. Sánchez-Rojas, J. M. Cano-Pavón and A. García de Torres*, Anal. Chim. Acta*, 2003, **494**, 97-103.

[37] M. V. Balarama Krishna, M. Ranjit, K. Chandrasekaran, G. Venkateswarlu and D. Karunasagar, *Talanta*, 2009, **79**, 1454-1463.

[38] J. L. Barriada, A. D. Tappin, E. H. Evans and E. P. Achterberg, *Trends Anal. Chem*., 2007, **26**(8), 809-817.

[39] L. Yang and R. E. Sturgeon, *J. Anal. At. Spectrom.*, 2002, **17**(2), 88-93.

[40] Z. Zhu and A. Zheng, *Spectroscopy,* 2017, **32**, 50-59.

[41] D. A. Atwood, *Radionuclides in the Environment*. John Wiley & Sons, Chichester, 1st edn, 2010.

---

[42] C. Poinssot. *Radionuclide Behaviour in the Natural Environment: Science, Implications and Lessons for the Nuclear Industry.* Eds.: C. Poinssot and H. Geckeis. Woodhead Publishing Series in Energy, 2012, Cambridge, UK.

[43] Q.-H. Hu, J.-Q. Wang and J.-S. Wang, *J. Environ. Radioact.,* 2010, **101**, 426-437.

[44] World Health Organization, *Guidelines for Drinking-Water Quality*, WHO, Geneva, fourth edition incorporating the first addendum, 2017. https://www.who.int/water_sanitation_health/publications/drinking-water-quality-guidelines-4-including-1st-addendum/en/.

[45] *Uranium Fact sheet, Environmental Protection Agency*, US EPA, 2013; https://www.wqa.org/Portals/0/Technical/Technical%20Fact%20Sheets/2014_Uranium.pdf.

[46] AERB Drinking water specifications in India. Department of Atomic Energy, Govt. of India, 2004; https://www.aerb.gov.in/english/.

[47] T. Laaninen. *Revision of the Drinking Water Directive.* European Union, 2019. http://www.europarl.europa.eu/RegData/etudes/BRIE/2018/625179/EPRS_BRI(2018)625179_EN.pdf.

[48] European environmental quality standards (EQS) variability study. Scientific Report from DCE – Danish Centre for Environment and Energy Nr. 198, 2016; http://dce.au.dk/en/.

[49] Z. Wang, J. Lin, S. Li, Q. Guo, W. Huang, W. Wen, G. Dan and Z. Tan, *J. Radioanal. Nucl. Chem*., 2018, **315**, 103-110.

[50] A. Habibi, C. Vivien, B. Boulet, C. Cossonnet, R. Gurriaran, M. Gleizes, G. Cote and D. Larivière, *J. Radionanal. Nucl Chem*., 2016, **310**, 217-227.

[51] A. Habibi, B. Boulet, M. Gleizes, D. Larivière and G. Cote, *Anal Chim Acta*, 2015, **883**, 109-116.

[52] J. X. Qiao, X. L. Hou, P. Steier and R. Golser, *Anal. Chem*., 2013, **85**, 11026-11033.

[53] J. Avivar, L. Ferrer, M. Casas and V. Cerda, *J. Anal. At. Spectrom*., 2012, **27**, 327-334.

[54] M. Kim, J. Stripeikis and M. Tudino, *Spectrochim. Acta Part B*, 2009, **64**, 500-505.

[55] X. Zhang, M. Chen, Y. Yu, T. Yang and J. Wang, *Anal. Methods*, 2011, **3**, 457-462.

[56] A. M. Zou, X. Y. Tang, M. L. Chen and J. H. Wang, *Spectrochim. Acta Part B*, 2008, **63**, 607-611.

[57] M. M. López-Guerrero, E. Vereda-Alonso, J. M. Cano-Pavón, M. T. Siles-Cordero and A. García de Torres, J. Anal. *At. Spectrom*., 2012, **27**, 682-688.

[58] S. Chen, L. Zhu, D. Lu, X. Cheng and X. Zhou, *Microchim Acta*, 2010, 196, 123-128.

[59] W. Hu, F. Zheng and B. Hu, *J. Hazard. Mater*., 2008, **151**, 58-64.

[60] Y. F. Huang, Y. Li, Y. Jiang and X. P. Yan. *J. Anal. At. Spectrom*. 2010, 25, 1467-1474.

[61] C. Huang, B. Hu, M. He and J. Duan, *J. Mass Spectrom*., 2008, **43**, 336-345.

[62] C. Xiong, Y. Qin and B. Hu, *J. Hazard. Mater*., 2010, **178**, 164-170.

---

[63] B. Magnusson and U. Örnemark (Eds.) *Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics*. (2nd ed. 2014). ISBN 978-91-87461-59-0. Available from http://www.eurachem.org.

[64] G. Ying, L. Rui and Y. Lu, *Chinese Sci. Bul*., 2013, **17**, 1980-1991.

[65] A. Calvo-Fornieles, A. García De Torres, E. Vereda-Alonso, M. T. Siles-Cordero and J. M. Cano-Pavón, *J. Anal. At. Spectrom.,* 2011, **26**, 1619-1626.

[66] A. N. Anthemidis, E. I. Daftsis and N. P. Kalogiouri, *Anal. Methods*, 2014, **6**, 2745-2750.

[67] L. O. B. Silva, L. A. Portugal, E. Palacio, L. Ferrer, V. Cerdà and S. L. C. Ferreira. *J. Anal. At. Spectrom*., 2014, **29**, 2398-2404.

[68] L. Fischer, M. Brunner, T. Prohaska and S. Hann., *J. Anal. At. Spectrom*., 2012, **27**, 1983-1991.

[69] M.M. López-Guerrero, M. T. Siles-Cordero, E. Vereda-Alonso, J. M. Cano-Pavón and A. Garcia de Torres, *J. Anal. At. Spectrom*., 2015, **30**, 1169-1178.

[70] I. Sánchez-Trujillo, A. García De Torres, E. I. Vereda-Alonso and J. M. Cano-Pavón, *J. Anal. At. Spectrom.*, 2013, **28**, 1772-1780.

[71] I. Sánchez-Trujillo, M. L. Alonso-Castillo, J. M. Cano-Pavón, E. I. Vereda-Alonso and A. García de Torres, *Anal. Methods*, 2013, **5**, 2551-2557.

[72] M. M. López-Guerrero, E. Vereda-Alonso, A. García De Torres and J. M. Cano-Pavón, *J. Anal. At. Spectrom*., 2017, **32**, 2281-2291.

[73] M. V. B. Krishna, K. Chandrasekaran and D. Karunasagar. *Talanta*, 2010, **81**, 462-472.

[74] I. Sánchez-Trujillo, E. Vereda-Alonso, J.M. Cano-Pavón and A. García De Torres, *J. Anal. At. Spectrom*., 2015, **30**, 2429-2440.

[75] M. Sigrist, A. Albertengo, H. Beldoménico and M. Tudino, *J. Hazard. Mater.,* 2011, **188**, 311-318.

[76] M. Miró and E. H. Hansen, *Anal. Chim. Acta*, 2013, **782**, 1-11.

[77] C. Mitani and A. N. Anthemidis, *Talanta*, 2015, **133**, 77-81.

[78] Y. Li and B. Hu, *At. Spectrosc*., 2009, **30**, 104-111.

[79] K. Chandrasekaran, D. Karunasagar and J. Arunachalam, *Anal. Methods*, 2011, **3**, 2140-2147.

[80] P. Berton, E .M. Martinis and R. G. Wuilloud, *J. Hazard. Mater*., 2010, **176**, 721-728.

[81] F. Pena, I. Lavilla and C. Bendicho, *Spectrochim. Acta Part B*, 2008, **63**, 498-503.

[82] A. N. Anthemidis and I. S. I. Adam, *Anal. Chim. Acta*, 2009, **632**, 216-220.

[83] C. Mitani and A. N. Anthemidis, *Anal. Chim. Acta*, 2013, **771**, 50-55.

[84] A. N. Anthemidis and K. – I. G. Ioannou, *Talanta*, 2009, **80**, 413–421.

[85] A. N. Anthemidis and K. I. G. Ioannou, *Anal. Chim. Acta*, 2010, **668**, 35-40.

[86] A. N. Anthemidis and K. I. G. Ioannou, *Talanta*, 2011, **84**, 1215–1220.

---

[87] A. N. Anthemidis and K. I. G. Ioannou, *Anal. Bioanal. Chem.*, 2012, **404**, 685–691.

88 H. Peng, N. Zhang, M. He, B. Chen and B. Hu, Int. J. Environ. Anal. Chem., 2016, 96, 212-224.

[89] J. E. O'Sullivan, R .J. Watson and E. C. V. Butler, *Talanta*, 2013, **115**, 999-1010.

[90] A. N. Anthemidis, S. Xidia and G. Giakisikli, *Talanta*, 2012, **97**, 181-186.

[91] B. Dai, M. Cao, G. Fang, B. Liu, X. Dong, M. Pan and S. Wang, *J. Hazard. Mater.*, 2012, **219-220**, 103-110.

[92] A. O. AlSuhaimi and T. McCreedy, *Arab. J. Chem.*, 2011, **4**, 195-203.

[93] A. N. Anthemidis, G. Giakisikli, S. Xidia, M. Miró, *Microchem. J.*, 2011, **98**, 66-71.

[94] C. Cui, M. He and B. Hu, *J. Hazard. Mater.*, 2011, **187**, 379-385.

[95] D. Chen, B. Hu, M. He and C. Huang, *Microchem. J.*, 2010, **95**, 90-95.

[96] I. Sánchez-Trujillo, E. Vereda-Alonso, M. T. Siles-Cordero, J. M. Cano-Pavón and A. García De Torres, *J. Anal. At. Spectrom.*, 2010, **25**, 1063-1071.

[97] D. Chen, B. Hu and C. Huang, *Talanta*, 2009, **78**, 491-497.

[98] P.-L. Lee, Y.-C. Sun and Y.-C. Ling, *J. Anal. At. Spectrom.*, 2009, **24**, 320-327.

[99] J. C. García-Mesa, P. Montoro-Leal, M. M. López-Guerrero and E. I. Vereda-Alonso, *Microchem. J.*, 2019, **150**, 104141.

[100] Y. Wang, X. Luo, J. Tang, X. Hu, Q. Xu and C. Yang, *Anal. Chim. Acta*, 2012, **713**, 92-96.

[101] P. H. Pacheco, P. Smichowski, G. Polla and L. D. Martinez, *Talanta*, 2009, **79**, 249-253.

[102] V. Yilmaz, Z. Arslan, O. Hazer and H. Yilmaz, *Microchem. J.*, 2014, **114**, 65-72.

[103] X.-W. Chen, A.-M. Zou, M.-L. Chen, J.-H. Wang and P. K. Dasgupta, *Anal. Chem.*, 2009, **81**, 1291-1296.

[104] M. Z. Corazza, B. F. Somera, M. G. Segatelli and C. R. T. Tarley, *J. Hazard. Mater.*, 2012, **243**, 326-333.

[105] X.-X. Zhang, L.-P. Zhang, T. Yang, L.-M. Shen, M.-L. Chen and J.-H. Wang, *J. Anal. At. Spectrom.*, 2012, **27**, 1680-1687.

[106] T. Yang, X.-X. Zhang, M.-L. Chen and J.-H. Wang. *Analyst*, 2012, **137**, 4193-4199.

[107] G. F. Lima, F. M. Oliveira, M. O. Ohara, M. G. Segatelli and C. R. T. Tarley, *Evaluation of histidine functionalized multiwalled carbon nanotubes for improvement in the sensitivity of cadmium ions determination in flow analysis,* In: Carbon Nanotubes - From Research to Applications, Dr. Stefano Bianco (Ed.), In Tech, Croatia, 2011.

[108] M. Gawin, J. Konefal, B. Trzewik, S. Walas, A. Tobiasz, H. Mrowiec and E. Witek, *Talanta*, 2012, **80**, 1305-1310.

[109] C. R. T.Tarley, F. N. Andrade, F. Midori de Oliveira, M. Z.Corazza, L. F. Mendes de Azevedo and M. G. Segatelli, *Anal. Chim. Acta*, 2011, **703**, 145-151.

---

[110] A. N. Anthemidis, I. S. I. Adam and G. A. Zachariadis, *Talanta*, 2010, **81**, 996-1002.

[111] Y. Bakricioglu, D. Bakircioglu and S. Akman, *J. Hazard. Mater*., 2010, **178**, 1015-1020.

[112] Z. Zhu and A. Zheng, *Molecules*, 2018, **23**, 489.

[113] C. K. Su, Y. T. Chen and Y. C. Sun, *Microchemical J*., 2019, **146**, 835-841.

[114] M. M. López-Guerrero, E. Vereda-Alonso, J. M. Cano-Pavón, M. T. Siles-Cordero and A. García De Torres, *J. Anal. At. Spectrom*., 2012, **27**, 682-688.

[115] S. Chen, L. Zhu, D. Lu, X. Cheng and X. Zhou, *Microchim. Acta*, 2010, **196**, 123-128.

[116] C. Xiong, M. He and B. Hu, *Talanta*, 2008, **76**, 772-779.

[117] S. S. Lins, C. F. Virgens, W. N. L. dos Santos, I. H.S. Estevam, and S. L. C. Ferreira, *Microchem. J*., 20149, **150**, 104075.

[118] A. Calvo-Fornieles, A. García de Torres, E. I. Vereda-Alonso and J. M. Cano-Pavón, *J. Anal. At. Spectrom*., 2013, **28**, 364-372.

[119] M. M. López-Guerrero, M. T. Siles-Cordero, E. Vereda-Alonso, A. García De Torres and J. M. Cano-Pavón. *Talanta*, 2014, **129**, 1-8.

REVIEWER REPORT(S)

We would like to thank all reviewers for their valuable and encouraging comments to improve the manuscript!

Responses address the suggestions and comments expressed in each review and changes based on these are pointed out clearly. The following changes have been performed based on the reviewers' comments and suggestions:

Referee: 1

This is a review article well-written and well-organized collecting the most relevant literature about on-line strategies for matrix separation and/or preconcentration and speciation of metals in natural waters prior to atomic spectrometric detection. The presented manuscript reflects well the state of the art the concerned topic, and the authors have offered their critical conclusions and future perspectives, however some recent developments, such as magnetic solid phase extraction (MSPE) or the methods on-line with High Resolution Continuous Source Electrothermal Atomic Absorption Spectrometry (HR-CS-ETAAS) have been missed. Thus, in my opinion the article is worth to be published in JAAS, however, authors should include in their discussion the above mentioned developments. Also some other remarks must be addressed before its final publication. All these suggestions have been listed below:

1. In the last years an improved technique SPE, magnetic SPE, based on magnetic nanosorbents has appeared as a promising technique. MSPE has been little used online with atomic detection despite of its advantages in front to MSPE “in batch”. There are some papers included into different Tables (1,2,3 and 5) which employ MSPE, however no discussion about this new development appears along the manuscript.

Answer: A general description about MNPs has been added to section 3.1, followed by a brief description of a study using MSPE for the extraction of Mn, Co, Cu, Zn and Pb (Lee et al. 2009).

In section 4, a method for the determination of precious metals by magnetic SPE-ICP-OES and CVG is mentioned.

2. On the same way, no method has been included with a relatively recent technique, HR-CS-ETAAS, despite of the advantages of this technique as improved signal stability, superior background correction potential, capabilities to monitor narrow molecular “lines” which permit the determination of non-metals, improved linearity by making use of side pixels, and possibility to sequential or

simultaneous multielemental determination. This instrument has been successfully coupled on-line with CVG/HG and SPE through the use of a FI system and a permanent modifier such as iridium. HRCS-ETAAS has opened the possibility of achieving even more rapid quantitation of some elements and with the incorporation of FI systems for automation of sample pretreatment, as well as chemical vapor generation renders into a feasible option for detection of elements, such as As, Hg, Sb, Sn, etc., in environmental control studies.

 J. Sardans, F. Montes, J. Penuelas, Spectrochim. Acta Part B, 2010, 20, 447-491.

 M.M. López Guerrero, M.T. Siles Cordero, E. Vereda Alonso, J.M. Cano Pavón and A. García de Torres, J. Anal. At. Spectrom., 2015, 30; 1169-1178.

 A. Cárdenas Valdivia, M.M. López Guerrero, E.I. Vereda Alonso, J.M. Cano Pavón and A. García de Torres, Microchem. J., 2018, 138, 109-115.

Answer: AAS methods based on HR-CS instrumentation were also added in the Introduction section.

A paragraph on HR-CS-ETAAS has been added and the above mentioned publications (2 and 3) have been referenced, further, details given in the 2018 Cárdenas Valdivia et al. publication were added to Table 5.

Answer: The first reference on Sardans et al. refers to soils and sediments and thus it is outside the scope of the review.

3. It is true that many acronyms are well known by potential readers of the article, however, in my opinion, the meaning of all the acronyms in the manuscript should be written the first time they appear in the text, e.g. in page 5, Introduction and Flowthrough approaches and interfaces sections, ICP-MS; ICP-OES; FAAS; qQq; SF.

In page 7, line 28, on the contrary, FAAS was described although had already appeared before, but not ETAAS. Other acronyms without definition are: USGS in page 11, line 38, or SI in page 12, line 25.

Answer: All acronyms were carefully revised throughout the manuscript and explained.

4. Section 3.3 Precious metals, authors commented that there were few publications reporting the automation and online separation/preconcentration of precious metals from natural waters, and they critically commented a method published more than 10 years ago (36), however the same research group has published improved and more recent articles, e.g.

 M.L. Alonso Castillo, A. García de Torres, E. Vereda Alonso, M.T. Siles Cordero and J.M. Cano Pavón, Talanta, 2012, 99, 853-858.

Answer: This reference has been added and information is given in the respective section and table.

5. Section 3.5. Metal speciation, page 14, line 49, in my opinion some reference of some Directive should be included.

Answer: This paragraph was revised since no environmental quality standards and limits, respectively, are set by legislations until now.

6. Page 15, line 8, the reference 57 was later repeated as 114, perhaps there was some confusion with a less recent paper about chromium speciation of the same research group based on SPE coupled on-line with ETAAS, in which it was used an original and fully automatic, home-made approach: the sample tip of the autosampler arm was replaced by a microcolumn containing the adsorbent resin, and a peristaltic pump together with a selection valve were readily controlled electronically via two switches on the autosampler try that were actuated when the autosampler arm was down.

 M.T. Siles Cordero, E.I. Vereda Alonso, A. García de Torres and J.M. Cano Pavón, J. Anal. At. Spectrom., 2004, 19, 398-403.

Answer: Reference 114 was redundant and hence, has been deleted. The additional reference has not been considered for this review manuscript as it does not fit in the respective timeframe.

7. Page 18, after line 50, Table 6 was unmentioned along the text.

Answer: The reference to Table 6 has been inserted in the text.

8. Table 6, this table has collected only four papers about methods employing CVG/HG techniques for the speciation of metals in natural waters. There is an article using MSPE on line with HG-ICP-MS for the inorganic As speciation that, in my opinion should be mentioned. Besides, the acronym MNPs (magnetic nanoparticles) appears as footnote on Table 6.

 P. Montoro Leal, E. Vereda Alonso, M.M. López Guerrero, M.T. Siles Cordero, J.M. Cano Pavón and A. García de Torres, Talanta, 2018, 184, 251-259.

Answer: The acronyms in the footnote of Table 6 have been revised and the Table has been enhanced with the method details of the above mentioned publication. In addition, a paragraph briefly describing the approach has been added in Section 4.

9. There are some other repeated references: 10 and 76; 20 and 101; and 58 and 115.

Answer: These references were checked and corrected.

Other minor remarks:

 Page 8, line 10, Giakisikli instead of Giakasikli

 Page 8, line 37, Is this format (e.g.20) correct?

- Page 22, lines 9-11, RSD units for Sb and Hg were missed (%)

Answer: That has been corrected.

Referee: 2

This manuscript is a well-structured and useful review, that evaluates the research achievements with regard to strategies for on-line sample treatment prior to atomic spectrometric determination of trace elements in natural waters and emphasizes on flow injection and related flow based approaches. It provides a critical overview of 119 references from the last 10 years. The article fully complies with the requirements for publication in JAAS and should be published with minor changes.

Some comments:

Figures in the manuscript are doubled Pages 41 – 44 and Pages 52-55

I would suggest removing the figures 2, 3 and 4, but if the editor do not agree, the figures should be of better quality.

Answer: We would like to keep these figures in as they make the paper more informative and readable, as expected in critical reviews in JAAS.

Page 40 - Caption in Figure 1 - Authors should provide an explanation of the abbreviations used in the figure, e.g. PP, peristaltic pump; SP, syringe pump….

Page 40 - Caption Figure 3 - Insufficient explanation of the figure.

Answer: Abbreviations (for Figure 1 and 3) and a more detailed explanation of Figure 3 have been added in the Figure captions.

Page 30, Line 5 - "99" must be in SuperScript format, the same is for Page 50, Line 6 “88”

Careful checking of all tables is required to print all units in the same line

e.g. "ng L-1" NOT "ng L-1

Answer: The formatting has been carefully checked throughout the manuscript.

Referee: 3

The manuscript presents a review of on-line strategies for matrix separation and/or preconcentration and speciation of metals in natural waters including marine waters, fresh waters, groundwater and precipitation prior to atomic spectrometric detection. In my opinion, this review is well written and well organized. I appreciated the presence of tables reporting the matrix, conditions adopted in each paper and figures of merit. In my opinion, this manuscript can be accepted for publication after revision.

Section 3.2: most of the studies in literature (presented in Table 3) reported the determination of REEs using quadrupole based ICP-MS or ICP-OES. The determination of REE using these techniques is impaired by the occurrence of several spectral interferences (mostly oxides in the case of ICP-MS). A comment about this should be added to section 3.2 and approaches used for the minimization of these interferences should be highlighted.

Answer: A paragraph concerning these comments has been added in the respective section.

Section 3.4, page 11, line 15: a comment can be added emphasizing that the method validation was not properly performed, once a certified reference material of sediment (BCR-320R) was used and not a matrix similar to the samples (such as seawater, well water, mineral water or fresh water).

Answer: A sentence concerning the lack of an appropriate CRM has been added.

Section 3.5, page 11: the first paragraph of this section has no references. References should be added to support authors statements and also when directives are mentioned.

Stephan – could you please add a reference?

Answer: The following reference has been added: J. R. Bacon, O. T. Butler, W: R. L. Cairns, J. M. Cook, C. M. Davidson, O. Cavoura and R. Mertz-Kraus, Atomic spectrometry update-a review of advances in environmental analysis, J. Anal. At. Spectrom., 2020; 35(1), 9-53. Further, directives are referenced.

Section 4, page 13, line 35: the authors mentioned the use of reducing agents such as sodium borohydride, but tin chloride can also be used for cold vapor generation of mercury. This information should be added to manuscript.

Answer: A sentence concerning this has been added in Section 4: “It should be mentioned that for the reduction of inorganic Hg, tin chloride can also be used. ”

Section 5, page 17, line 26: The authors mentioned that cloud point extraction techniques are summarized in Table 7, but it just shows works using LLME. Also, cloud point extraction techniques are just mentioned but no works were shown in the manuscript. If this technique is used for the analysis of natural waters, it should be discussed during the manuscript and works should be shown.

Answer: All of the methods reviewed but one in the period surveyed are focused on LLME variants for real sample analysis, and thus the reference to on-line CPE has been eliminated

Section 5, page 17, line 44: What do the authors mean with “a number of intriguing LPME variants”? Please, let it clear to the readers.

Answer: The word “intriguing” has been replaced by “appealing”

Section 5, page 18, line 1: The authors concluded this section mentioning that the main issue of FI/SI systems incorporating LPE/LPME is that method validation is not properly performed (performed with CRMs which are not similar to sample matrix). However, this is an issue that was also observed for the other methods, such as SPE, CVG and HG. I think that, to conclude this section, the authors could add a discussion comparing the recoveries, LODs and sample throughput of the LPE/LPME in comparison with SPE, CVG and/or HG.

Answer: Further discussion of the limitations of FI/SI-LPE/LPME methods has been added to this section. It should be noted that an overall comparison of the various sample preparation approaches is not feasible because the figures of merit are analyte, matrix and detection technique dependant. However, the analytical performance of the various approaches is comprehensively summarized in the tables.

Section 6: Not only in this section, but also during the entirely manuscript, the authors could emphasize and discuss more thoroughly the advantages and disadvantages of each matrix separation/preconcentration method (SPE, CVG, HG and LPME). A comparison between the analytical performances of the different methods could be added to this section.

Answer: Each of the sections of the manuscript has been written critically with focus on the merits and pitfalls of the various on-line sample preparation methods as applied to real samples. However, we have expanded the conclusion section to highlight that SPE is by far the sample preparation approach that offer superior performance in terms of reliability, enrichment capability and throughput.

Table 7, line 31: the sample volume unit is missing (16.2 ?).

Answer: The unit has been added.

Figure 1: The meaning of the abbreviations, such as “PP”, “S”, “R”, “E”, should be included on the figure caption.

Answer: The abbreviations have been added to the Figure.

References: All references should be carefully revised. Page 14, line 33: the authors referred to reference 65 when mentioning a work for Sb, Bi and Sn determination in sea water, but reference 65 is actually a work for Sb speciation. In Table 5, the reference for Sb, Bi and Sn determination is number 118. Also, duplicated references were also found (20 and 101, 58 and 115).

Answer: The references were carefully checked again and corrected.

On-line sample treatment coupled with atomic spectrometric detection for the determination of trace elements in natural waters

Lisa Fischer[a], Stephan Hann[a], Paul J. Worsfold[b] and Manuel Miró[c]

[a] Department of Chemistry, University of Natural Resources and Life Sciences, Vienna (BOKU), Muthgasse 18, 1190 Vienna, Austria

[b] Biogeochemistry Research Centre, SoGEES, University of Plymouth, Plymouth PL48AA, Devon, UK.

[c] FI-TRACE group, Department of Chemistry, University of the Balearic Islands, Carretera de Valldemossa km 7.5, E-07122 Palma de Mallorca, Spain

Keywords. Natural waters, trace elements, atomic spectrometry, flow injection, sequential injection, solid phase extraction, cold vapour generation, hydride generation, liquid membrane extraction, speciation.

Abstract

This review discusses the application of on-line strategies for sample treatment prior to atomic spectrometric detection. These strategies are based on flow injection and related flow-based approaches and focus on publications that have been published in the last ten years and have been explicitly applied to real world natural water samples (open ocean, coastal and estuarine water, river water, lake water and groundwater) and matrix relevant certified reference materials. The focus is on the use of solid phase extraction for matrix removal and analyte preconcentration. For convenience of searching, methods are grouped by element type, i.e. transition metals (plus zinc, cadmium, lead and arsenic), rare earth elements (the 15 lanthanides plus scandium and yttrium), precious metals (platinum group elements plus silver and gold) and actinide elements (the transuranic elements plus actinium, thorium, polonium and uranium). There is a separate section on methods for elemental speciation. Other on-line treatment strategies covered are cold vapour and hydride generation, and liquid phase microextraction. Comprehensive method details and analytical figures of merit are provided for key selected papers covering each of these strategies in associated tables.

1 Introduction

Natural waters include marine waters (e.g. open ocean, shelf sea, coastal and estuarine), fresh waters (e.g. river, stream, lake), groundwater and precipitation (e.g. rain, snow, ice). Each of these reservoirs has a different chemical composition, including their trace element profile (see e.g. [1, 2]), that varies spatially and temporally but all are interconnected via the global water cycle. Biogeochemical processes[3] impact on the fluxes of trace elements between these compartments and their physico-chemical speciation[4] within each compartment.

The need to quantify trace elements in natural waters is driven by several factors. Some elements or elemental species are toxic[5], even at low concentrations, whilst others are essential micronutrients[6]. Others can be used to elucidate transport processes or act as specific markers for aquatic processes or events[7]. The low concentrations of many elements or their compounds in natural waters requires sensitive detection techniques such as inductively coupled plasma-mass spectrometry (ICP-MS), often hyphenated with some form of separation[8] or preconcentration/matrix removal[9]. This review focusses on the use of flow injection (FI) manifolds and advanced flow setups for on-line sample treatment, coupled mainly with flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma-optical emission spectrometry (ICP-OES) and ICP-MS detection, for the determination of trace elements and their compounds in natural waters published since 2008 (for previous reviews on the role of flow analysis in sample preparation see e.g. [10, 11]). Flow-based methods coupled to high resolution-continuum source (HR-CS)-AAS have also been considered[12, 13]. Advantages compared with standard AAS include improved signal stability and background correction and the use of a high-pressure xenon short-arc lamp as a continuous radiation source for sequential or simultaneous multi-element analysis.

2 Flow-through approaches and interfaces

The three main cornerstones of FI, i.e. controllable dispersion, reproducible timing and controlled sample injection, have been fully exploited in combination with atomic spectrometric detection, for which the transport of aerosols into the atomizer is regarded as the 'Achilles heel' of atomic spectrometric techniques. Flow injection approaches were conceived for sample introduction of a metered aqueous sample volume to a detection system (FAAS in the case of elemental analysis), capitalizing on the high (carrier) wash to sample ratio. Hereto, the nebulizer and burner are continuously cleaned by a carrier solution, thus alleviating problems of clogging, even in high salt matrix samples. In fact, FI setups hyphenated to ICP-triple quadrupole-mass spectrometry (ICP-qQq-MS)/ICP-sector field-mass spectrometry (ICP-SFMS), based on the continuous operating nature of both the flow setup and detection technique, are now regarded as the second dawn for high-throughput (multi-) elemental and molecular automatic analysis. The advances in sample injectors (e.g. nano-valves) and improved designs of nebulizers and spray chambers that enable continuous injection of, e.g. organic eluates and alcoholic solvents, have helped to overcome the limitations of FI-ICP couplings in terms of the nature of the sample to be injected[14, 15], in as much as high carbon content matrices have been traditionally excluded from ICP analysis. Nowadays the utilization of organic solvents in ICP-MS is performed on a routine basis with robust interfaces allowing the controlled addition of oxygen in order to eliminate carbon deposition on cones and other parts of the ICP-MS introduction system[14, 15]. In quadrupole MS based systems, the implementation of reaction/collision cell technology has enabled the development of strategies for the reduction or elimination of almost all polyatomic interferences that would otherwise hamper the accurate determination of the elements amenable to this technique. Tandem QMS systems are now state-of-the-art and regarded as equivalent with ICP-SFMS systems in terms of selectivity and limits of detection.

With regard to system configuration, on-line hyphenation of FI with ICP involving the use of a mechanically movable element, namely a rotary valve, has been the interface of choice for practitioners to integrate sample handling seamlessly with analysis. Nonetheless, at-line automatic interfacing, achieved by exploiting advanced robotic arms or autosamplers, is a simple means of conditioning the sample/extract prior to analysis[16]. However, coupling of flow approaches to discontinuously operating detectors ETAAS is not straightforward. The second generation of FI, so-called Sequential Injection (SI), has however paved the way for automatic sample handling across a multi-position selection valve as a core element of the flow system and a bi-directional syringe pump as a liquid driver with on-line sample injection of minute volumes (< 50 μL) into the graphite tube[17]. This is accomplished by integrating a flow line (usually polytetrafluorethylene (PTFE) tubing) in the ETAAS autosampler arm, which connects the selection valve with the graphite tube at pre-set injection times. Advantage is taken of the fact that the ensuing sample might be processed in the SI manifold while running the ETAAS program of the previous sample. A conceptual diagram of the combination of on-line FI/SI sample preparation with atomic spectrometric detectors is shown in Fig. 1.

FI, SI and related techniques can also be used as automatic platforms for accommodating appropriate pre-treatment schemes prior to the actual detection when handling troublesome samples for which matrix clean-up and/or analyte preconcentration to attain suitable detectability are required.

3 On-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the determination of metal concentrations in natural waters.

3.1 Transition metals, zinc, cadmium, lead and mercury

This section focusses on the use of on-line solid phase preconcentration for the determination of transition metals (V, Mn, Fe, Co, Ni and Cu) and includes group 12 elements (Zn, Cd (and Hg)), along with other metals (Pb) and metalloids (As). These elements can be classified in different ways depending on the context in which they are being determined. Their interaction with biota is a particularly important classification and these elements can be described as micronutrients (e.g. Fe, Co), toxic elements (e.g. Pb, Cd) or both (depending on the concentration, e.g. Cu).

The major analytical challenge is the potential for contamination during sampling, storage and analysis as concentrations in natural waters (particularly seawater) are typically very low (≤ nM). In this regard flow manifolds incorporating on-line solid phase extraction (SPE) are attractive due to the confined and controlled nature of the sample handling step, the ability to preconcentrate the analyte(s) and the removal of major sea salt ions that would otherwise interfere with the detection step (see e.g. [11] and [17]). Filtration of samples and refrigeration immediately after collection are essential for obtaining high quality data. The application of flow manifolds, coupled with the use of high purity reagents and a meticulous approach to cleaning of all laboratory ware, are essential prerequisites for minimising the blank signal and hence achieving the desired limit of detection (LOD).

Transition metals can often be determined simultaneously using e.g. ICP-MS or ICP-OES detection and the key analytical performance data for selected papers are summarised in Table 1. It is also possible to determine individual elements using e.g. FAAS or ETAAS and performance data for selected papers are similarly summarised in Table 2. Particularly noteworthy features from these papers are considered in more detail below.

The most important component of the flow manifold for these methods is the on-line SPE micro/mini-column. The chemistry of the SPE phase used for on-line preconcentration and matrix removal, i.e. the nature of the support material and the attached chelating ligand or sorptive material, and the design of the column, e.g. column dimensions, shape and fabrication material, and the elution mode (e.g., the use of back-flushing elution) are important considerations. The most common ligands are iminoacetate based chelates ((iminodiacetic acid (IDA), nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA)), quinolinol based chelates ((8-hydroxyquinoline (8HQ)) and dithiocarbamate based chelates. Nobias-chelate PA1 is a chelating resin that has both, EDTA and IDA chelating groups immobilized on a hydrophilic methacrylate polymer. It is popular because it is commercially available, functions over a relatively wide pH range and has a high affinity for several transition metals[9]. This paper reported an enrichment factor (also called a preconcentration factor) of ~200 for Co, Cu, Fe, Mn, Ni and Zn with a 9 mL sample volume, which allowed excellent detection limits to be achieved. As a general comment it is recommended that all papers using on-line SPE state the method used to calculate the enrichment factor and the experimental details used to obtain the data. Toyopearl AF-Chelate 650 is another popular polymeric resin incorporating IDA chelating groups that has been used to estimate the uncertainties associated with on-line preconcentration and ICP-MS detection of trace metals in seawater[18]. A schematic diagram of the FI manifold used for this work is shown in Fig. 2.

It is also possible to react the transition metal with the ligand on-line and then use a reversed-phase material such as octadecyl-chemically modified silica for trapping the neutral chelate. In an interesting example, Giakisikli and Anthemidis[19] formed a cadmium complex with diethyldithiocarbamate (DDTC) on-line and then preconcentrated the complex on octadecylsilane functionalized maghemite magnetic particles. The complex was then eluted with isobutyl methyl ketone.

Proprietary resins include 1,5-bis (2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide (PSTH) which was immobilized on aminopropyl-controlled pore glass and incorporated within the injection valve of a simple flow manifold[20]. However, enrichment factors were relatively low, ranging from 2.2 – 6.8 for a range of transition metals. Another proprietary resin utilised a natural product (chitosan) as the support material and EDTA as the immobilised chelating ligand[21], achieving enrichment factors of 14 – 35 for a range of transition (and rare earth) metals for a sample volume of only 5 mL. A conventional mini-column (4 cm length x 2 mm i.d.) was incorporated within a 6-port switching valve as part of a fully automated system.

Unconventional advanced sorbents exploiting nanotechnology, based on the large surface area of nanomaterials, have also been adapted for metal assays in natural waters. For example, multi-walled carbon nanotubes (MWCNTs) have been used for preconcentration, with ligands such as *L*-tyrosine immobilised on the walls of the tubes to enhance interaction with transition metals via cation-π interactions[22]. An enrichment factor of 180 was reported for Co using FAAS detection.

Recent developments in microchip fabrication have been used to design compact, on-line miniaturized preconcentration devices. One example is the use of dipole–ion interactions between the highly electronegative C–Cl moieties of 2,2'-azobisisobutyronitrile, which was cross-linked to the channel interior of a poly(methyl methacrylate) fabricated chip, and the positive charges on the transition metal ions in the sample[23]. Using this approach, detection limits ranging from 1.6 – 42 ng L^{-1} were achieved for Co, Cu, Mn, Ni and Pb in river water[24].

Within the last decade, magnetic SPE based on magnetic nanosorbents has received considerable interest for matrix separation/preconcentration. The principle involves magnetisable materials used as sorbents and their attraction by a magnetic field for the isolation of target analytes after extraction from the sample matrix. A recent review article reports several applications based on magnetic nanoparticles (MNPs) for SPE of a suite of trace metals in water and other matrices using inorganic nanoparticles such as silica-coated MNPs, magnetic alumina and titania or magnetic layered double oxides, and organic sorbents including magnetic carbon materials (graphene/graphene oxide), magnetic carbon nanotubes and nitrides and magnetic organic polymers or ionic liquids. These extraction procedures are mostly performed in batch mode but the authors explicitly emphasise the possibility of automation[25]. An on-line method based on magnetite-based MNPs as sorbent coupled to ICP-MS for the determination of Mn, Co, Cu, Zn and Pb in water (and other matrices) was first reported in 2009[26]. Effective separation of matrix constituents and excellent recovery for the CASS-2 CRM was achieved; however, the resulting LODs were not significantly lower compared to direct analysis as only 20 µl sample volume was processed.

It is essential that robust quality assurance procedures are used to ensure that the results are fit for purpose. For water quality management it is important that results are sufficiently accurate to monitor environmental threshold levels such as the EU maximum admissible concentration values. This requires the use of appropriate (matrix matched) certified reference materials (CRMs) or waters with consensus values such as those produced by the GEOTRACES programme[27]. All publications should report at least one (preferably more) CRM/consensus value for each element, including appropriate statistical assessment of the results. Unfortunately, this is not the case in many reports compiled in Tables 1 and 2 (indicated by °) for which CRMs of matrices other than waters, including biological matrices (e.g., urine or seafood tissues) or environmental solids (e.g. sediments and soils) have been inappropriately selected. For elucidating environmental processes, a key requirement is to be able to statistically distinguish changes in recorded data from analytical uncertainty. Thus, a rigorous assessment of all uncertainties in the sampling and analysis steps should be undertaken[18].

3.2 Rare earth elements

In this section, on-line matrix separation and preconcentration methods based on solid phase extraction for the quantification of rare earth elements (REEs) are discussed. The group of REEs comprises the 15 lanthanoids as well as Sc and Y. They can be further divided into light REEs (Sc, La, Ce, Pr, Nd, Sm, Eu) and heavy REEs (Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). They are not regulated with respect to threshold levels and maximum admissible concentrations in water but there is a growing interest in knowing their concentrations in the aquatic environment. They have been confirmed as critical raw materials by the European Commission in 2014[28] due to their significant economic importance as they are widely used in numerous applications such as the automotive industry and nuclear, oil and green technologies[29]. This, however, increases the emission of REEs into the aquatic environment, resulting in anthropogenic anomalies, e.g. Gd due to its intense use in Gd-based magnetic resonance imaging contrast agents. The assessment of anthropogenic contamination requires a knowledge of naturally occurring concentrations of REEs, which are generally in the low ng L^{-1} range in seawater and fresh water and are found in varying concentrations, depending on the surrounding bedrock geochemistry, in groundwater. Hence, direct measurement with state-of-the-art atomic spectrometry techniques is not sensitive enough, particularly if the sample has to be diluted to decrease the total dissolved solid concentration, as required when ICP-MS is applied, to obtain accurate data. Only a handful of methods dealing with the determination of REEs using an on-line approach have been published in the last decade. It is important to stress (again) that the use of an automated flow-manifold is advantageous due to the increased efficiency and the lower risk of contamination and other accidental errors. Table 3 summarizes key analytical performance data of selected publications reporting the determination of REEs in lake water, river water, coastal water and open ocean seawater by ICP-OES and ICP-(SF)MS. All of these methods use on-line SPE mini- or micro-columns incorporating in-house fabricated chelating resins based on the natural polymer chitosan and functionalized with either EDTA-type chitosan[21] or N-(2-hydroxyethyl)glycine as chelating moieties[30]. These resins were used in a fully automated manifold coupled to ICP-OES for the extraction of REEs including Sc and Y from river waters at a pH of 5 with recoveries, assessed from spike experiments, in the range of 90 – 110%[21, 30]. Preconcentration factors were estimated by comparison of peak heights obtained by processing a standard solution with the preconcentration system and conventional nebulization. High preconcentration factors, in the range of 83 – 120 (EDTA-type chitosan) and 83 – 102 (N-(2-hydroxyethyl)glycine-type chitosan) were obtained, except for Y and Sc which were ≤ 30, by processing a sample volume of 20 mL. Due to the operation of the manifold in a “multi-mode” with three synchronized collection systems, up to 12 samples h^{-1} could be analysed for a suite of metals. However, LODs of ≥ 0.002 ng mL^{-1} are relatively high compared with other methods surveyed in this review (see Table 3), which might be attributed to the use of ICP-OES as the detection system.

Resins with IDA and EDTA chelating groups (also referred to as polyaminopolycarboxylic acid groups – PAPC) packed in a chelating column and sold as Nobias PB1M were used by Zhu *et al.* for the determination of REEs in coastal seawater[31], lake water[32] and seawater[33] in an on-line SI manifold directly coupled to ICP-(SF)MS. Initially, 10 mL of seawater were processed within 6 min and a preconcentration factor of 9.6 was obtained, leading to LODs in the range of 0.005 – 0.09 pg mL^{-1}. Recoveries were determined based on spiked sample solutions and the trueness of the method was estimated by comparing published and measured values obtained by the repetitive analysis of CRM NASS-5[31].

Even faster analysis could be performed with an automatic column changing system as reported by the same authors[32]. Elution and measurement of one sample, including the time required for column changing, was performed in 3 min but sample loading was carried out off-line. They compared Nobias PB1M with InterSep ME1, a chelating resin with only IDA moieties. For both resins, a pH of 5.0 was optimal for adsorption and similar recoveries, ranging from 97 – 103%, and precision (RSDs of the peak areas) were obtained with identical elution conditions.

Far lower LODs, ranging from 0.0008 – 0.004 pg mL^{-1}, could be obtained using an automatic pH-adjustment system for SPE of REEs on Nobias-PB1M from seawater by preconcentrating 50 mL of sample[33]. As sample pH is crucial for the sorption efficiency of the target metals and each sample manipulation step (i.e. a manual pH adjustment) increases the risk of contamination, the main focus of this work[33] was the development of a device for automated and contactless pH-adjustment and monitoring, involving the addition of a quantity of aqueous ammonia solution into the sample via a nebuliser, which was controlled by an electromagnetic valve while the transmitted light at 550 nm (the pH indicator was methyl red) was spectrophotometrically monitored. The system has been used to pH adjust sample volumes of 20 to 100 mL within < 5 min per sample prior to REEs determination using the automatic column changing system described above[32]. Blank values measured were significantly lower compared with those obtained by applying “conventional” pH-adjustment with glass- or all-plastic pH electrodes, leading to improved LODs. Spike recovery experiments with two concentration levels were performed to validate the method but CRMs were not analysed.

The use of the commercially available seaFAST^{TM} system (Elemental Scientific Inc.), coupled to ICP-QMS, has been reported by Hathorne *et al.*[34] LODs in the range of 2 – 302 ppq, determined from a 2% HNO_3 solution, were reported by preconcentrating 7 mL of seawater on the commercially available chelating resin Nobias PA1, which has similar chelating moieties to Nobias PB1M. The system allows automated in-line buffering of the sample and is equipped with trace metal clean-up columns in the up-take capillaries, which deliver buffer solution and carrier. This resulted in extremely low background signals and hence low signal/noise ratios for most REEs. By adjusting the pH value of the samples loaded onto the column to pH 6.0, yields in the range of 94 – 102% were obtained. Yields were estimated by comparing time resolved peaks of a matrix matched (NaCl) standard solution containing 5 ng L^{-1} of REEs after preconcentration with signals obtained from standards diluted in the eluent by bypassing the column. The authors state the susceptibility to errors during the determination of column yields (absolute recoveries) if there is any inconsistency in the acid strengths of eluted and directly analysed standards, which leads to the conclusion that the accurate determination of column recovery is not easy. Trueness of the reported method was appropriately assessed by standard additions of deep Atlantic seawater samples, isotope dilution analysis (for Nd) and by measuring reference samples such as NASS-5 as well as 1:10 diluted VIDAC18 reference mine waste water and SCREE and PPREE reference acid mine waters produced by the United States Geological Survey (USGS), and diluted in different matrices with an appropriate content of NaCl to mimic seawater matrixes.

In addition to commercially available chelating resins, a graphene oxide-TiO_2 composite was synthesized as a novel and inexpensive type of carbon-based nanomaterial and packed into a micro-column for the online preconcentration and ICP-OES detection of La, Ce, Eu, Dy and Yb (additionally Cu and Pb)[35]. High adsorption capacity, fast sorption kinetics, and stability over a wide pH range have been reported due to the unique characteristics of the material, e.g. the large surface area and various oxygen containing groups which offer binding sites for metal ions such as heavy metals and REEs. Adsorption kinetics have been well studied in this work and the adsorption capacity obtained was indicated to be comparable with related SPE materials. Preconcentration factors of 10 could be obtained, yielding LODs in the range of 0.13 – 2.64 ng mL^{-1}. They are, however, orders of magnitude higher compared with those obtained using the chelating resins described above, in particular those obtained using EDTA/IDA functionalized resins, and significantly higher than those obtained with chitosan based chelating resins[21, 30], even though the detection system in this case was also ICP-OES, and thus the graphene oxide-TiO_2 composite is not a viable low-cost alternative for the preconcentration of REEs from natural water samples.

It is worth stressing that the accurate quantification of REEs by atomic spectrometric detection techniques in hampered by an exhaustive list of spectral interferences. Emission wavelengths in ICP-OES are interfered by overlapping and partially overlapping spectral lines, and molecular- and background interferences. Various techniques are available to overcome these interferences, particularly the careful selection of interference-free emission wavelengths when ICP-OES detection is performed[21, 30]. A more detailed discussion of interferences and ways to overcome them is described in He *et al.*, 2017[36].

Spectral interferences in ICP-MS include numerous isobaric, as well as polyatomic interferences. Although some of the metals belonging to the group of REEs have 6 or 7 isotopes (e.g. Nd, Sm, Gd, Dy, Er, Yb), most of them have isobaric interferences (e.g. ^{152}Sm, ^{154}Sm, ^{156}Dy, ^{158}Dy and ^{160}Dy

on the respective Gd isotope). Polyatomic interferences are, in particular, lower mass oxides and hydroxides which interfere on higher mass REEs (e.g. $^{139}La^{16}O^+$ on $^{155}Gd^+$ and $^{141}Pr^{16}O^+$ on $^{157}Gd^+$ – the only two Gd isotopes with no isobaric interferences). ICP-QMS equipped with an octopole reaction/collision cell with He as collision gas has been used to overcome oxide and polyatomic interferences[33, 119], however, as stated in Zhu end Zheng (2018)[119], the formation of lighter REEO$^+$ is inevitable. ICP-SFMS operated in the “high-resolution mode” ($m/\Delta m > 10000$) could separate some of these polyatomic interferences but with a significant loss in sensitivity, and hence, detection capability. Therefore, this possibility has been scarcely applied (e.g., the “low-resolution mode” has been used in the studies published by Zhu *et al.* (2009 and 2010)[31, 32]). A prerequisite is to minimize oxide formation rate by monitoring the CeO^+/Ce^+ and UO^+/U^+ ratios, and the interference ratio of MO^+/M^+ when mathematical interference correction is performed, as applied by[31, 32, 33]. Desolvation units such as the CETAC Aridus™ II or the APEX membrane desolvaters (Elemental Scientific Inc. Omaha, Nebraska) can significantly reduce the oxide formation rate down to < 0.05%; however, these devices have not been used in this context (for more detailed information the reader is referred to Fisher and Kara (2016)[37] and references therein.

3.3 Precious metals

In this section, on-line matrix separation and preconcentration methods based on solid phase extraction for the quantification of precious metals are discussed (see Table 3 for details of selected methods). The determination of precious metals, including the platinum group elements (PGEs) Ru, Rh, Pd, Os, Ir and Pt, as well as Ag and Au, in natural waters is still in its infancy. Naturally occurring concentrations are in the sub-ng L^{-1} - pg L^{-1} range, thus requiring powerful extraction and preconcentration methods. However, the interest in the determination of, in particular, PGE concentrations in the aquatic environment is steadily increasing because of anthropogenic emissions resulting from their use in industrial, chemical, electrical and pharmaceutical applications and in catalytic converters for cars[38]. Silver has also been used in a wide variety of chemistry, electronics, medicine and other industrial fields and is highly toxic to marine organisms due to bio-accumulation[39]. Time consuming as well as potentially harmful methods based on liquid-liquid extraction using ammonium 1-pyrrolidinedithiocarbamate/diethylammonium diethyldithiocarbamate (APDC/DDDC) and co-precipitation and flotation techniques are being replaced by methods based on SPE using chelating sorbents, prior to detection by atomic spectrometry. Due to the characteristic of these metals to mainly occur as anionic chloro-complexes in the aqueous phase, as facilitated by the chloride content in seawater[40, 41], (strong) anion exchangers have traditionally been used. However, few publications report the automation and online separation/preconcentration of precious metals from natural waters. More than 10 years ago, a method was published for the determination of Pt using a chelating ion exchange resin (silica gel modified with 1,5-bis(di-2-pyridyl)methylene thiocarbohydrazide - DPTH-gel) in an on-line flow system coupled to ETAAS[42]. Since this publication is not within the timeframe herein selected, it will not be discussed further; nevertheless, it is worth mentioning that the LOD obtained by this method is not sufficiently low for monitoring naturally occurring concentrations of these metals. An improved method, based on the extraction of Pt, Pd and Ir on 1.5-bis(2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass (PSTH-cpg) in an on-line mode coupled to ICP-MS [43], could achieve LODs in the low ng L^{-1} range with a sample volume of only 3.3 mL (details are given in Table 3). However, the concentrations of the target analytes could still not be quantified in unspiked seawater and river water samples, clearly indicating that the sample volume processed by the on-line flow system does not provide adequate preconcentration factors for the determination of PGEs in natural waters.

As a viable alternative to commercial strong anion exchangers, polyaniline (PANI) has been evaluated for the on-line preconcentration of Pd from natural waters including ground water, lake water and seawater as a low cost and easy to synthesize alternative to other sorbents[44]. The extraction mechanism is based on anion exchange and preconcentration factors of 125 have been reported by applying a sample volume of 250 mL, thus resulting in LODs of 0.0004 – 0-003 ng mL^{-1} (LODs given for individual Pd isotopes) with ICP-MS detection. These however are still not sufficiently low for monitoring natural Pd concentrations. It should be mentioned here that chemical vapour generation of these elements for introduction into atomic spectrometric sources has been tested and evaluated (please see On-line sample preparation techniques based on cold vapour- and hydride generation techniques for matrix separation and preconcentration of metals and metal species in natural waters. 4 and Table 5).

Several methods were published for the automatic on-line preconcentration and matrix separation of Ag from seawater more than 10 years ago e.g.[45, 46] using the strong anion exchanger Dowex®1x8 with trimethylbenzylammonium functional groups immobilized on a styrene-divinylbenzene gel but only one method has been published recently for the analysis of estuarine samples[47] using the same sorbent. This resin is very popular for the extraction of Ag chloro-complexes as it has a high adsorption capacity. With a sample consumption of only 7.5 mL, a LOD of 0.06 ng kg^{-1} was obtained. This LOD is comparable with those obtained by the two previous methods[45, 46]. The advantage of the latter method, however, is the lower sample volume required (7.5 mL vs 12 mL) and the low column volume of only 18 µL. Validation was performed with SLEW-3 and CASS-4 certified reference materials. These are not certified for Ag but the authors demonstrated the trueness and good precision of the method by comparing these values with previously reported concentrations.

3.4 Actinides

In this section, on-line matrix separation and preconcentration methods based on solid phase extraction for the quantification of actinides (Th, U) are discussed (see Table 3 for details of selected methods). The actinide elements encompass Ac, Th, Pa, U and the transuranic elements, whereas U and Th are the most abundant actinides naturally occurring in all environmental compartments[48]. Additionally, anthropogenic sources of these radionuclides and their synthetic isotopes (^{232}U, ^{233}U, ^{236}U and ^{229}Th) include technological applications (metallurgy, ceramic and nuclear industries), phosphorous mineral fertilizers and pesticides, uranium mining and milling, coal combustion, fuel processing, nuclear power plants and nuclear tests[49, 50]. Due to the high chemical and radiological toxicity of their soluble compounds, permissible limits of U in drinking water are regulated by the Word Health Organisation (WHO; 30 µg L^{-1}) [51], Environmental protection Agency (EPA; 30 µg L^{-1}) [52] and the Atomic Energy Regulatory Board (AERB; 60 µg L^{-1}) [53]. In the last revision of the Drinking Water Directive of the European Commission (EC)[54], U was included in the list of parameters of naturally occurring but harmful substances to be monitored. In addition, environmental quality standards for freshwater have been elaborated by some member states, ranging from 0.015-25 µg L^{-1} [55] within the EU Water Framework Directive. The WHO also set guidance levels for radionuclides in drinking water, i.e. 10 Bq L^{-1} for ^{238}U (81 µg L^{-1}) and 1 Bq for ^{232}Th (246 µg L^{-1})[51]. Thus, concentrations in the (aquatic) environment need to be monitored. Various methods, mostly employing SPE on actinide specific resins such as TEVA, UTEVA, TRU and DGA resins, based on flow analysis in combination with atomic spectrometric detection, have been reported for the determination of actinides in natural waters e.g. [56, 57 ,58 ,59]. They were, however, operated with off-line detection, mostly by applying two or more different resins to cover a wider range of analytes and perform in-line extraction chromatographic separation and hence are not within the scope of this manuscript.

One method has been published for the simultaneous determination of U and Th at environmentally relevant concentrations in various water matrices based on a fully automated lab-on-valve FI system coupled to ICP-QMS[60]. The performance characteristics are outlined in Table 3. Extraction and simultaneous elution, i.e. no separation involved, was based on SPE using the UTEVA chromatographic resin functionalised with dipentyl pentylphosphate (DP[PP]) moieties (also called diamyl amylphosphate (DAAP). The authors estimated a resin durability of

150 injections (up to 8 mL sample volume) and reported recoveries of > 95%, determined by analyte-spike recovery experiments, and clearly pointed out the low cost of the method as only 30 mg of resin were packed on-line in the column. They also reported the suppressive effect of high concentrations of phosphate due to the formation of a non-extractable charge neutral complex with Th^{4+} cations. Addition of Al^{3+} counteracts this due to the formation of Al^{3+}-phosphate complexes which inhibits Th-phosphate complexation. It should, however, be mentioned that method validation has not been properly performed with matrix certified reference materials; instead the authors used a BCR-320R sediment material.

3.5 Metal speciation

There are many publications on the use of ICP-MS and ICP-OES, as well as AAS, combining on-line sample preparation with elemental speciation analysis of metal(loid)s in natural waters[61]. Arsenic is the most commonly studied metal, followed by Cr and, to a lesser extent, Hg, Sb, Fe, Se and V. In general, elemental speciation involves the differentiation between oxidation states or organic/inorganic elemental fractions. Historically, research and development on elemental speciation analysis was mainly curiosity driven; however, biogeochemical, biological and toxicological effects as well as bioavailability of the elements are highly dependent on their chemical form. Nonetheless, legal institutions and governmental agencies such as WHO, US EPA and EC (e.g. via the EU Water Framework Directive[62]) still define environmental quality standards and limits only for the total elemental concentrations, including all (toxic) compounds. On-line SPE is mainly used for separation of elemental species or fractions of interest in combination with atomic spectrometric detection and only very few studies deal with the on-line combination of SPE with liquid chromatographic separation. The key analytical performance data for selected papers using on-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the speciation of metals in natural waters are summarised in Table 4.

Chromium speciation with SPE was performed on-line in several studies using either ETAAS[63, 64, 65] or ICP-MS[66, 67, 68, 69] as the detection technique. In general, these studies achieved LODs in the low ng L^{-1} range and trueness was, in most cases, demonstrated using CRMs. In 2008, Hu *et al.*[68] reported a useful method for the simultaneous speciation of inorganic As(III)/As(V) and Cr(III)/Cr(VI) in natural waters. They used mesoporous Al_2O_3, which was prepared by sol-gel technology, as a capillary micro-extraction coating material. The column retained AsO_4^{3-} and $Cr_2O_7^{2-}$/CrO_4^{-} under acidic condition while cationic As(III) and Cr(III) were not retained. Elution of the retained species was performed under alkaline conditions. They reported LODs of 0.7 and

18 ng L^{-1} for As(V) and Cr(VI), and 3.4 and 74 ng L^{-1} for As(III) and Cr(III), respectively. Evidently, such differential approaches can also be performed on-line with ETAAS. Zou *et al*.[65] combined a *C. vulgaris* cell (green microalgae) mini-column in sequential combination with an anion exchange resin mini-column for the retention of Cr(III) and Cr(VI), respectively. Utilizing a SI system, Cr(III) and Cr(VI) were eluted by 0.04 mol L^{-1} and 1.0 mol L^{-1} nitric acid, respectively, and quantified on-line with ETAAS. LODs were 0.02 µg L^{-1} for Cr(III) and 0.03 µg L^{-1} for Cr(VI), which unfortunately does not meet the California Public Health Goal set to 0.02 µg L^{-1} for Cr(VI).

Selenium speciation is of great interest as the toxicity, bioavailability, and essential nature of this element is highly depending on its chemical form. Huang *et al*.[70] published a double column method combining nanometre-sized Al_2O_3 and mesoporous TiO_2 which was chemically modified by dimercaptosuccinic acid. A schematic diagram of the flow manifold used for this work is shown in Fig. 3. The inorganic selenium species Se(IV) and Se(VI) were selectively adsorbed by Al_2O_3 while the organic Se species, i.e. the seleno-amino acids selenocysteine and selenomethionine, which were not retained on the first column, were retained on the chemically modified, mesoporous TiO_2. Sequential elution enabled the selective and sensitive determination of the four species (LODs were in the range of 45 - 210 ng L^{-1}) in lake water.

Vanadium, like Se, is one of the major essential elements, but also has toxic properties depending on both the concentration and oxidation state. Xiong *et al*. [71] speciated V(IV) and V(V) on a conical micro-column packed with cetyltrimethylammonium bromide-modified alkyl silica. The species showed different pH dependent retention behaviour: V(V) was quantitatively retained in the pH range 2.0 – 7.0, while V(IV) was not retained at pH 2.0 - 3.5 but quantitatively retained at pH 5.0 - 7.0. V(IV) was quantified by subtracting V(V) from total V. The LOD for V(V) was 0.03 µg L^{-1}.

It can be concluded that FI in combination with elemental speciation analysis is mature in terms of the technical developments, which have been achieved over many decades. The situation regarding CRMs certified for elemental species is still not well developed, as for many matrices no reliable materials are available. Regarding validation, the authors of this work wish to emphasise that in order to assure comparability of different studies in terms of LODs and LOQs and in terms of their applicability to control legal limits, improvements towards setting a harmonized procedure are much needed. Evidently there are several ways to calculate these values for transient signals, but most of the time the procedures are not fully described or completely missing. Accordingly, we propose adoption of the well elaborated procedure outlined in the EURACHEM guide "The Fitness for Purpose of Analytical Methods"[72] for calculating LODs and LOQs for methods which use peak areas for calibration and quantification purposes.

4 On-line sample preparation techniques based on cold vapour- and hydride generation techniques for matrix separation and preconcentration of metals and metal species in natural waters.

Cold vapour generation (CVG) and hydride generation (HG) techniques have been used in on-line flow systems to separate the analyte from the matrix, in some instances in combination with sorptive preconcentration using chelating sorbents. A precondition, however, is the formation of volatile species upon reaction with reducing agents such as sodium borohydride in an acidic environment. The classical elements determined by HG are Ge, Sn, As, Bi, Sb, Se and Te after chemical transformation into their gaseous hydrides, whereas e.g. Hg and Cd are determined by CVG after volatile species are generated. It should be mentioned that for the reduction of inorganic Hg, tin chloride can also be used. Through gas/liquid phase separation by an argon gas carrier stream, the volatile hydrides/elements are transported into the plasma or graphite furnace. Matrix separation is based on the fact that non-volatile interfering elements such as major ions do not form hydrides, and thus remain in the liquid phase and are drained off to waste. Hydride analyte transport efficiencies up to 100%, leading to higher signal/noise ratios, and hence lower LODs, in comparison with conventional liquid sample introduction, are reported[73]. HG/CVG is an important sample introduction technique when coupled on-line to atomic spectrometric detectors[73] but careful optimization of the hydride generation process is required, e.g. the concentration of the reducing agent because too high a concentration of $NaBH_4$ may lead to foaming and the production of droplets as well as the generation of excessive hydrogen gas. These factors result in plasma instability[74], especially when coupled to ICP-based detectors.

Methods employing CV and HG techniques for the matrix separation and preconcentration of metals in natural waters are summarized in Table 5.

Only a limited number of papers have been published within the last decade reporting the determination of As[75], Cd[76] and Hg[77] in natural waters after HG and CV generation with $NaBH_4$ without preconcentration on chelating sorbents. For example, for the quantification of Hg, the CV technique, even without preconcentration, LODs are reported to improve by a factor of 24 when CV-ICP-QMS is used compared with solution nebulization based ICP-QMS due to reduced signal suppression from matrix effects[77].

Nevertheless, also in combination with CV and HG techniques, matrix effects with a negative effect on the accuracy and sensitivity of these methods have been observed. To overcome matrix interferences arising from e. g. Ca, Mg, K and Na, as well as various transition metals (Cu, Fe, Ni, Co) present in natural waters at high(er) concentrations, SPE based on ion-exchange has been applied prior to HG/CV generation in various applications (see Table 5). The challenge here is to find the optimum acid concentration for both the elution of the retained metal species from the preconcentration column (stronger acids usually enhance recovery) and efficient hydride generation as this process is strongly dependent on the pH and acid strength. For example, Sb, Bi and Sn were preconcentrated from seawater on DPTH bonded to silica gel (DPTH-gel) packed in a mini-column prior to HG-ICP-QMS analysis[78]. As hydride generation efficiency depends on the oxidation state of the elements, *L*-cysteine was used as a pre-reducing and masking agent. Increased signal intensities could be obtained for Sn, whereas those for Sb and Bi were not affected by *L*-cysteine addition. Enrichment factors of 2.5 – 8.6 were achieved with a sample volume of 4.8 mL. Limits of detection were in the sub µg L^{-1} range and sufficiently low for the determination of these elements in diluted CRMs and real seawater samples. A similar approach has been applied to the determination of these elements and, in addition, Hg from seawater and river water[13**Error! Bookmark not defined.**]. DPTH was functionalized on mesoporous silica, packed in a mini-column and elution was performed with HCl (plus thiourea for Hg) while in [78] HNO_3 alone was used instead. A comparison between these two methods showed similar performance for Sb, Bi and Sn with respect to trueness (estimated from TMDA 54.4 and TM 24.3 fortified lake water CRMs), precision, relative recovery and the detection capability of ICP-QMS vs ETAAS.

Sánchez-Trujillo *et al.*[79] addressed a problem associated with simultaneous multi-element determinations for Pb, Cd and Hg using CVG-ICP-QMS, i.e., different optimal conditions are required for individual elements. Catalysts such as thiourea and Co were used for more efficient reaction of Cd, and hexacyanoferrate (III) was proposed as an oxidizing reagent for the conversion of Pb(II) to Pb(IV) ([79] and therein cited publications). The elimination of interferences on the determination of other elements requires the use of appropriate sorbent materials, oxidizing agents and catalysers. In fact, two mini-columns packed with DPTH-gel were incorporated in the flow manifold in parallel, *viz*., in the injection loop of two rotary valves, and loaded with sample adjusted to pH 5.0. Elution with thiourea in HNO_3 was performed, and whereas the eluted metals from the first column were mixed with a reducing agent consisting of $NaBH_4$ and $K_3Fe(CN)_6$ for the generation of PbH_4 (and Hg^0 vapour), those eluted from the second column were mixed solely with $NaBH_4$ for Cd^0 and Hg^0 vapour generation. Hence, the most efficient vapour generation conditions for each element were obtained. Enrichment factors in the range of 14.4 – 27.3 were obtained and LODs were in in the low ng L^{-1} range. However, these are at least 3 times higher than those obtained by HG/CVG methods developed for the single element determination of e.g. Hg[77], Cd[76] and Pb[80] (see Table 5), probably due to the addition of reagents for pH adjustment, oxidation and improved elution efficiency contributing to the blank signal.

Noble metals are not traditionally analysed by CVG due to the unknown identity and formation efficiency of their hydrides and volatile species but recent studies have shown its suitability for the determination of Pt, Pd, Ir[81], and also Os, Rh, Ag and Au [82, 83.] using $NaBH_4$ as the reducing agent. The target analytes were preconcentrated using SPE on DPTH-gel81 packed in a mini-column and MSPE on DPTH immobilized on iron oxide magnetic nanoparticles (DPTH-MNPs)82 and DPTH immobilized on magnetic graphene oxide (DPTH-GO)[83], which were retained in a knotted reactor by an external magnetic field, with the analytes eluted with thiourea in HCl or HNO_3 prior to online ICP-OES detection. Detailed methodological information is given in Table 5. Since chemical vapours of noble metals are unstable, rapid transition and separation from the liquid phase into the gas phase and introduction into the detection system is required, thus making this procedure very sophisticated. The spray chamber has been used as a gas-liquid separator in these studies. By mixing the analytes with the reducing reagent via a T-junction just before the nebulizer the formation of volatile species is improved but efficiencies were lower compared with “conventional” SPE without CVG[81]. *In situ* CVG using a commercially available multi-mode sample introduction (MMSI) system for CVG and liquid nebulization, which also served as gas/liquid separator, was a pre-requisite for the applicability of this approach for efficient vapour generation. It was shown that hydride formation in the presence of $NaBH_4$ was appropriate for Ag, Pt, Pd and Os whilst Au, Ir and Rh signals did not improve compared with non-CVG results, hence requiring the use of compromised conditions[82]. A preferred or missing formation rate of noble metal volatile species has not been reported by García-Mesa (2019)[83]. Widely ranging enrichment factors – depending on the applied method and the analytes – were reported and LODs were in the low µg L^{-1} and sub-µg L^{-1} ranges, i.e. not sufficiently low for the determination of ambient noble metal concentrations in natural waters.

Sample introduction techniques based on CV and HG have also been used in this context with elemental speciation analysis. Details of selected methods are summarized in Table 6. Two studies have addressed the separation of inorganic mercury and methyl mercury. Krishna *et al.* [84] developed a speciation approach for the two fractions employing efficient preconcentration of natural water samples (pH 7) on a polyaniline microcolumn and subsequent selective elution of MeHg and iHg using 2% HCl and a mixture of HCl–thiourea (2% HCl + 0.02% thiourea) respectively. This successful combination of preconcentration, speciation and CVG-ICP-MS (all on-line) enabled quantification of the two species in the high ng L^{-1} range. Sánchez-Trujillo *et al.* [85] published a similar concept using on-line CVG-ICP-MS after on-line enrichment/speciation of the two Hg-fractions on mesoporous silica functionalized with 1,5-bis(2-pyridyl) methylene thiocarbohydrazide. Selective elution of CH_3Hg^+ and Hg^{2+} was obtained with 0.2% HCl and 0.1% thiourea in 0.5% HCl, respectively. Total mercury (calculated as the sum of the two fractions) was determined in LGC 6016 (Estuarine Water) and was in good agreement with the results obtained by the same group in an earlier study[79]. The LODs in this work were lower than those obtained in the earlier study using the polyaniline material, which can be explained mainly by the use of a next generation ICP-MS detection system. In a similar approach to that used in many other studies, method LODs in the two above mentioned studies were calculated from background noise, its standard deviation and the height of a measured standard solution. It is noteworthy that this method allows relative inter-comparison of different methods but is not capable to give reliable LODs or LOQs, as quantification is routinely performed via peak integration (peak area), whereas in these cases LODs/LOQs are calculated via peak height.

HG was used in studies on the speciation of different oxidation states of As[86, 87] and Sb[74]. One report concerning As used a differential approach by passing natural water sample through a strong anion exchanger cartridge, on which As(V) was selectively retained, whereas As(III) passed through the column and was detected via HG AAS[86]. The concentration of As(V) was then determined by subtracting the As(III) concentration from the total As concentration of the sample. LODs were of the order of 0.5 µg L^{-1}. The authors discussed the limitations of their work regarding organic As species (which would also pass through the column and lead to false positive As(III) results) and present a method that is fast and reliable and suitable for the analysis of low salinity natural waters for As(III). A very recent study has been published by Montoro-Leal *et al.*[87] using functionalized Fe_3O_4 magnetic nanoparticles packed in two knotted reactors for inorganic As speciation in environmental waters following a similar differential approach. However, speciation was based on different reduction conditions; thus, different concentrations of borohydride were used. This method showed a high sample throughput and very low detection limits of 2.7 and 3.2 ng L^{-1} for As(III) and total inorganic As and has been validated for the determination of As in highly saline samples such as seawater. For the speciation of inorganic Sb, selective sorption materials were used in a FI approach with sequential elution and on-line HG-ICP-MS detection[74]. Accuracy was demonstrated for the sum of the quantified Sb species by the analysis of the CRMs SLRS-5 River Water and TMDA-54.4 Fortified Lake Water. It should be mentioned that, due to the lack of species-specific CRMs, it is difficult to assess method accuracy with regard to the target species. In such cases inter-comparison with independent methods available in-house, or inter-comparison with other competent laboratories is mandatory for method validation/verification in terms of trueness.

5 On-line sample preparation techniques based on liquid-liquid-micro extraction techniques for matrix separation and preconcentration of metals in natural waters.

There are a limited number of published papers dealing with liquid-phase microextraction (LPME) in flow systems for trace element analysis in surface waters as compared with those using SPE[10]. This is attributed to operational difficulties in achieving (i) reliable dispersion of the aqueous and organic phases across the conduits of flow platforms, (ii) quantitative separation under the flow regime of the analyte-containing organic phase after extraction and (iii) high enrichment factors on account of the limited organic to liquid-phase ratios in miniaturized systems. Moreover, metal species usually need to be derivatized prior to LPME[88] , in contrast to SPE for which there is a plethora of commercially available sorbents with a wide range of chelating moieties for direct extraction and preconcentration at the appropriate pH. The key analytical performance data for selected papers LPME approaches for the matrix separation and preconcentration of metals in natural waters are summarised in Table 7.

Some of the FI-based papers on LPME for trace metal determinations merely report semi-automatic methods. The flow platform is used for automation of the detection step after batch LPE[89], or phase separation by modification of the ionic strength or temperature and retrieval of the metal-containing phase for detection[90].

Computer-controlled flow methodologies using programmable flow, such as sequential injection analysis and its variants[91, 92, 93], have been designed for the miniaturization of LPME schemes, endowing these methods with green chemical credentials whilst also ameliorating extraction efficiencies and enrichment factors. For example, Anthemidis and co-workers have developed a number of appealing LPME variants, such as dynamic single-drop LPME[92, 93], countercurrent LPME[88] and dispersive LPME (DLPME)[94, 95, 96 ,97] that were fully automated as a front-end to FAAS or ETAAS for direct on-line injection of the metal-enriched organic phase. In those articles dealing with DLPME[94, 95 ,96, 97], the aqueous sample, organic solvent containing the chelating reagent and dispersing solvent were merged on-line to generate droplets of the organic phase for efficient extraction of the neutral chelates followed by on-line trapping of the metal containing organic droplets into reversed-phase materials packed in flow-through micro-columns. A schematic diagram of a flow manifold integrating in-line DLPME as a front end to ETAAS is shown in Fig. 4.

The main issue observed by a number of FI/SI systems incorporating LPE/LPME, alike SPE, is that method validation is performed with overly simplistic CRMs (e.g. lyophilised solutions[91]) or entirely different matrices (e.g., sediments and mussel tissues) that do not properly simulate the composition of the target matrices (river water, seawater) analysed in those papers[97, 88 ,93].

Moreover, FI/SI-based LPME methods sometimes use environmentally unfriendly solvents, and on-line coupling to standard ICP instrumentation is more complicated as compared with SPE because of potential incompatibility of the extracting medium (back-extraction is usually recommended instead), thus making multi-elemental analysis troublesome.

6 Conclusions and perspectives

FI has become a mature approach for metal determination and non-chromatographic speciation analysis, but still constitutes a viable platform and vehicle for on-line implementation of in-house and commercially available sorptive (nano)materials prior to atomic spectrometric detection systems for trace and ultra-trace analysis. When comparing theon-line sample preparation approaches discussed herein (i.e., LPME, SPE, CV/HG), SPE is by far the most attractive because it offers superior performance in terms of versatility, reliability and enrichment capability for trace elements in freshwater systems. The analytical detection techniques have not greatly evolved in terms of sensitivity and instrumental detection limits over the last 10 years and thus efficient sorbent phases and ligands for element preconcentration and clean-up analysis of natural waters are still required. It should however be noted that some of the analytical methods reported in the literature that include enrichment protocols are not sensitive enough for the analysis of natural waters and thus spike concentration levels that are not environmentally relevant of natural waters are used for method validation instead. Likewise, inappropriate reference materials, such as biological materials, sediments and wastewaters, have been selected for evaluation of the trueness of methods applied to natural waters. It is therefore recommended that QC/QA tools and uncertainty measurements should be adopted in fully validated protocols using FI approaches.

The last two decades have also witnessed the advent of novel miniaturized and portable devices based on mesofluidic Lab-on-Valve and microfluidic Lab-on-chip platforms, yet application to continuous on-line monitoring is still in its infancy.

Acknowledgement

Manuel Miró acknowledges financial support from the Spanish State Research Agency (AEI) and Ministry of Science, Innovation and Universities (MCIU) through projects CTM2017-84763-C3-3-R (MCIU/AEI/FEDER, EU) and CTM2017-90890-REDT (MCIU/AEI/FEDER, EU).

Table 1: Multi-element on-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the determination of the total metal concentration of transition metals and metalloids in natural waters. (All units as in the original publication)

Analyte	**Matrix**	**Solid phase**	**Detection technique**	**Sample treatment/ Elution**	**Figures of merit**				**Validation**	**Sample volume**	**Enrich-ment factor**	**Sample through--put**	**Ref**
					DL	**Linear range**	**Precision**	**Relative Recovery**					
Mn, Co, Ni, Cu, Pb	River water	PMMA microchip (treated with saturated NaOH)	ICP-MS	pH 6 (NH_4Ac)/ 0.5% HNO_3	Mn: 2.62 ng L^{-1} Co: 1.69 ng L^{-1} Ni: 42.54 ng L^{-1} Cu: 13.85 ng L^{-1} Pb: 1.64 ng L^{-1}	Up to 5 μg L^{-1}	2.9-3.6% (n=3)	83-110%	NIST 1640a trace elements in natural water	20 μL	≥2	19.35 h^{-1}	[24]
Zn, Cu, Cd, Cr, V, As	River water, lake water (*well water)	MWCNTs-silica	ICP-OES	pH 8.5/ 2 M HCl	Zn: 0.27 μg L^{-1} Cu: 0.11 μg L^{-1} Cd: 0.45 μg L^{-1} Cr: 0.91 μg L^{-1} V: 0.55 μg L^{-1} As: 0.67 μg L^{-1}	LOD–100 μg L^{-1}	3.1-8.6% at 10 μg L^{-1} (n=7)	82-115%	GSBZ50009-88, GSBZ 50029-94 environmental waters	6 mL	10	n.a.	[98]
Co, Fe, Pb, V	Seawater	Toyopearl AF-Chelate-650	ICP-MS	pH 5 (NH_4Ac)/ 1 M HNO_3	0.021-0.34 nmol L^{-1}	n.a.	4-23%	76.111%	NASS-5 seawater, GEOTRACES reference samples	7.5 mL	10-15	8.25 min/ sample	[18]
Mn, Co, Ni, Cu, Cd, Pb	River water	PMMA	ICP-MS	pH 8 (maleate buffer)/ 0.5% HNO_3	Mn: 20.6 ng L^{-1} Co: 5.44 ng L^{-1} Ni: 11.86 ng L^{-1} Cu: 4.90 ng L^{-1} Cd: 16.11 ng L^{-1} Pb: 3.48 ng L^{-1}	0.05-100 μg L^{-1}	< 9% CV (long term)	82-118%	NIST 1643a artificial saline water	50 μL	n.a.	13.33 h^{-1}	[23]
Mn, Fe, Co, Ni, Cu, Zn	Seawater	Nobias PA 1	ICP-SFMS	pH 5.7, pH 7.0 ($AcNH_4$)/ 1.6 M HNO_3	Mn: 0.002 Co: 0.00029 Fe: 0.014 Ni: 0.013 Cu: 0.003 Zn: 0.016 nmol kg^{-1}	n.a.	1-3% for Ross seawater (long term)	96-107%	GEOTRACES reference samples	9 mL	200	8.75 min/ sample	[9]

Cd, Co, Cu, Ni, Pb, Zn	Oceanic waters	IDA	ICP-MS	pH 6.0 (AcNH$_4$)/ 0.8 M HNO$_3$	Co: 3.2 pM Ni: 23 pM Cu: 46 pM Zn: 71 pM Cd: 2.7 pM Pb: 1.5 pM	up to: Co: 0.89 nM Ni: 24 nM Cu: 9.6 nM Zn: 20 nM Cd: 2.8 nM Pb: 0.59 nM	3.4-8.6% for SAFe D2	92-102%	NASS-5 seawater, GEOTRACES reference sample (SAFe)	7 mL	10	6 min/ sample	[99]
Co, Cr, Ni, Cd, Mn, Zn, Cu, Pb	Seawater	PTSH-cpg resin	ICP-MS	pH 8.0±0.5 (borate/ boric acid buffer)/ 5% (m/m) HNO$_3$	Co: 0.002 µg L^{-1} Cr: 0.057 µg L^{-1} Ni: 0.117 µg L^{-1} Cd: 0.004 µg L^{-1} Mn: 0.21 µg L^{-1} Zn: 0.260 µg L^{-1} Cu: 0.030 µg L^{-1} Pb: 0.020 µg L^{-1}	DL-60 µg L^{-1}	< 5% (at twice the DL, n=10)	82-111%	SLEW 3 and LGC6016 estuarine water, CASS-5 coastal seawater, SLRS-5 river water, TMDA-54.4 fortified lake water	2.1 mL	2.2-6.8	8.6 h^{-1}	[20]
Cd, Pb, Cu	River water, lake water, (*urine)	SCX Bond Elut® Plexa™ PCX	FAAS	pH 2 (HNO$_3$)/ 1 mol L^{-1} HCl	Cd: 0.1 µg L^{-1} Pb: 1.8 µg L^{-1} Cu: 0.5 µg L^{-1}	Cd: 0.4-20 µg L^{-1} Pb: 7.5-450 µg L^{-1} Cu: 1.8-100 µg L^{-1}	Cd: 2.9% at 2 µg L^{-1} Pb: 3.1% at 30 µg L^{-1} Cu: 2.7% at 10 µg L^{-1} (n=10)	95-99%	NIST CRM 1643e trace elements in water, (°BCR 278-R trace elements in mussel tissue)	2 mL	90-95	30 h^{-1}	[100]
V, Cr, Cu, As, Pb	River water and tap water (*amongst others)	S-CS-MWCNTs	ICP-MS	pH 7 (HNO$_3$, NH$_3$ H$_2$O)/ 0.5 mol L^{-1} HNO$_3$	V: 0.002 µg L^{-1}, Cr: 0.0038 µg L^{-1} Cu: 0.0035 µg L^{-1} As: 0.0013 µg L^{-1} Pb: 0.0036 µg L^{-1}	0.005-10 µg L^{-1}	V: 3.8% Cr: 1.4% Cu: 3.1% As: 4.6% Pb: 1.6% at 1 µg L^{-1} (n=11)	91-105%	GBW08607 riverine water, (°GBW10024 scallop)	20 mL	V. 111 Cr: 95 Cu: 60 As: 52 Pb: 128	n.a.	[101]
Cd, Co, Ni	Seawater	8-HQ	ICP-MS	AcNH$_4$ buffer/ 1 M HNO$_3$	Cd: 0.008 ng mL^{-1} Co: 0.006 ng mL^{-1} Ni: 0.009 ng mL^{-1}	Cd and Co: 0-0.5 ng mL^{-1} Ni: 0.1-1.0 ng mL^{-1}	Cd: 2.47% Co: 2.09% Ni: 3.03% at 0.25 ng mL^{-1} (n=3)	99-110%	CASS-2 coastal seawater, SLEW-1 estuarine water	40 µL	n.a.	n.a.	[102]
Cd, Pb	Coastal seawater, river water, (*tap water)	OASIS HLB	FAAS	On-line complex formation with DDTP/ Methanol	Cd: 0.09 µg L^{-1} Pb: 0.9 µg L^{-1}	Cd: 0.3-12.0 µg L^{-1} Pb: 3.1-200 µg L^{-1}	Cd: 2.9% at 4 µg L^{-1} Pb: 2.6% at 20 µg L^{-1}	95-99%	NIST CRM 1643e trace elements in water	12 mL	Cd: 155 Pb: 180	24 h^{-1}	[103]

Cu, Mn, Ni	River- and lake water	Alumina hollow fibre	ICP-OES	pH 8.5 (NH_4NO_3)/ 2.5 mol L^{-1} HCl	Cu: 0.88 ng mL^{-1} Mn: 0.61 ng mL^{-1} Ni: 0.38 ng mL^{-1}	Up to 200 ng mL^{-1}	6.2-7.9% at 10 ng mL^{-1} (n=7)	87-110%	GSBZ50009-88 environ-mental water	3 mL	10	5 h^{-1}	[104]
V, Cu, Pb, Cr	River- and lake water	Modified meso-porous TiO_2	ICP-OES	pH 6.5 (NH_4Cl/ NH_3 H_2O)/ 1 M HNO_3	V: 0.09 µg L^{-1} Cu: 0.23 µg L^{-1} Pb: 50 µg L^{-1} Cr: 0.15µg L^{-1}	0.3-50 µg L^{-1}	V: 1.7% Cu: 3.9% Pb: 4.6% Cr: 2.9% at 5 µg L^{-1} (n=7)	89-107%	GSBZ50009-88 environ-mental water	6 mL	20	10 h^{-1}	[105]
Co, Cr, Cd, Mn, Zn, Ni	Seawater, river water	DPTH-gel	ICP-MS	pH 8.6 (boric acid/Na tetra-borate)/ 2% (m/m) HNO_3	0.004-0.530 µg L^{-1}	DL-60 µg L^{-1}	0.3-4% at double the conc. used for Dl of the analytes (n=5)	93-110%	SLEW-3 estuarine water, NASS-5 seawater, SLRS-4 river water, TMDA-54.4 fortified water	5 mL	2.3-32.9	10 h^{-1}	[106]
V, Cu, Pb, Cd, Hg	Lake- and river water	Chitosan modified ordered mesoporous silica	ICP-OES	pH 6.5 (NH_4Cl/NH_3 H_2O)/ 1 M HCl	V: 0.33 ng mL^{-1} Cu: 0.30 ng mL^{-1} Pb: 0.96 ng mL^{-1} Cd: 0.05 ng mL^{-1} Hg: 0.93 ng mL^{-1}	n.a.	V: 2.8% Cu: 6.7% Pb: 1.8% Cd: 4.0% Hg: 5.3% at 10 ng mL^{-1} (n=7)	> 90%	GSBZ50009-88 environ-mental water sample	6 mL	20	10 h^{-1}	[107]
Cd, Co, Cu, Mn, Ni, Pb, V, Zn	River water	EDTriA-type chitosan	ICP-OES	pH 5 ($AcNH_4$)/ 1.5 M HNO_3	0.002-0.15 ng mL^{-1}	n.a.	< 10%	90-110%	SRLS-4 river water	5 mL	14-35	28 h^{-1}	[30]
Cd, Co, Cu, Mn, Ni, Pb, V, Zn	River water	Glycine-type chitosan	ICP-OES	pH 5 ($AcNH_4$)/ 1.5 M HNO_3	0.004-0.17 ng mL^{-1}	n.a.	< 10%	90-110%	SRLS-4 river water	5 mL	14-106	27 h^{-1}	[21]
Mn, Co, Cu, Zn, Pb	(*CRMs)	Fe-based MNPs-PAA	ICP-MS	pH 9 ($AcNH_4$)/ 1% HNO_3	0.04-0.06 µg L^{-1} Cu and Zn: 0.6 µg L^{-1}	0.5-50 µg L^{-1}	4% at 5 µg L^{-1} (n=3)	96-109%	CASS-2 nearshore seawater, (°RSM 2670a trace elements in urine)	20 µL	n.a.	5 min/ sample	[26]

Abbreviations:

8-HQ: 8-hydroxyquinoline (8-quinolinol)
cpg: controlled pore glass
DPTH gel: 1-(di-2-pyridyl)methylene thiocarbonohydrazide bonded to silica gel
EDTriA-type chitosan: ethylenediamine N,N,N'-triacetate-type chitosan
IDA: iminodiacetate
MNPs-PAA: magnetic nanoparticles with polyacrylic acid
MWCNTs: multi-walled carbon nanotubes
OASIS HLB: poly(divinylbenzene-N-vinylpyrrolidone) co-polymeric beads
PCX: polymeric cation exchanger
PMMA: poly(methyl methacrylate)
S-CS-MWCNTs: Schiff base-chitosan grafted multiwalled carbon nanotubes
SCX: strong cation exchanger

Table 2: Single-element on-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the determination of the total metal concentration of transition metals and metalloids in natural waters. (All units as in the original publication)

Analyte	**Matrix**	**Solid phase**	**Detection technique**	**Sample treatment/Elution**	**Figures of merit**				**Validation**	**Sample volume**	**Enrichment factor**	**Sample throughput**	**Ref**
					DL	**Linear range**	**Precision**	**Relative Recovery**					
Co	Underground water, (*tap water)	Fe_3O_4 nanoparticles	ETAAS	None/ Ethanol	6 ng L^{-1}	0.01-5µg L^{-1}	2.8% at 0.5 µg L^{-1} (n=11)	96-99%	(°GBW 07303 stream sediment, GBW10017 powdered milk)	2 mL	30	18 h^{-1}	108
Co	(*Only CRM)	*L*-tyrosine functional-ized MWCNTs	FAAS	pH 7.0 ($AcNH_4$)/ 10% (v/v) HNO_3	50 ng L^{-1}	DL-250 µg L^{-1}	2.7-3.4% at 10 µg L^{-1} (n=10)	102%	QC METAL LL2 metals in natural waters	10 mL	180	>600 s/ sample	22
Cu	Coastal and estuarine water	TMA	ICP-OES	pH 5.5 ($AcNH_4$)/ 2% (v/v) HNO_3	0.4 µg L^{-1}	0-50 µg L^{-1}	3.2% at 5.0 µg L^{-1}	91-103%	(°CRM22 fish otoliths, SRM 1400 bone ash)	10 mL	5	n.a.	109
As	(*Cave water, tap water)	Live HeLa cells immobilized on Sephadex G-50 beads	GFAAS	pH 3.0 (phosphate buffer)/ 2 M HNO_3	0.05 µg L^{-1}	0.15-2.5 µg L^{-1}	1.7% at 1.25 µg L^{-1} and 3.4% 0.5 µg L^{-1} (n=9)	97-98%	SRLS-4 river water	450 µL	11	13 h^{-1}	110
Cd	Ground-, river- and coastal seawater	SiMAG-Octadecyl	ETAAS	pH 2.0±0.2 (HNO_3); on-line addition of DDTC/ IBMK	3 ng L^{-1}	9-350 ng L^{-1}	3.9% at 50 ng L^{-1} (n=11)	94-98%	NIST CRM 1643e trace elements in water	5 mL	19	8 h^{-1}	19
Cd	Mineral water, (*tap water, synthetic seawater)	3-MPTMS-MWCNTs	FAAS	pH 7.5 (phosphate buffer)/ 1 M HCl	0.15 µg L^{-1}	1-60 µg L^{-1}	4.04% at 1 µg L^{-1} and 2.34% at 55.0 µg L^{-1} (n=10)	92-110%	NIST SRM 1643e trace elements in natural waters, (°NIST SRM 1573a tomato leaves)	20 mL	31.5	14 h^{-1}	111

Cd	Spring water, rain water, snow water	Fe-based MWNTs	ETAAS	pH 6.0 (NaOH)/ 0.002 mol L^{-1} H_3PO_4 and 0.1 mol L^{-1} HN_4NO_3	1.3 ng L^{-1}	0.003-0.2 µg L^{-1}	2.2% at 0.1 µg L^{-1} (n=11)	97-105%	GBW08608 trace elements in water, (°GBW07404 soil)	1000 µL	31.2	12 h^{-1}	112
Cd	Spring water, rain water, seawater, (*tap water)	*S. cerevisiae* cell-loaded cytopore® beads	GFAAS	pH 6-7 (0.1 mol L^{-1} NaOH)/ 0.8 mol L^{-1} HNO_3	1.1 ng L^{-1}	5-100 ng L^{-1}	3.3% at 50 ng L^{-1} (n=11)	69-102%	(°GBW 07404 soil)	1 mL	30	20 h^{-1}	113
Cd	Mineral water, lake water, (*tap water)	Histidine functionalized MWCNTs	FAAS	pH 8.50 (ammoniacal buffer)/ 0.8 M HNO_3	0.20 µg L^{-1}	2-140 µg L^{-1}	3.11% at 40 µg L^{-1} (n=10)	96-104%	(°Tort 2 Lobster Hepato-pancreas)	15 mL	17.7	16 h^{-1}	114
Cd	River water, spring water, ground water, (*tap water)	Salen/Cd(II) complex imprinted polymer	FAAS	pH 6.8 (Britton-Robinson buffer)/ 1% HNO_3	0.11 µg L^{-1}	1-10 µg L^{-1}	6.3% at 1 µg L^{-1} (n=5)	92-107%	ES-H-2 ground water, (°EU-H-3 waste water)	16 mL	117	20 h^{-1}	115
Pb	Mineral water, (*tap water, synthetic seawater amongst other samples)	IIHC	TS-FFAAS	pH 6.46 (phosphate buffer)/ 0.5 mol L^{-1} HNO_3	0.75 µg L^{-1}	2.5-65.0 µg L^{-1}	5% at 10.0 µg L^{-1} and 3.6% at 60.0 µg L^{-1} (n=10)	93-110%	(°DORM-3 fish protein, MESS-3 and PACS-2 marine sediments)	20 mL	128	n.a.	116
Pb	Ground water, river water, coastal seawater	PEEK	FAAS	On-line complex formation with 0.5% (m/v) DDPA in water/ IBMK	0.32 µg L^{-1}	3.6-300 µg L^{-1}	2.2% at 50 µg L^{-1} (n=11)	95-97%	NIST CRM 1643e trace elements in water, (°IAEA-433 marine sediment, BCR 278-R trace elements in mussel tissue)	22 mL	110	20 h^{-1}	117
Pb	Seawater, (*tap water)	Filamentous fungal biomass-loaded TiO_2 NPs	FAAS	pH 4.0 (HNO_3)/ 1 M HCl	0.78 µg L^{-1}	2.5-10 µg L^{-1}	9.1-1.8% at 2.5-100 µg L^{-1} (n=5)	96-104%	NASS-5 seawater	250 mL	868	n.a.	118

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Abbreviations:
IIHC: ion imprinted polyvinylimidazole-silica hybrid copolymer
MPTMS: mercaptopropyltrimethoxysilane
MWCNTs: multi-walled carbon nanotubes
NP: nanoparticle
PEEK: polyether ether ketone
SiMAG: silica maghemite
TMA: 2-thiozylmethycrylamide
WCNT: wall coated nanotubes

Table 3: On-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the determination of the total metal concentration of rare earth elements, precious metals and actinides in natural waters. (All units as in the original publication)

Analyte	Matrix	Solid phase	Detection technique	Sample treatment /Elution	Figures of merit				Validation	Sample volume	Enrich-ment factor	Sample through-put	Ref
					DL	Linear range	Precision	Relative Recovery					
Rare earth elements													
REEs (incl. Y)	Seawater	Toyopearl AF Chelate 650M®	ICP-MS	pH 5.5±0.2 ($AcNH_4$)/ 0.8 M HNO_3	0.002 ng kg^{-1} (Tm)- 0.078 ng kg^{-1}(Ce)	Up to 200 ng kg^{-1} Tm: 100 ng kg^{-1}	Y6% (n=5)	93-106%	CASS-4, SLEW-3 coastal seawaters	6 mL	n.a.	11 h^{-1}	119
La, Ce, Eu, Dy, Yb	Lake water, river water, seawater	GO-TiO_2	ICP-OES	pH 5 / 1 M HNO_3	0.13-2.64 ng mL^{-1}	0.5-1000 ng mL^{-1}	3.2-8.6% at 10 ng mL^{-1} (n=7)	> 90%	(°GBW07301a stream sediment)	7 mL	10	12 h^{-1}	35
REEs	Seawater	SDCC (Nobias PB 1 M)	ICP-MS	pH 6 ($AcNH_4$)/ 2 M HNO_3	0.00008-0.04 pg mL^{-1}	n.a.	< 3.3% for seawater (n=4)	97-100%	Previous results	50 mL	n.a.	n.a.	33
REEs (incl. Y)	Seawater	Nobias PA 1	ICP-MS	pH 6 ($AcNH_4$)/ 1.5 M HNO_3 + 0.4% acetic acid	1-36 ppq	0.1-10 ppt	< 15-23% for 2000 m seawater sample (n=50)	94-102%	NASS-5 seawater, (°VIDAC18 Portuguese mineral water (1:10 diluted))	7 mL	15	15 min/ sample	34
REEs	Lake water	SDCC (Nobias PB 1 M) and InterSEP ME1	ICP-SFMS	pH 5 ($AcNH_4$)/ 2 M HNO_3	0.013-0.15 pg mL^{-1}	n.a.	1.03%	96-104%	NMIJ 7201-1 river water	10 mL	n.a.	3 min/ sample	32
REEs (incl. Sc and Y)	River water	EDTriA-type chitosan	ICP-OES	pH 5 ($AcNH_4$)/ 2 M HNO_3	0.002-0.095 ng mL^{-1}	n.a.	< 10% at 1 ng mL^{-1}	> 95%	SRLS-4 river water	20 mL	83-120	12 h^{-1}	21
REEs (incl. Sc and Y)	River water	Chitosan based chelating resin	ICP-OES	pH 5 ($AcNH_4$)/ 1.5 M HNO_3	0.002-0.25 ng mL^{-1}	n.a.	< 10%	90-110%	SRLS-4 river water	20 mL	21-102	11 h^{-1}	30
REEs	Coastal seawater	SDCC (PAPC)	ICP-SFMS	pH 5 ($AcNH_4$)/ 2 M HNO_3	0.005 -0.09 pg mL^{-1}	n.a.	<10%	93-99%	NASS-5 seawater	10 mL	9.6	6 min/ sample	31

Precious metals													
Ag	Estuarine - and seawater	Dowex AG1X	ICP-MS	None/ 2.5 M HNO_3	0.06 ng kg^{-1}	LD-1000 ng kg^{-1}	< 3% (n=5)	99-102%	SLEW-3 estuarine water, CASS-4 coastal seawater	7.5 mL	n.a.	7 h^{-1}	47
Pd	Groundwater, lake water, seawater	Polyaniline	ICP-OES, ICP-MS	No acidification/ 3% HCl + 0.06% thiourea	0.0004 ng mL^{-1}	100 (ICP-OES)/0.22 (ICP-MS) ng mL^{-1}	< 3%	> 99%	Standard additions	250 mL	125	n.a.	44
Pt, Pd, Ir	(*spiked seawater and river water samples)	PSTH-cpg	ICP-MS	pH: 3.2/ 0.03% (m/v) thiourea in 3.2% (v/v) HNO_3	Pt: 78.5 ng L^{-1} Pd: 55.5 ng L^{-1} Ir: 0.1 ng L^{-1}	Up to 600 ng L^{-1}	3% (n=10)	93-107%	(°NIST-2557 autocatalyst)	3.3 mL	Pt: 18 Pd: 2.3 Ir: 43	10 h^{-1}	43
Actinides													
Th, U	Seawater, well water, mineral water, fresh water, (*tap water)	UTEVA	ICP-MS	Acidified to 3M HNO_3/ 0.05 M $H_2C_2O_4$/ 0.01 M HNO_3	Th: 0.4 ng L^{-1} U: 2.8 ng L^{-1}	0-200 µg L^{-1}	1.7% at 2.5 ng L^{-1} (n=5)	> 90%	(°BCR-320R channel sediment)	8 mL	13	9 h^{-1}	60

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Note: Only additional sample treatment other than filtration and preservation with acid is mentioned here.
Abbreviations:
3-MPTMS: 3-mercaptopropyltrimethoxysilane
AC-TBAH: tetrabutylammonium hydroxide-modified activated carbon
AF-MMPs: amine-functionalized magnetite microspheres
APS: 3-aminopropyltriethoxysilane
Bromo-PADAP: 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol
CNTs: carbon nanotubes
CTAB: cetyltrimethylammonium bromide
DDTC: diethyldithiocarbamate
DPTH gel: 1-(di-2-pyridyl)methylene thiocarbonohydrazide bonded to silica gel
EDTriA-type chitosan: ethylenediamine N,N,N'-triacetate-type chitosan
GO-TiO_2: graphene oxide titanium dioxide
IIHC: ion imprinted polyvinylimidazol-silica hybrid copolymer

MNPs-PAA: magnetic nanoparticles with polyacrylic acid
MWCNTs: multi-walled carbon nanotubes
OASIS HLB: poly(divinylbenzene-N-vinylpyrrolidone) co-polymeric beads
PAPC: divinylbenzene-methacrylate copolymeric resin containing polyaminopolycarboxylic acid groups = ethylendiaminetriacetic acid and iminodiacetic acid groups
PDDA: poly(diallyldimethylammonium chloride
PMMA: poly(methyl methacrylate)
PSTH-cpg: 1.5-bis(2-pyridyl)3-sulphophenyl methylene thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass
Salen/Cd(II) complex: (cadmium(II) 2,2'-{ethane-1,2-diylbis[nitrilo(E)methylylidene]} diphenolate)
S-CS-MWCNTs: Schiff base-chitosan grafted multiwalled carbon nanotubes

Table 4: On-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the speciation of metals in natural waters. (All units as in the original publication)

Analyte	**Matrix**	**Solid phase**	**Sample treatment/ Elution**	**Detection technique**	**Figures of merit**				**Validation**	**Sample volume**	**Enrich-ment factor**	**Sample through-put**	**Ref**
					DL	**Linear range**	**Precision**	**Relative Recovery**					
Fe(II)/ Fe(III)	Ground water, River water, seawater (*tap water)	Non-functional-ized acrylate resin	Fe(II): pH 5 (evacuation by air); Fe(III): pH 4 (evacuation by water)	ICP-MS	Fe(II): 1 ng L^{-1} Fe(III): 1-2 ng L^{-1}	5-5000 ng L^{-1}	n.a.	Total Fe: 97-115% Fe(III): 89-110% Fe(II): 89-108%	SLEW-3, 1640a, 1643e trace metals in natural waters	1 mL	Fe(III) pH 4: 10.1 Fe (II)pH 5: 13.3 Fe(III) pH 5: 20.9	7.5 h^{-1}	[120]
V(V)/ V(IV)	Seawater, fresh water	CTAB-modified alkyl silica	pH 2.5 and 6.0/ 1 M HNO$_3$	ICP-OES	V(V): 0.03 µg L^{-1}	0.1-500 µg L^{-1}	V(V): 4.3% total V: 4.0% at 5 µg L^{-1} (n=9)	>90%	GSBZ50029-94 environmental water	3 mL	27.9	24 h^{-1}	[71]
Cr(III)/ Cr(VI)	Seawater (surface coastal)	Amberlite IRA 910, DPTH-gel	pH 5.5 (NaAc)/ 2 M HNO$_3$	ICP-MS	0.03 µg L^{-1}/ 0.009 µg L^{-1}	DL-60 µg L^{-1}	2.6%/ 3.2% at 0.3 µg L^{-1} (n=10)	98-113%	SLEW-3, LGC6016 estuarine waters, TMDA-54.4 fortified lake water (1:100)	4 mL	2.4/3.7	7.5 h^{-1}	[66]
Cr(VI)	Snow water, spring water, river water	PDDA-MWNTs	pH 6/ 0.1 M ammonium nitrate	ETAAS	0.016 µg L^{-1}	0.05-1.5 µg L^{-1}	3.9% at 0.5 µg L^{-1} (n=11)	100%	GBW08608 trace elements in water	1000 µL	8.6	9 h^{-1}	[64]
Cr(III)/ Cr(VI)	Mineral water, lake water, (*waste water)	SWCNTs	pH 3 (HNO$_3$, CH$_3$COONa)/ 1.2 M HNO$_3$	ICP-MS	0.01 ng mL^{-1}/ 0.024 ng mL^{-1}	0.1-100 ng mL^{-1}	<2.1%/ 4.0% at 1 ng mL^{-1} (n=9)	>90%	spiking experiments	20 mL	63	n.a.	[67]
Cr(VI)	Mineral water, river water (*effluent water)	Functional-ized meso-porous silica (APS)	pH 2 (HCl)/ 0.1 M NH$_2$OH·HCl in 1 M HCl	ETAAS	1.2 ng L^{-1}	n.a.	2.5 % at 0.50 µg L^{-1} (n=10)	100%	Recovery studies; total conc.: SRM 1643e trace elements in water	2 mL	27	21 h^{-1}	[63]

Cr(III)/ Cr(VI)	Lake water, mineral water (*tap water)	Mesoporous Al_2O_3	pH 4.0 (NH_3 H_2O/HNO_3)/ 0.01 M NaOH	ICP-MS	3.4 ng L^{-1}/ 74 ng L^{-1}	n.a.	2.8%/ 3.9% at 1 ng mL^{-1} (n=7)	>90%	GSBZ50027-94, GSBZ50004-88 environmental waters	0.5 mL	5	8 h^{-1}	68
Cr(III)/ Cr(VI)	River water (* tap water)	*C. Vulgaris*/ 717 anion exchanger	pH 6/ 0.04 M/1.0 M HNO_3	ETAAS	0.02 µg L^{-1}/ 0.03 µg L^{-1}	0.1-2.5 µg L^{-1}/ 0.12-2.0 µg L^{-1}	1.9%/ 2.5% at 1.0 µg L^{-1} (n=11)	100%/99 %	GBW08608 trace elements in water	600 µL	10.5/ 11.6	n.a.	65
As(III)/ As(V)	Lake water, mineral water, (*tap water)	Mesoporous Al_2O_3	pH 4.0 (NH_3 H_2O/HNO_3)/ 0.01 M NaOH	ICP-MS	0.7 ng L^{-1}/ 18 ng L^{-1}	n.a.	3.1%/ 4.0% at 1 ng mL^{-1} (n=7)	>90%	GSBZ50027-94, GSBZ50004-88 environmental waters	0.5 mL	5	8 h^{-1}	68
As(III)/ As(V)	River water, lake water, well water, rain water	(CTAB)-modified alkyl silica sorbent	None/ 1 M HNO_3	ICP-OES	As(V): 0.15 µg L^{-1}	0.5-1000 µg L^{-1}	As(V): 4.0% at 5.0 µg L^{-1} (n=9)	n.a.	BW3209 (0602), BW3210 (0602), GSBZ 50031-94 (203706) environmental waters	3 mL	26.7	24 h^{-1}	121
Se(IV)/ Se(VI)	River water, lake water, well water, rain water	(CTAB)-modified alkyl silica sorbent	None/1 M HNO_3	ICP-OES	Se(VI): 0.10 µg L^{-1}	0.5-1000 µg L^{-1}	Se(VI): 3.6% at 5 µg L^{-1} (n=9)	n.a.	BW3209 (0602), BW3210 (0602), GSBZ 50031-94 (203706) environmental waters	3 mL	27.6	24 h^{-1}	121
Se(IV)/ Se(VI), SeCys/ Se-Met	Lake water, (*biological samples)	Nanometre sized Al_2O_3/ mesoporous TiO_2	pH 3.5/pH 6/ 0.2 M NaOH	ICP-MS	45-210 ng L^{-1}	n.a.	7.0-9.7% at 0.8 ng mL^{-1} (n=7), 3.6-5.8% at 5 ng mL^{-1} (n=7)	n.a.		4 mL	1-5	5 h^{-1}	70

*Matrices in brackets indicated with a * are not within the scope of this review.*
n.a.: not available.

Note: Only additional sample treatment other than filtration and preservation with acid is mentioned here.
Abbreviations:
3-MPTMS: 3-mercaptopropyltrimethoxysilane
AC-TBAH: tetrabutylammonium hydroxide-modified activated carbon
AF-MMPs: Amine-functionalized magnetite microspheres
APS: 3-aminopropyltriethoxy silane
CTAB: cetyltrimethylammonium bromide
DDTC: diethyldithiocarbamate
DPTH-gel: 1-(di-2-pyridyl)methylene thiocarbonohydrazide bonded to silica gel

EDTriA-type chitosan: ethylenediamine N,N,N'-triacetate-type chitosan
MWCNTs: multi-walled carbon nanotubes
PAPC: divinylbenzene-methacrylate copolymeric resin containing polyaminopolycarboxylic acid groups = ethylendiaminetriacetic acid and iminodiacetic acid groups
PDDA: poly(diallyldimethylammonium) chloride
PMMA: poly(methyl)-methacrylate
PSTH-cpg: 1.5-bis(2-pyridyl)3-sulphophenyl methylene thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass
S-CS-MWCNTs: Schiff base-chitosan-grafted multiwalled carbon nanotubes
SSDC: syringe driven chelating column (packed with divinylbenzene-methacrylate co-polymeric resin containing polyaminopolycarboxylic acid groups (PAPC) = ethylendiaminetriacetic acid and iminodiacetic acid groups
SWCNTs: micro-column packed single-walled carbon nanotubes
TAR: 4-(2-thiazolylazo)resorcinol
TMA: 2-thiozylmethycrylamide
UTEVA: Uranium and TEtraValent Actinides - diamyl amylphosphonate (DAAP) functionalized

Table 5: Methods employing cold vapour generation (CVG) and hydride generation (HG) techniques for the matrix separation and preconcentration of metals in natural waters. (All units as in the original publication)

Analyte	**Matrix**	**Solid phase**	**Detection technique**	**Sample treatment/ Elution/Reduction**	**Figures of merit**				**Validation**	**Sample volume**	**Enrich-ment factor**	**Sample through-put**	**Ref**
					DL	**Linear range**	**Precision**	**Relative Recovery**					
Hg	Natural water samples	Dithizone chelate	AFS	pH: 4.0/ 1.5 mol L^{-1} HCl/ 1.5% (m/v) NaBH$_4$ in 0.5% (w/v) NaOH	0.02 µg L^{-1}	0.06-3.0 µg L^{-1}	5.2% (n=7) at 0.5 µg L^{-1}	90-105%	Standard addition/ recovery experiments	50 mL	29	5 h^{-1}	[122]
Pt, Pd, Os, Ir, Rh, Ag, Au	Spiked seawater (*tap water, environmental samples)	DPTH-MNPs	ICP-OES	Water samples: pH 1 (HCl); (*acid digests: pH 0.9 (NaOH)/ 2.5% thiourea (w/v) in 6% (w/w) HCl/ 2.1% (w/v) NaBH$_4$ in 0.1% (w/v) NaOH)	Pd: 1.5 µg L^{-1} Ag: 0.03 µg L^{-1} Os:0.65 µg L^{-1} Au: 0.62 µg L^{-1} Ir: 0.57 µg L^{-1} Pt: 0.63 µg L^{-1} Rh: 100 µg L^{-1}	n.a.	2.6-8.5% at 0.74-14.7 µg L^{-1}	92-108%	TMDA 54.4 fortified lake water, SRM 1643e trace elements in fresh water (°NIST 2557 autocatalyst)	12 mL	Pd: 20 Ag: 206 Os: 9 Au: 18 Ir: 17 Pt: 144 Rh: 3	17 h^{-1}	[82]
Ag, Au, Ir, Os, Pd, Pt, Sb, Hg	Seawater, mineral water (*spiked tab water	Function-alized magnetic graphene oxide	ICP-OES	pH 3.0 (0.2 M glycin/HCl)/ 2% (wt/vol) thiourea in 4% (wt/vol) HNO$_3$/ 2.6% (wt/vol) NaBH$_4$ in 0.2% (wt/vol) NaOH	Ag: 0.5 µg L^{-1} Au: 0.6 µg L^{-1} Ir: 0.2 µg L^{-1} Os: 1.2 µg L^{-1} Pd: 2.6 µg L^{-1} Pt: 0.4 µg L^{-1} Sb: 1.5 µg L^{-1} Hg: 0.05 µg L^{-1}1	Ag: 3.0-5000 Au: 4.8-3500 Ir: 6.5-400 Os: 7.7-400 Pd: 8.3-5000 Pt:2.8-5000 Sb: 9.0-5000 Hg: 0.2-1000 µg L^{-1}	Ag: 3.2% Au: 2.6% Ir: 3.1% Os: 3.8% Pd: 4.0% Pt: 3.8% Sb: 4.5% Hg: 1.6% at 25 µg L^{-1} (n=11)	Ag: 90-106% Au: 90-104% Ir: 93-113% Os: 90-104% Pd: 95-106% Pt: 86-106 Sb: 93-117% Hg: 93-105%	TMDA 54.4 fortified lake water	16.8 mL	Ag: 22 Au: 29 Ir: 9 Os: 33 Pd: 6 Pt: 28 Sb: 9 Hg: 3	13 h^{-1}	83
As, Sb, Hg	Seawater	DPTH-MNPs	HR-CS-ETAAS	pH: 5 (acetic acid/sodium acetate buffer)/ 5.0% (wt/wt) HCl/ 0,1% (wt/vol) NaBH$_4$ in 0.1% (wt/vol) NaOH	As:0.25 µg L^{-1} Sb: 0.003 µg L^{-1} Hg: 0.22 µg L^{-1}	n.a.	2.2-2.9 % (n=11) at As: 8 µg L-^{1}, Sb: 0.2 µg L^{-1}, Hg: 1.5 µg L^{-1}	90.4-110%	TM 24.3 and TMDA 54.4 fortified lake water	12 mL	As: 23.4 Sb: 2.9 Hg: 3.3	16.7 h^{-1}	78

Sb, Bi, Sn, Hg	Seawater, river water	DPTH-silica gel	HR-CS-ETAAS	pH 2.2 (glycine/HCl)/ Sb, Bi, Sn: 3.1% HCl, Hg: 4.6% thiourea/ 0.6% (w/v) $NaBH_4$ in 0.1% (w/v) NaOH	Sb: 0.009 µg L^{-1} Bi: 0.001 µg L^{-1} Sn: 0.18 µg L^{-1} Hg: 0.17 µg L^{-1}	0.025-2.5 µg L^{-1}	1.9-2.4% at 1 µg L^{-1} (n=11)	91-103%	TM 24.3, TMDA 54.4 fortified lake waters	3 mL	Sb: 4 Bi: 18 Sn: 7 Hg: 9	7.5 h^{-1}	13
Pt, Pd, Ir	Spiked seawater	DPTH-gel	ICP-OES	pH: 7.5 (borate-boric acid buffer)/0.07% (wt/v) thiourea in 2 mol L^{-1} HCl/0.5% (wt/v) $NaBH_4$ in 0.1% (wt/v) NaOH	Pt: 1.4 µg L^{-1} Pd: 0.5 µg L^{-1} Ir: 0.6 µg L^{-1}	0.05 – 3 mg L^{-1}	Pt: 2.8% Pd: 2.7% Ir: 2.9% (n=10)	94.5-105.8%	(°NIST 2557 autocatalyst)	6.6 mL	Pt: 6.3 Pd: 6.7 Ir: 6.3	11 h^{-1}	81^{s}
Pb, Cd, Hg	Natural waters including seawater	DPTH-silica gel	ICP-MS	pH 5.0 (acetic acid/sodium acetate)/ 1.5% (w/w) thiourea in 1.5% (w/w) HNO_3/ Pb: 1.25% (w/v) $NaBH_4$ + 3% (w/v) $K_3Fe(CN)_6$; Cd and Hg: 1.25% (w/v) $NaBH_4$ in 0.1% (w/v) NaOH	Pb: 9 ng L^{-1} Cd: 17 ng L^{-1} Hg: 12 ng L^{-1}	DL-30.0 µg L^{-1}	2.5-2.9% at 0.5 µg L^{-1} (n=9)	985-105%	TMDA-54.4 fortified lake water, LGC6016 estuary water, CASS-5 seawater	5.4 mL	Pb: 16.4 Cd: 25.1 Hg:27.3	10.4 h^{-1}	79
Sb, Bi, Sn	Seawater	DPTH-silica gel	ICP-MS	pH 3.5 (0.75% cysteine added)/ 4% HNO_3/ 0.5% $NaBH_4$ in 0.1% NaOH	Sb: 0.01 µg L^{-1} Bi: 0.002 µg L^{-1} Sn: 0.142 µg L^{-1}	DL-60.0 µg L^{-1}	1.1-1.5% (n=10)	97-108%	Diluted TMDA-54.5, TM-24.3 natural waters	4.8 mL	Sb: 7.0 Bi: 8.6 Sn: 2.5	12 h^{-1}	78
As	River water, tap water, mineral water, (*waste water)	None	AAS	0.01 mol L^{-1} HCl/ 4.0 mol L^{-1} HCl/ 1.0% (m/v)NaBH4 in 0.1% (m/v) NaOH	0.05 µg L^{-1}	0.15-6.0 µg L^{-1}	3.2% at 2.0 µg L^{-1} (n=10)	96-102%	Reference method based on on-line FI-HG-AAS (FIAS 400)	3 mL	n.a.	9 h^{-1}	75
Sb	River- and seawater	DPTH-silica gel	ETAAS	pH 5.0 (acetic acid/ sodium acetate)/ 2.0% thiourea in 4.0% HNO_3/ 0.5% (w/v) $NaBH_4$ in 0.1% (w/v) NaOH	1 ng L^{-1}	0.025-2.5 µg L^{-1}	0.9% at 1 µg L^{-1} (n=11)	98-108%	TMDA 54.4 fortified lake water, SLRS-5 estuarine water	5 mL	22	20 h^{-1}	123
Cd	Seawater, ground water	None	AAS	2 mol L^{-1} HCl/ 0.75% (m/v) thiourea in 0.05 mol L^{-1} HCl/ 6% (w/v) $NaBH_4$ in 0.5% (m/v) NaOH	5.8 ng L^{-1}	19.3 ng L^{-1}-5 µg L^{-1}	1.4-2.9% at 0.25 and 2.5 µg L^{-1}	94-101%	CASS-4 seawater	2 mL	n.a.	87 h^{-1}	76

Pb	Seawater, river water	PSTH-cpg	ETAAS	pH 6.0 (NaH_2PO_4/Na_2HPO_4)/ 1% (v/v) HCl/ 2.6% (m/v) $NaBH_4$ + 3% (m/v) ($K_3Fe(CN)_6$) in 0.5% (m/v) NaOH	3.0 ng L^{-1}	n.a.	2.5% at 50 ng L^{-1} (n=10)	97-105%	TMDA 54.4 fortified lake water, LG6016 estuarine water	6.4 mL	20	18 h^{-1}	[80]
Hg	River water	None	ICP-MS, MC-ICP-MS	Stabilization ($K_2Cr_2O_7$), isotope dilution/ 0.2% (w/w) $NaBH_4$ in 0.05% (w/w) NaOH	0.25 ng L^{-1}	n.a.	0.6-2.9% for ERM-CA615 (n=3)	n.a.	ERM-CA615 ground water	500 µL	10-50	40 h^{-1}	[77]

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Abbreviations:
cpg: controlled pore glass
DPTH: 1-(di-2-pyridyl)methylene thiocarbonohydrazide
MNP: magnetic nanoparticle
PSTH: 1.5-bis(2-pyridyl)3-sulphophenyl methylene thiocarbonohydrazide

Table 6: Methods employing cold vapour- and hydride generation techniques for the speciation of metals in natural waters. (All units as in the original publication)

Analyte	Matrix	Solid phase	Detection technique	Sample treatment/ elution/reduction	Figures of merit				Validation	Sample volume	Enrich-ment factor	Sample through-put	Ref
					LOD	Linear range	Precision	Relative Recovery					
As(III)/ As(V))/ total iAs	Seawater, well-water	PSTH-MNPs	ICP-MS	pH 4.0 (acetic acid/sodium acetate)/ 0.1% (m/v) thiourea + 2.8% (m/v) *L*-cysteine in 7% (w/w HNO_3/ As(III): 0.1% (w/v) $NaBH_4$ in 0.5% NaOH As(V): 0.5% (w/v) $NaBH_4$ in 0.5% NaOH	As(III): 2.7 ng L^{-1} iAs: 3.2 ng L^{-1}	As(III): 0.01-50 µg L^{-1} total iAs: 0.03-100 µg L^{-1}	As(III): 2.5% iAs: 2.7% (n=8)	90-110%	SLEW—estuarine water, CASS-5 sea water, TMDA 54.4 fortified lake water, SPS-SW 2 Batch 125 surface water	9.6 mL	As(III): 1.9 total iAs: 2.1	14.4 h^{-1}	87
As(III)/ As(V)/ total iAs	Groundwater	Cl-SAX	AAS	None - neutral sample/ As(III): 3.5 mol L^{-1} HCl/ 0.35% (m/v) $NaBH_4$ in 0.025% NaOH	As(III): 0.5 µg L^{-1} iAs: 0.6 µg L^{-1}	1.7-25 µg L^{-1}	<2% at 5 µg L^{-1} (n=3)	98-106%	NIST 1643e trace elements in water	500 µL	n.a.	60 h^{-1}	86
iHg/ MeHg	Seawater	DPTH-silica gel	ICP-MS	pH 5.0 (acetic acid/sodium acetate)/ MeHg: 0.2% HCl, iHg: 0.5% HCl + 0.1% thiourea/ 0.25% (w/v) $NaBH_4$ in 0.5% (w/v) NaOH	MeHg: 0.011 µ L^{-1} iHg: 0.024 µg L^{-1}	DL-70 µg L^{-1}	MeHg: 2.8% iHg: 2.6% at 2 µg L^{-1} (n=10)	92-107%	LGC 6016 estuarine water, (°SRM 2976 mussel tissue)	4.6 mL	MeHg: 4.7 iHg: 11	7.1 h^{-1}	85
Sb(III)/ Sb(V)	Seawater, river water, lake water	PSTH-cpg/ Amberlite IRA-910	ICP-MS	pH 8.4 (boric acid/borax)/ 0.04% thiourea in 5% HNO_3/ 0.2% (m/v) $NaBH_4$ in 0.05% NaOH	Sb(III): 0.05-80 µg L^{-1} Sb(V): 0.05-80 µg L^{-1}	Sb(III): 0.013 µg L^{-1} Sb(V): 0.021 µg L^{-1}	Sb(III): 4.6% Sb(V): 3.0% (n=10)	97-105%	SLRS-5 river water, TMDA-54.4 lake water	2.2 mL	Sb(III): 5.5 Sb(V): 3.9	9 h^{-1}	74

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Note: Only additional sample treatment other than filtration and preservation with acid is mentioned here.

Abbreviations:

Cl-SAX: Silica-based chloride-form strong anion exchange resin
PSTH-MNPs: (Fe_3O_4) magnetic nanoparticles functionalized with [1,5-bis (2-pyridyl) 3-sulfophenylmethylene] thiocarbonohydrazide
PANI: polyaniline
DPTH-silica gel: 1,5-bis(di-2-pyridyl)methylene thiocarbonohydrazide bonded to silica gel

PSTH-cpg: [1,5-bis(2-pyridyl)-3-sulfonphenyl methylene]thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass

Table 7: Methods employing liquid-liquid-micro-extraction for the matrix separation and preconcentration of metals in natural waters. (All units as in the original publication)

Analyte	Matrix	Detection technique	Sample treatment	Disperser/ complexing solution	Figures of merit				Validation	Sample volume	Enrichment factor	Sample throughput	Ref
					DL	Linear range	Precision	Relative Recovery					
Pb	Coastal water, ditch water	FAAS	pH 2 (HNO_3)	DDPA/chloroform	1.5 $\mu g\ L^{-1}$	5.0-280 $\mu g\ L^{-1}$	2.7% at 40.0 $\mu g\ L^{-1}$ (n=9)	95-102%	CRM 1643e trace elements in natural water, (°BCR 278-R mussel tissue)	6 mL	130	13 h^{-1}	[88]
Pb	Lake water, coastal water	FAAS	pH 2 (HNO_3)	APDC/chloroform	1.8 $\mu g\ L^{-1}$	6.0-300 $\mu g\ L^{-1}$	2.9% at 50 $\mu g\ L^{-1}$ (n=10)	94-98%	CRM 1643e trace elements in natural water, (°BCR 278-R mussel tissue)	10 mL	125	7 h^{-1}	[93]
Tl	River water, lake water, coastal seawater (*tap water)	FAAS	pH 2.0 (HNO_3)	Methanol containing 0.6% (v/v) ([Hmim][PF_6]; Elution: MIBK; Support: PUF micro column	0.86 $\mu g\ L^{-1}$	2.8-120 $\mu g\ L^{-1}$	2.7% at 20 $\mu g\ L^{-1}$	94-98%	SRM 1643e trace elements in natural water, (°SRM 2704 river sediment)	15 mL	290	16 h^{-1}	[97]
U	Ground water, seawater	ICP-OES, ICP-MS	pH 1	APDC/CTAB; extraction into chloroform, back extraction into HNO_3	ICP-OES: 2.0 $\mu g\ L^{-1}$ ICP-MS: 30 $ng\ L^{-1}$	ICP-OES: 5-200 $\mu g\ L^{-1}$; ICP-MS: 50-5000 $ng\ L^{-1}$	ICP-OES: 5% ICP-MS: 4% (n=6)	90-105% at 10 and 5 $\mu g\ L^{-1}$	BCR 403 North Seawater, laser fluorimetry	10 mL	11-25	n.a.	[89]
Ag	River water, seawater, (*waste water)	FAAS	0.1 $mol\ L^{-1}$ HNO_3	DDTC in 0.3% (m/v) methanol; Elution: MIBK; Support: PEEK-microcolumn	0.15 $\mu g\ L^{-1}$	0.40-20 $\mu g\ L^{-1}$	2.9% at 5 $\mu g\ L^{-1}$ (n=10)	96-99%	NIST CRM 1643e trace elements in natural water	16.2 mL	186	12 h^{-1}	[96]
Pb, Cd	Natural waters (river water, coastal seawater)	ETAAS	None	Methanol containing 2% (v/v) xylene a + 0.2% (m/v) APDC; Elution: MIBK; Support: PTFE-tubing	Pb: 10 $ng\ L^{-1}$ Cd: 2 $ng\ L^{-1}$	Pb: 0.04-1.5 $\mu g\ L^{-1}$ Cd: 0.006-0.150 $\mu g\ L^{-1}$	Pb: 3.8% at 0.5 $\mu g\ L^{-1}$ Cd: 4.1% at 0.03 $\mu g\ L^{-1}$	94-98% (n=3)	NIST CRM 1643e trace elements in natural water	8.1 mL	Pb: 80 Cd: 34	10 h^{-1}	[95]

V	River water, (*tap water)	ETAAS	pH 4.0 (acetic acid/ acetate)	(5-Br-PADAP) + ([C4mim][PF6]) RTIL; Elution: 10% (v/v) HNO_3 (in acetone); Support: Florisil	4.8 ng L^{-1}	DL-15 µg L^{-1}	4.1% at 5 µg L^{-1} (n=10)	96-103% (n=6)	NIST CRM 1643e trace elements in natural water	5 mL	n.a.	6 h^{-1}	90
Cd	Seawater, river water	ETAAS	pH 2.0±0.2 (HNO_3)	DDPA/DIBK	0.01 µg L^{-1}	0.03-0.6 µg L^{-1}	3.9% at 0.1 µg L^{-1} (n=9)	94-98%	NIST CRM 1643e trace elements in natural water	15 mL	10	6 h^{-1}	92
Cu, Pb	River water, coastal water	FAAS	pH 1.4 (HNO_3)	Methanol containing 2% (v/v) xylene + 0.3% (m/v) DDPA; Elution: MIBK; Support: PTFE-micro column	Cu: 0.04 µg L^{-1} Pb: 0.54 µg L^{-1}	0.16-12.0 µg L^{-1}	Cu: 2.1% at 2.0 µg L^{-1} Pb: 1.9% at 30 µg L^{-1} (n=10)	96-100%	NIST CRM 1643e trace elements in natural water	12 mL	Cu: 560 Pb: 265	12 h^{-1}	94
Cr	Spring water, river water, seawater	ETAAS	pH 3.5 (phthalate buffer)	APDC	0.02 µg L^{-1}	0.5-6 µg L^{-1}	7% (n=6)	90-103%	(°CRM 544 lyophilized solution (no real matrix))	2.5 mL	20	n.a.	91

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Note: Only additional sample treatment other than filtration and preservation with acid is mentioned here.
Abbreviations:
APDC: ammonium pyrrolidine dithiocarbamate
([C4mim][PF6])RTIL: 1-butyl-3-methylimidazolium hexafluorosphosphate room temperature ionic liquid
([Hmim][PF6]): 1-hexyl-3-methylimidazolium hexafluorophosphate ionic liquid
(5-Br-PADAP): 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol
CTAB: cetyltrimethyl ammonium bromide
DDPA: ammonium diethyldithiophosphate
DDTC: sodium diethyldithiocarbamate
DIBK: di-isobutyl ketone
MIBK: methyl isobutyl ketone
PUF: polyurethane foam

Figure captions

Figure 1: A conceptual diagram of the combination of on-line FI/SI sample preparation with atomic spectrometric detectors.

Abbreviations: LPME: liquid phase microextraction; SPE: solid phase extraction; HG/CVG-GLS: hydride generation/cold vapour generation-gas liquid separator; PP: peristaltic pump; SP: syringe pump; MPW: multi position valve; HC: holding coil; IV: injection valve; S: sample; R: reagent; E: eluent; W: waste.

Source: adapted from Miró and Hansen (2013)[10]

Figure 2: A conceptual diagram of the combination of on-line FI/SI sample preparation with atomic spectrometric detectors. Reproduced from [18] (Talanta 133 (2015) 164, authored by Robert Clough, Hagit Sela, Angela Milne, Maeve C. Lohan, Serife Tokalioglu and Paul J. Worsfold), with permission from Elsevier.

Figure 3: FI microcolumn preconcentration/separation system for simultaneous speciation of Se(IV) and Se(VI), selenocysteine and selenomethionine, prior to ICP detection.

Abbreviations: P1/P2: peristaltic pumps; C1/C2: micro columns; V: valves.

a) Separation of inorganic ((Se(IV) and Se(VI)) and organic Se species (Se-Met and Se Cys_2) on C1 and C2, respectively. ($SeCys_2$ retained on C2, Se-Met was detected by ICP-MS)
b) Elution of Se-Cys_2 from C2 with 0.5 mol L^{-1} NaOH and ICP-MS detection.
c) Elution of inorganic Se from C1 with 0.2 mol L^{-1} NaOH and pH adjustment
d) Separation of inorganic Se species on C2. (Se(IV) retained on C2, Se(VI) was detected by ICP-MS)
e) Elution of Se(IV) with 0.5 mol L^{-1} NaOH and ICP-MS detection.

Source and a more detailed description can be found in [70].

Figure 4: Schematic illustration of a sequential injection system for automatic DLPME of trace elements as a front end to ETAAS.

Abbreviations: S: sample; MeOH (APDC, xylene), extracting solvent composed of 2.0% (v/v) xylene and 0.2% (m/v) APDC in methanol which acts as dispersant; P: peristaltic pump; SP: syringe pump; MV: multi-position valve; V: head valve; HC: holding coil; C: micro-column containing sorbent; CC: confluence connector; DT: delivery tube; GF: graphite furnace of ETAAS. Reprinted from [95] (A.N. Anthemidis, K.-I.G. Ioannou / Analytica Chimica Acta 668 (2010) 35–40, Copyright (2010)), with permission from Elsevier.

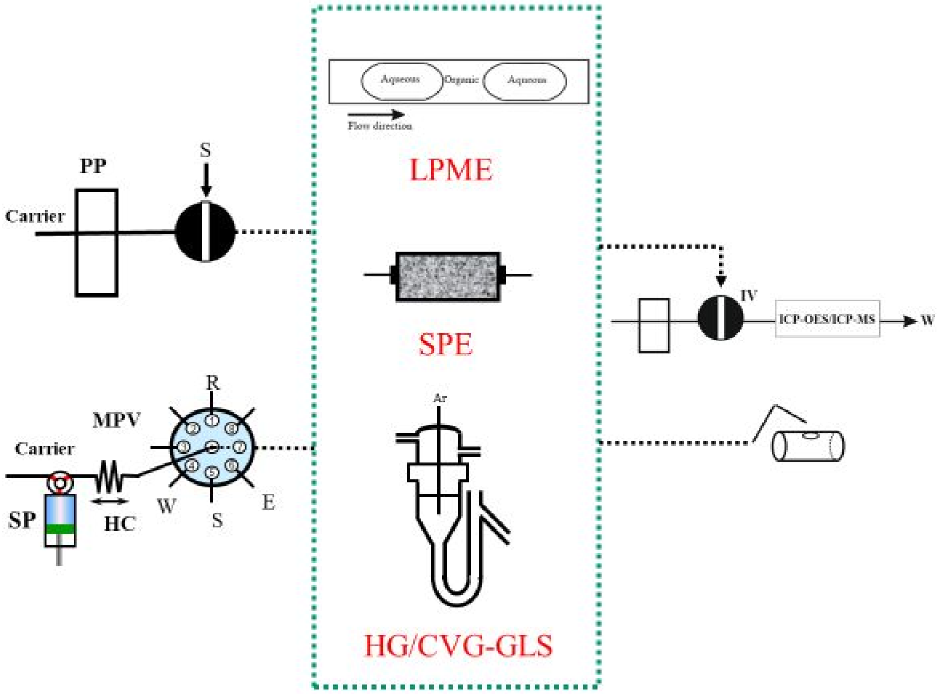
Aqueous
Organic
Aqueous
Flow direction
LPME
PP
S
Carrier
SPE
IV
ICP-OES/ICP-MS
W
R
MPV
Carrier
SP
HC
W
S
E
Ar
HG/CVG-GLS

Fig. 1

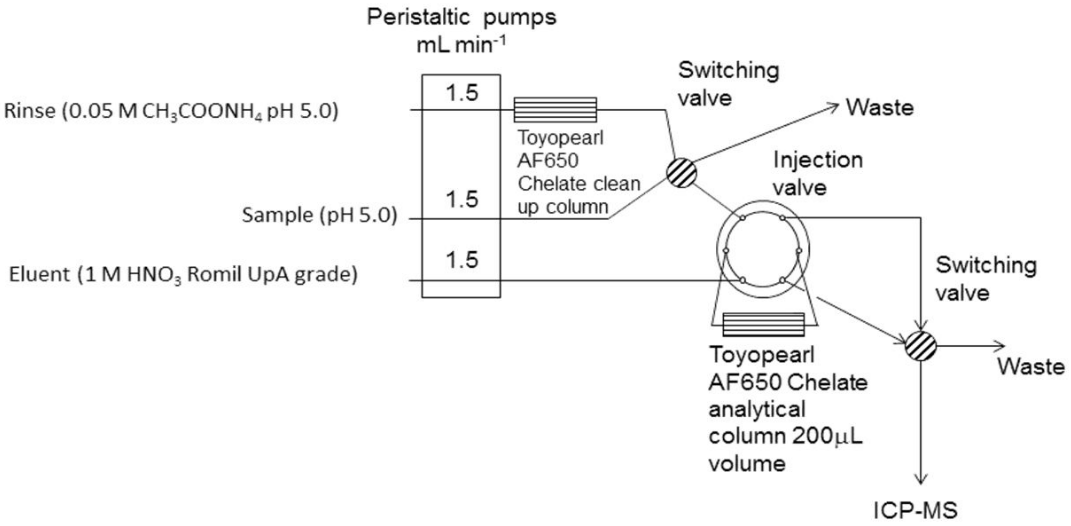
Peristaltic pumps
mL min^{-1}
1.5
1.5
1.5
Rinse (0.05 M CH_3COONH_4 pH 5.0)
Sample (pH 5.0)
Eluent (1 M HNO_3 Romil UpA grade)
Toyopearl AF650 Chelate clean up column
Switching valve
Waste
Injection valve
Switching valve
Waste
Toyopearl AF650 Chelate analytical column 200μL volume
ICP-MS

Fig. 2

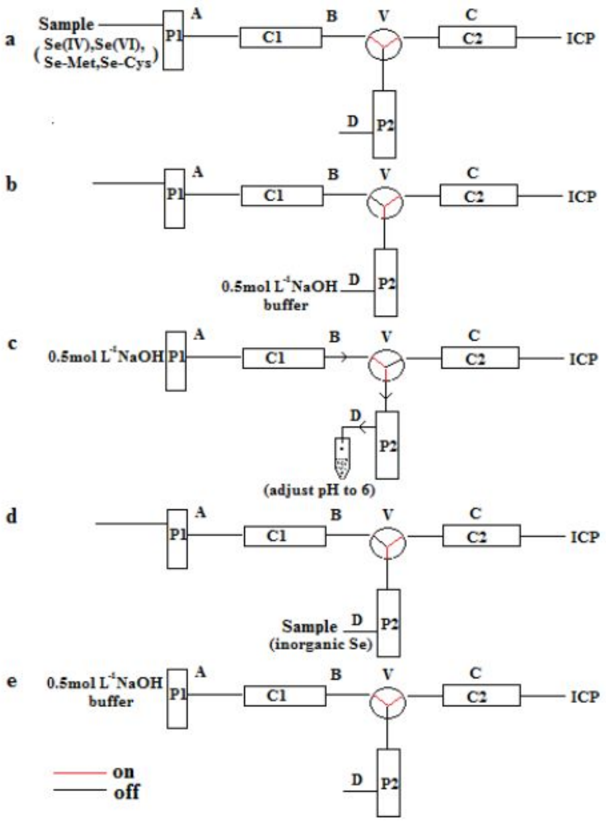
a
Sample
(Se(IV),Se(VI), Se-Met,Se-Cys)
P1
A
C1
B
V
C
C2
ICP
D
P2
b
0.5mol L⁻¹NaOH buffer
c
0.5mol L⁻¹NaOH
(adjust pH to 6)
d
Sample (inorganic Se)
e
0.5mol L⁻¹NaOH buffer
on
off

Fig. 3

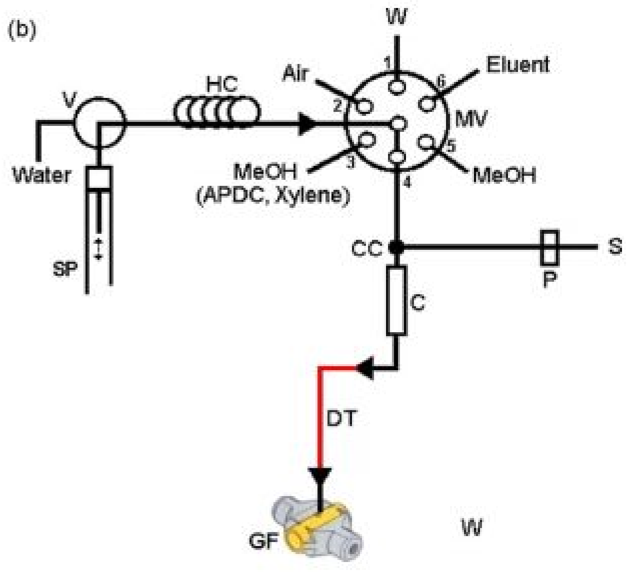
(b)
W
1
Air
Eluent
6
HC
V
2
MV
5
3
4
Water
MeOH
(APDC, Xylene)
MeOH
CC
S
P
SP
C
DT
GF
W

Fig. 4

References

---

[1] J. Gaillardet, J. Viers and B. Dupré, *Treatise on Geochemistry: Second Edition*, Elsevier Inc. 2013, pp. 195-235.

[2] Y. Sohrin and K.W. Bruland, *Trends Anal. Chem.,* 2011, **30**, 1291-1307.

[3] W. H. Schlesinger and E. S. Bernhardt*, Biogeochemistry: An analysis of global change.* Third Edition, Elsevier Inc. 2013.

[4] R. Clough, C. F. Harrington, S. J. Hill, Y. Madrid and J. F. Tyson, *J. Anal. At. Spectrom.,* 2018, **33**, 1103-1149.

[5] B. Buszewksi, W. Piekoszewsky, P. Pomastowski, K. Rafinska, M. Sugajski and T. Kowalkowski, *Recent Advances in Trace Elements*, Wiley Blackwell 2017, pp: 33-60.

[6] S. J. Ussher, E. P. Achterberg and P. J. Worsfold, *Environ. Chem.,* 2004, **1**, 67-80.

[7] P. Lindahl, S. H. Lee, P. Worsfold and M. Keith-Roach, *Mar. Environ. Res.*, 2010, **69**, 73-84.

[8] M. Marcinkowska and D. Baralkiewicz, *Talanta*, 2016, **161**, 177-204.

[9] M. E. Lagerström, M. P. Field, M. Séguret, L. Fischer, S. Hann and R. M. Sherrell, *Mar. Chem.,* 2013, **155**, 71-80.

[10] M. Miró and E. H. Hansen*, Anal. Chim. Acta*, 2013, **782**, 1-11.

[11] P. J. Worsfold, R. Clough, M. C. Lohan, P. Monbet, P. S. Ellis, C. R. Quétel, G. H. Floor and I. D. Mc Kelvie., *Anal. Chim. Acta*, 2013, **803**, 15-40.

[12] A. Cárdenas Valdivia, M.M López Guerrero, E. I. Vereda Alonso, J. M. Cano Pavón and A-Garcia de Torres, *Microchem. J.,* 2018, **138**, 109-115.

[13] M.M. López-Guerrero, M. T. Siles-Cordero, E. Vereda-Alonso, J. M. Cano-Pavón and A. Garcia de Torres, *J. Anal. At. Spectrom*., 2015, **30**, 1169-1178.

[14] A. Leclercq, A. Nonell, J. L. Todolí Torró, C. Bresson, L. Vio, T. Vercouter and F. Chartier, *Anal. Chim. Acta*, 2015, **885**, 33-56.

[15] A. Leclercq, A. Nonell, J. L. Todolí Torró, C. Bresson, L. Vio, T. Vercouter and F. Chartier, *Anal. Chim. Acta*, 2015, **885**, 57-91.

[16] G. R. D. Prabhu and P. L. Urban, *Trends Anal. Chem.,* 2017, **88**, 41–52.

[17] E. H. Hansen and M. Miró, *Flow Injection Analysis-Comprehensive Analytical Chemistry* (S. D. Kolev and I. McKelvie, Eds), Chap. 14, pp. 375-405, Elsevier, The Netherlands, 2008.

[18] R. Clough, H. Sela, A. Milne, M. C. Lohan, S. Tokalioglu and P.J. Worsfold, *Talanta*, 2015, **133**, 162-169.

[19] G. Giakisikli and A. N. Anthemidis, *Talanta*, 2013, **110**, 229-235.

[20] I. Sánchez-Trujillo, E. Vereda-Alonso, A. García de Torres and J.M. Cano-Pavón, *Microchem. J.,* 2012, **101**, 87-94.

---

[21] R. K. Katarina, M. Oshima and S. Motomizu, *Talanta*, 2009, **78**, 1043-1050.

[22] P. H. Pacheco, P. Smichowski, G. Polla and L. D. Martinez, *Talanta,* 2009, **79**, 249-253.

[23] T. T. Shih, I. H. Hsu, S. N. Chen, P. H. Chen, M. J. Deng, Y. Chen, Y. W. Lin and Y. C. Sun, Analyst, 2015, 140, 600-608.

[24] T. T. Shih, C. C. Hsieh, Y. T. Luo, Y. A. Su, P. H. Chen, Y. C. Chuang, Y. C. Sun, *Anal. Chim. Acta*, 2016, **916**, 24-32.

[25] M. Hemmati, M. Rajabi and A. Asghari, *Microchim. Acta*, 2018. **185**, 160.

[26] P.-L. Lee, Y.-C. Sun and Y.-C. Ling, *J. Anal. At. Spectrom*., 2009, **24**, 320-327.

[27] R. Schlitzer, R. F. Anderson, E. M. Dodas, M. Lohan, W. Geibert, A. Tagliabue, A. Bowie, C. Jeandel, M. T. Maldonado, W. M. Landing, D. Cockwell, C. Abadie, W. Abouchami, E. P. Achterberg, A. Agather, A. Aguliar-Islas, H. M. van Aken, M. Andersen, C. Archer, M. Auro, H. J. de Baar, O. Baars, A. R. Baker, K. Bakker, C. Basak, M. Baskaran, N. R. Bates, D. Bauch, P. van Beek, M. K. Behrens, E. Black, K. Bluhm, L. Bopp, H. Bouman, K. Bowman, J. Bown, P. Boyd, M. Boye, E. A. Boyle, P. Branellec, L. Bridgestock, G. Brissebrat, T. Browning, K. W. Bruland, H. J. Brumsack, M. Brzezinski, C. S. Buck, K. N. Buck, K. Buesseler, A. Bull, E. Butler, P. Cai, P. C. Mor, D. Cardinal, C. Carlson, G. Carrasco, N. Casacuberta, K .L. Casciotti, M. Castrillejo, E. Chamizo, R. Chance, M. A. Charette, J. E. Chaves, H. Cheng, F. Chever, M. Christl, T. M. Church, I. Closset, A. Colman, T. M. Conway, D. Cossa, P. Croot, J. T. Cullen, G. A. Cutter, C. Daniels, F. Dehairs, F. Deng, H. T. Dieu, B. Duggan, G. Dulaquais, C. Dumousseaud, Y. Echegoyen-Sanz, R. L. Edwards, M. Ellwood, E. Fahrbach, J. N. Fitzsimmons, A. Russell Flegal, M. Q. Fleisher, T. van de Flierdt, M. Frank, J. Friedrich, F. Fripiat, H. Fröllje, S. J. G. Galer, T. Gamo, R. S. Ganeshram, J. Garcia-Orellana, E. Garcia-Solsona, M. Gault-Ringold, E. George, L. J. A. Gerringa, M. Gilbert, J. M. Godoy, S. L. Goldstein, S. R. Gonzalez, K. Grissom, C. Hammerschmidt, A. Hartman, C. S. Hassler, E. C. Hathorne, M. Hatta, N. Hawco, C. T. Hayes, L. E. Heimbürger, J. Helgoe, M. Heller, G. M. Henderson, P. B. Henderson, S. van Heuven, P. Ho, T. J. Horner, Y. T. Hsieh, K. F. Huang, M. P. Humphreys, K. Isshiki, J. E. Jacquot, D. J. Janssen, W. J. Jenkins, S. John, E. M. Jones, J. L. Jones, D. C. Kadko, R. Kayser, T. C. Kenna, R. Khondoker, T. Kim, L. Kipp, J. K. Klar, M. Klunder, S. Kretschmer, Y. Kumamoto, P. Laan, M. Labatut, F. Lacan, P. J. Lam, M. Lambelet, C. H. Lamborg, F. A. C. Le Moigne, E. Le Roy, O. J. Lechtenfeld, J. M. Lee, P. Lherminier, S. Little, M. López-Lora, Y. Lu, P. Masque, E. Mawji, C. R. McClain, C. Measures, S. Mehic, J. L. M. Barraqueta, P. van der Merwe, R. Middag, S. Mieruch, A. Milne, T. Minami, J. W. Moffett, G. Moncoiffe, W.S. Moore, P. J. Morris, P. L. Morton, Y. Nakaguchi, N. Nakayama, J. Niedermiller, J. Nishioka, A. Nishiuchi, A. Noble, H. Obata, S. Ober, D.C. Ohnemus, J. van Ooijen, J. O'Sullivan, S. Owens, K. Pahnke, M. Paul, F. Pavia, L. D. Pena, B. Peters, F. Planchon, H. Planquette, C. Pradoux, V. Puigcorbé, P. Quay,

---

F. Queroue, A. Radic, S. Rauschenberg, M. Rehkämper, R. Rember, T. Remenyi, J. A. Resing, J. Rickli, S. Rigaud, M. J. A. Rijkenberg, S. Rintoul, L. F. Robinson, M. Roca-Martí, V. Rodellas, T. Roeske, J. M. Rolison, M. Rosenberg, S. Roshan, M. M. Rutgers van der Loeff, E. Ryabenko, M. A. Saito, L. A. Salt, V. Sanial, G. Sarthou, C. Schallenberg, U. Schauer, H. Scher, C. Schlosser, B. Schnetger, P. Scott, P. N. Sedwick, I. Semiletov, R. Shelley, R. M. Sherrell, A. M. Shiller, D. M. Sigman, S. K. Singh, H. A. Slagter, E. Slater, W. M. Smethie, H. Snaith, Y. Sohrin, B. Sohst, J. E. Sonke, S. Speich, R. Steinfeldt, G. Stewart, T. Stichel, C. H. Stirling, J. Stutsman, G. J. Swarr, J. H. Swift, A. Thomas, K. Thorne, C. P. Till, R. Till, A. T. Townsend, E. Townsend, R. Tuerena, B. S. Twining, D. Vance, S. Velazquez, C. Venchiarutti, M. Villa-Alfageme, S. M. Vivancos, A. H. L. Voelker, B. Wake, M. J. Warner, R. Watson, E. van Weerlee, M. Alexandra Weigand, Y. Weinstein, D. Weiss, A. Wisotzki, E. M. S. Woodward, J. Wu, Y. Wu, K. Wuttig, N. Wyatt, Y. Xiang, R.C. Xie, Z. Xue, H. Yoshikawa, J. Zhang, P. Zhang, Y. Zhao, L. Zheng, X. Y. Zheng, M. Zieringer, L. A. Zimmer, P. Ziveri, P. Zunino and C. Zurbrick, *Chem. Geol.*,2018, **493**, 210-223.

[28] European Commission. *Critical Raw Materials for the EU. Report of the Ad-hoc Working Group on Defining Critical Raw Materials*. 2014. Ref. Ares (2015)1819503 - 29/04/2015, Brussels.

[29] S. Massari and M. Ruberti*, Resour. Policy*, 2013, **38**, 36-43.

[30] R. K. Katarina, M. Oshima and S. Motomizu, *Talanta*, 2009, **79**, 1252-1259.

[31] Y. Zhu, T. Umemura, H. Haraguchi, K. Inagaki and K. Chiba, *Talanta*, 2009, **78**, 891-895.

[32] Y. Zhu, A. Itoh, T. Umemura, H. Haraguchi, K. Inagaki and K. Chiba, *J. Anal. At. Spectrom*., 2010, **25**, 1253-1258.

[33] Y. Zhu, A. Hioki and K. Chiba, *J. Anal. At. Spectrom*., 2013, **28**, 883-889.

[34] E. C. Hathorne, B. Haley, T. Stichel, P. Grasse, M. Zieringer, M. Frank, *Geochem. Geophys. Geosyst.*, 2012, **13**, 1-12.

[35] Y. Zhang, C. Zhong, Q. Zhang, B. Chen, M. He and B. Hu, *RSC Adv*., 2015, **8** 5996-6005.

[36] M. He, B. Hu, B. Chen and Z. Jiang, *Physical Sciences Reviews,* 2017, 20160059.

[37] A. Fisher and D. Kara, *Anal. Chim. Acta*, 2016, *935*, 1-29.

[38] M. M. González-García, F. Sánchez-Rojas, C. Bosch-Ojeda, A. García de Torres and J. M. Cano-Pavón, *Anal. Bioanal. Chem.*, 2003, **375**, 1229-1233.

[39] Ratte H. T, *Environ. Toxicol. Chem.*, 1999, **18**, 89–108.

[40] R. H. Byrne, *Geochem. Trans*., 2002, **3**(2), 11-16.

[41] F. L. Bernardis, R. A. Grant and D. C. Sherrington, *Reac. Funct. Polym*., 2005, **65**, 205-2017.

[42] C. B. Ojeda, F. Sánchez-Rojas, J. M. Cano-Pavón and A. García de Torres*, Anal. Chim. Acta*, 2003, **494**, 97-103.

---

[43] M. L. Alonso Castillo, A. García de Torres, E. Vereda Alonso, M. T. Siles Codero and J. M. Cano Pavón, *Talanta*, 2012, **99**, 853-858.

[44] M. V. Balarama Krishna, M. Ranjit, K. Chandrasekaran, G. Venkateswarlu and D. Karunasagar, *Talanta*, 2009, **79**, 1454-1463.

[45] J. L. Barriada, A. D. Tappin, E. H. Evans and E. P. Achterberg, *Trends Anal. Chem.*, 2007, **26**(8), 809-817.

[46] L. Yang and R. E. Sturgeon, *J. Anal. At. Spectrom.*, 2002, **17**(2), 88-93.

[47] Z. Zhu and A. Zheng, *Spectroscopy,* 2017, **32**, 50-59.

[48] D. A. Atwood, *Radionuclides in the Environment*. John Wiley & Sons, Chichester, 1st edn, 2010.

[49] C. Poinssot. *Radionuclide Behaviour in the Natural Environment: Science, Implications and Lessons for the Nuclear Industry.* Eds.: C. Poinssot and H. Geckeis. Woodhead Publishing Series in Energy, 2012, Cambridge, UK.

[50] Q.-H. Hu, J.-Q. Wang and J.-S. Wang, *J. Environ. Radioact.,* 2010, **101**, 426-437.

[51] World Health Organization, *Guidelines for Drinking-Water Quality*, WHO, Geneva, fourth edition incorporating the first addendum, 2017. https://www.who.int/water_sanitation_health/publications/drinking-water-quality-guidelines-4-including-1st-addendum/en/.

[52] *Uranium Fact sheet, Environmental Protection Agency*, US EPA, 2013; https://www.wqa.org/Portals/0/Technical/Technical%20Fact%20Sheets/2014_Uranium.pdf.

[53] AERB Drinking water specifications in India. Department of Atomic Energy, Govt. of India, 2004; https://www.aerb.gov.in/english/.

[54] T. Laaninen. *Revision of the Drinking Water Directive.* European Union, 2019. http://www.europarl.europa.eu/RegData/etudes/BRIE/2018/625179/EPRS_BRI(2018)625179_EN.pdf.

[55] European environmental quality standards (EQS) variability study. Scientific Report from DCE – Danish Centre for Environment and Energy Nr. 198, 2016; http://dce.au.dk/en/.

[56] Z. Wang, J. Lin, S. Li, Q. Guo, W. Huang, W. Wen, G. Dan and Z. Tan, *J. Radioanal. Nucl. Chem.*, 2018, **315**, 103-110.

[57] A. Habibi, C. Vivien, B. Boulet, C. Cossonnet, R. Gurriaran, M. Gleizes, G. Cote and D. Larivière, *J. Radionanal. Nucl Chem.*, 2016, **310**, 217-227.

[58] A. Habibi, B. Boulet, M. Gleizes, D. Larivière and G. Cote, *Anal Chim Acta*, 2015, **883**, 109-116.

[59] J. X. Qiao, X. L. Hou, P. Steier and R. Golser, *Anal. Chem.*, 2013, **85**, 11026-11033.

[60] J. Avivar, L. Ferrer, M. Casas and V. Cerda, *J. Anal. At. Spectrom.*, 2012, **27**, 327-334.

---

[61] J. R. Bacon, O. T. Butler, W: R. L. Cairns, J. M. Cook, C. M. Davidson, O. Cavoura and R. Mertz-Kraus, *J. Anal. At. Spectrom.*, 2020, **35**(1), 9-53.

[62] Official Journal of the European Union, Directive 2008/105/EC of the European Parliament and of the council of 16 December 2008 (L 348/84).

[63] M. Kim, J. Stripeikis and M. Tudino, *Spectrochim. Acta Part B*, 2009, **64**, 500-505.

[64] X. Zhang, M. Chen, Y. Yu, T. Yang and J. Wang, *Anal. Methods*, 2011, **3**, 457-462.

[65] A. M. Zou, X. Y. Tang, M. L. Chen and J. H. Wang, *Spectrochim. Acta Part B*, 2008, **63**, 607-611.

[66] M. M. López-Guerrero, E. Vereda-Alonso, J. M. Cano-Pavón, M. T. Siles-Cordero and A. García de Torres, J. Anal. *At. Spectrom*., 2012, **27**, 682-688.

[67] S. Chen, L. Zhu, D. Lu, X. Cheng and X. Zhou, *Microchim Acta*, 2010, **196**, 123-128.

[68] W. Hu, F. Zheng and B. Hu, *J. Hazard. Mater*., 2008, **151**, 58-64.

[69] Y. F. Huang, Y. Li, Y. Jiang and X. P. Yan*. J. Anal. At. Spectrom*. 2010, 25, 1467-1474.

[70] C. Huang, B. Hu, M. He and J. Duan, *J. Mass Spectrom*., 2008, **43**, 336-345.

[71] C. Xiong, Y. Qin and B. Hu, *J. Hazard. Mater*., 2010, **178**, 164-170.

[72] B. Magnusson and U. Örnemark (Eds.) *Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics*. (2nd ed. 2014). ISBN 978-91-87461-59-0. Available from http://www.eurachem.org.

[73] G. Ying, L. Rui and Y. Lu, *Chinese Sci. Bul*., 2013, **17**, 1980-1991.

[74] A. Calvo-Fornieles, A. García De Torres, E. Vereda-Alonso, M. T. Siles-Cordero and J. M. Cano-Pavón, *J. Anal. At. Spectrom.,* 2011, **26**, 1619-1626.

[75] A. N. Anthemidis, E. I. Daftsis and N. P. Kalogiouri, *Anal. Methods*, 2014, **6**, 2745-2750.

[76] L. O. B. Silva, L. A. Portugal, E. Palacio, L. Ferrer, V. Cerdà and S. L. C. Ferreira. *J. Anal. At. Spectrom*., 2014, **29**, 2398-2404.

[77] L. Fischer, M. Brunner, T. Prohaska and S. Hann., *J. Anal. At. Spectrom*., 2012, **27**, 1983-1991.

[78] A. Calvo-Fornieles, A. García de Torres, E. I. Vereda-Alonso and J. M. Cano-Pavón, *J. Anal. At. Spectrom*., 2013, **28**, 364-372.

[79] I. Sánchez-Trujillo, A. García De Torres, E. I. Vereda-Alonso and J. M. Cano-Pavón, *J. Anal. At. Spectrom.*, 2013, **28**, 1772-1780.

[80] I. Sánchez-Trujillo, M. L. Alonso-Castillo, J. M. Cano-Pavón, E. I. Vereda-Alonso and A. García de Torres, *Anal. Methods*, 2013, **5**, 2551-2557.

[81] A. Calvo Fornieles, A. García de Torres, E. Vereda Alonso and J. M. Cano Pavón, *Microchem. J.*, 2016, **124**, 82-89.

[82] M. M. López-Guerrero, E. Vereda-Alonso, A. García De Torres and J. M. Cano-Pavón, *J. Anal. At. Spectrom*., 2017, **32**, 2281-2291.

---

[83] J. C. García-Mesa, P. Montoro Leal, M. M. López Guerrero and E. I. Vereda Alonso, *Microchem. J.*, 2019, **150**, 104141.

[84] M. V. B. Krishna, K. Chandrasekaran and D. Karunasagar. *Talanta*, 2010, **81**, 462-472.

[85] I. Sánchez-Trujillo, E. Vereda-Alonso, J.M. Cano-Pavón and A. García De Torres, *J. Anal. At. Spectrom*., 2015, **30**, 2429-2440.

[86] M. Sigrist, A. Albertengo, H. Beldoménico and M. Tudino, *J. Hazard. Mater.,* 2011, **188**, 311-318.

[87] P. Montoro Leal, E. Vereda Alonso, M. M. López Guerrere, M. T. Siles Cordero, J. M Cano Pavón, A. García Torres, Talanta, 2018, **184**, 251-259.

[88] C. Mitani and A. N. Anthemidis, *Talanta*, 2015, **133**, 77-81.

[89] K. Chandrasekaran, D. Karunasagar and J. Arunachalam, *Anal. Methods*, 2011, **3**, 2140-2147.

[90] P. Berton, E .M. Martinis and R. G. Wuilloud, *J. Hazard. Mater*., 2010, **176**, 721-728.

[91] F. Pena, I. Lavilla and C. Bendicho, *Spectrochim. Acta Part B*, 2008, **63**, 498-503.

[92] A. N. Anthemidis and I. S. I. Adam, *Anal. Chim. Acta*, 2009, **632**, 216-220.

[93] C. Mitani and A. N. Anthemidis, *Anal. Chim. Acta*, 2013, **771**, 50-55.

[94] A. N. Anthemidis and K. – I. G. Ioannou, *Talanta*, 2009, **80**, 413–421.

[95] A. N. Anthemidis and K. I. G. Ioannou, *Anal. Chim. Acta*, 2010, **668**, 35-40.

[96] A. N. Anthemidis and K. I. G. Ioannou, *Talanta*, 2011, **84**, 1215–1220.

[97] A. N. Anthemidis and K. I. G. Ioannou, *Anal. Bioanal. Chem*., 2012, **404**, 685–691.

[98] H. Peng, N. Zhang, M. He, B. Chen and B. Hu, Int. J. Environ. Anal. Chem., 2016, 96, 212-224.

[99] J. E. O'Sullivan, R .J. Watson and E. C. V. Butler, *Talanta*, 2013, **115**, 999-1010.

[100] A. N. Anthemidis, S. Xidia and G. Giakisikli, *Talanta*, 2012, **97**, 181-186.

[101] B. Dai, M. Cao, G. Fang, B. Liu, X. Dong, M. Pan and S. Wang, *J. Hazard. Mater*., 2012, **219-220**, 103-110.

[102] A. O. AlSuhaimi and T. McCreedy, *Arab. J. Chem*., 2011, **4**, 195-203.

[103] A. N. Anthemidis, G. Giakisikli, S. Xidia, M. Miró, *Microchem. J*., 2011, **98**, 66-71.

[104] C. Cui, M. He and B. Hu, *J. Hazard. Mater*., 2011, **187**, 379-385.

[105] D. Chen, B. Hu, M. He and C. Huang, *Microchem. J*., 2010, **95**, 90-95.

[106] I. Sánchez-Trujillo, E. Vereda-Alonso, M. T. Siles-Cordero, J. M. Cano-Pavón and A. García De Torres, *J. Anal. At. Spectrom*., 2010, **25**, 1063-1071.

[107] D. Chen, B. Hu and C. Huang, *Talanta*, 2009, **78**, 491-497.

[108] Y. Wang, X. Luo, J. Tang, X. Hu, Q. Xu and C. Yang, *Anal. Chim. Acta*, 2012, **713**, 92-96.

[109] V. Yilmaz, Z. Arslan, O. Hazer and H. Yilmaz, *Microchem. J*., 2014, **114**, 65-72.

---

[110] X.-W. Chen, A.-M. Zou, M.-L. Chen, J.-H. Wang and P. K. Dasgupta, *Anal. Chem*., 2009, **81**, 1291-1296.

[111] M. Z. Corazza, B. F. Somera, M. G. Segatelli and C. R. T. Tarley, *J. Hazard. Mater*., 2012, **243**, 326-333.

[112] X.-X. Zhang, L.-P. Zhang, T. Yang, L.-M. Shen, M.-L. Chen and J.-H. Wang, *J. Anal. At. Spectrom*., 2012, **27**, 1680-1687.

[113] T. Yang, X.-X. Zhang, M.-L. Chen and J.-H. Wang. *Analyst*, 2012, **137**, 4193-4199.

[114] G. F. Lima, F. M. Oliveira, M. O. Ohara, M. G. Segatelli and C. R. T. Tarley, *Evaluation of histidine functionalized multiwalled carbon nanotubes for improvement in the sensitivity of cadmium ions determination in flow analysis,* In: Carbon Nanotubes - From Research to Applications, Dr. Stefano Bianco (Ed.), In Tech, Croatia, 2011.

[115] M. Gawin, J. Konefal, B. Trzewik, S. Walas, A. Tobiasz, H. Mrowiec and E. Witek, *Talanta*, 2012, **80**, 1305-1310.

[116] C. R. T.Tarley, F. N. Andrade, F. Midori de Oliveira, M. Z.Corazza, L. F. Mendes de Azevedo and M. G. Segatelli, *Anal. Chim. Acta*, 2011, **703**, 145-151.

[117] A. N. Anthemidis, I. S. I. Adam and G. A. Zachariadis, *Talanta*, 2010, **81**, 996-1002.

[118] Y. Bakricioglu, D. Bakircioglu and S. Akman, *J. Hazard. Mater*., 2010, **178**, 1015-1020.

[119] Z. Zhu and A. Zheng, *Molecules*, 2018, **23**, 489.

[120] C. K. Su, Y. T. Chen and Y. C. Sun, *Microchemical J*., 2019, **146**, 835-841.

[121] C. Xiong, M. He and B. Hu, *Talanta*, 2008, **76**, 772-779.

[122] S. S. Lins, C. F. Virgens, W. N. L. dos Santos, I. H.S. Estevam and S. L. C. Ferreira, *Microchem. J*., 2019, **150**, 104075.

[123] M. M. López-Guerrero, M. T. Siles-Cordero, E. Vereda-Alonso, A. García De Torres and J. M. Cano-Pavón. *Talanta*, 2014, **129**, 1-8.

On-line sample treatment coupled with atomic spectrometric detection for the determination of trace elements in natural waters

Lisa Fischer[a], Stephan Hann[a], Paul J. Worsfold[b] and Manuel Miró[c]

[a] Department of Chemistry, University of Natural Resources and Life Sciences, Vienna (BOKU), Muthgasse 18, 1190 Vienna, Austria

[b] Biogeochemistry Research Centre, SoGEES, University of Plymouth, Plymouth PL48AA, Devon, UK.

[c] FI-TRACE group, Department of Chemistry, University of the Balearic Islands, Carretera de Valldemossa km 7.5, E-07122 Palma de Mallorca, Spain

Keywords. Natural waters, trace elements, atomic spectrometry, flow injection, sequential injection, solid phase extraction, cold vapour generation, hydride generation, liquid membrane extraction, speciation.

Abstract

This review discusses the application of on-line strategies for sample treatment prior to atomic spectrometric detection. These strategies are based on flow injection and related flow-based approaches and focus on publications that have been published in the last ten years and have been explicitly applied to real world natural water samples (open ocean, coastal and estuarine water, river water, lake water and groundwater) and matrix relevant certified reference materials. The focus is on the use of solid phase extraction for matrix removal and analyte preconcentration. For convenience of searching, methods are grouped by element type, i.e. transition metals (plus zinc, cadmium, lead and arsenic), rare earth elements (the 15 lanthanides plus scandium and yttrium), precious metals (platinum group elements plus silver and gold) and actinide elements (the transuranic elements plus actinium, thorium, polonium and uranium). There is a separate section on methods for elemental speciation. Other on-line treatment strategies covered are cold vapour and hydride generation, and liquid phase microextraction. Comprehensive method details and analytical figures of merit are provided for key selected papers covering each of these strategies in associated tables.

1 Introduction

Natural waters include marine waters (e.g. open ocean, shelf sea, coastal and estuarine), fresh waters (e.g. river, stream, lake), groundwater and precipitation (e.g. rain, snow, ice). Each of these reservoirs has a different chemical composition, including their trace element profile (see e.g. [1, 2]), that varies spatially and temporally but all are interconnected via the global water cycle. Biogeochemical processes[3] impact on the fluxes of trace elements between these compartments and their physico-chemical speciation[4] within each compartment.

The need to quantify trace elements in natural waters is driven by several factors. Some elements or elemental species are toxic[5], even at low concentrations, whilst others are essential micronutrients[6]. Others can be used to elucidate transport processes or act as specific markers for aquatic processes or events[7]. The low concentrations of many elements or their compounds in natural waters requires sensitive detection techniques such as inductively coupled plasma-mass spectrometry (ICP-MS), often hyphenated with some form of separation[8] or preconcentration/matrix removal[9]. This review focusses on the use of flow injection (FI) manifolds and advanced flow setups for on-line sample treatment, coupled mainly with flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma-optical emission spectrometry (ICP-OES) and ICP-~~/~~MS detection, for the determination of trace elements and their compounds in natural waters published since 2008 (for previous reviews on the role of flow analysis in sample preparation see e.g. [10, 11]). Flow-based methods coupled to high resolution-continuum source (HR-CS)-AAS have also been ~~also~~ considered. [12, 13]. Advantages compared ~~to~~with standard AAS include improved signal stability and background correction and the use of a high-pressure xenon short-arc lamp as a continuous radiation source for sequential or simultaneous multi-element analysis.

2 Flow-through approaches and interfaces

The three main cornerstones of FI, i.e. controllable dispersion, reproducible timing and controlled sample injection, have been fully exploited in combination with atomic spectrometric detection, for which the transport of aerosols into the atomizer is regarded as the 'Achilles heel' of atomic spectrometric techniques. Flow injection approaches were conceived for sample introduction of a metered aqueous sample volume to a detection system (FAAS in the case of elemental analysis), capitalizing on the high (carrier) wash to sample ratio. Hereto, the nebulizer and burner are continuously cleaned by a carrier solution, thus alleviating problems of clogging, even in high salt matrix samples. In fact, FI setups hyphenated to ICP-triple quadrupole-mass spectrometry (ICP-qQq-MS)/ICP-sector field-mass spectrometry (ICP-SFMS)~~(SF)MS,~~, based on the continuous operating nature of both the flow setup and detection technique, are now regarded as the second dawn for high-throughput (multi-) elemental and molecular automatic analysis. The advances in sample injectors (e.g. nano-valves) and improved designs of nebulizers and spray chambers that enable continuous injection of, e.g. organic eluates and alcoholic solvents, have helped to overcome the limitations of FI-ICP couplings in terms of the nature of the sample to be injected[14, 15], in as much as high carbon content matrices have been traditionally excluded from ICP analysis. Nowadays the utilization of organic solvents in ICP-MS is performed on a routine basis with robust interfaces allowing the controlled addition of oxygen in order to eliminate carbon deposition on cones and other parts of the ICP-MS introduction system[14, 15]. In quadrupole MS based systems, the implementation of reaction/collision cell technology has enabled the development of strategies for the reduction or elimination of almost all polyatomic interferences that would otherwise hamper the accurate determination of the elements amenable to this technique. Tandem QMS systems are now state-of-the-art and regarded as equivalent with ICP-SFMS systems in terms of selectivity and limits of detection.

With regard to system configuration, on-line hyphenation of FI with ICP involving the use of a mechanically movable element, namely a rotary valve, has been the interface of choice for practitioners to integrate sample handling seamlessly with analysis. Nonetheless, at-line automatic interfacing, achieved by exploiting advanced robotic arms or autosamplers, is a simple means of conditioning the sample/extract prior to analysis [16]. However, coupling of flow approaches to discontinuously operating detectors ~~such as electrothermal atomic absorption spectrometry (~~ETAAS~~)~~ is not straightforward. The second generation of FI, so-called Sequential Injection (SI), has however paved the way for automatic sample handling across a multi-position selection valve as a core element of the flow system and a bi-directional syringe pump as a liquid driver with on-line sample injection of minute volumes (< 50 µL) into the graphite tube[17]. This is accomplished by integrating a flow line (usually polytetrafluorethylene (PTFE) tubing) in the ETAAS autosampler arm, which connects the selection valve with the graphite tube at pre-set injection times. Advantage is taken of the fact that the ensuing sample might be processed in the SI manifold while running the ETAAS program of the previous sample. A conceptual diagram of the combination of on-line FI/SI sample preparation with atomic spectrometric detectors is shown in Fig. 1.

FI, SI and related techniques can also be used as automatic platforms for accommodating appropriate pre-treatment schemes prior to the actual detection when handling troublesome samples for which matrix clean-up and/or analyte preconcentration to attain suitable detectability are required.

3 On-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the determination of metal concentrations in natural waters.

3.1 Transition metals, zinc, cadmium, lead and mercury

This section focusses on the use of on-line solid phase preconcentration for the determination of transition metals (V, Mn, Fe, Co, Ni and Cu) and includes group 12 elements (Zn, Cd (and Hg)), along with other metals (Pb) and metalloids (As). These elements can be classified in different ways depending on the context in which they are being determined. Their interaction with biota is a particularly important classification and these elements can be described as micronutrients (e.g. Fe, Co), toxic elements (e.g. Pb, Cd) or both (depending on the concentration, e.g. Cu).

The major analytical challenge is the potential for contamination during sampling, storage and analysis as concentrations in natural waters (particularly seawater) are typically very low (≤ nM). In this regard flow manifolds incorporating on-line solid phase extraction (SPE) are attractive due to the confined and controlled nature of the sample handling step, the ability to preconcentrate the analyte(s) and the removal of major sea salt ions that would otherwise interfere with the detection step (see e.g. [11] and [17]). Filtration of samples and refrigeration immediately after collection are essential for obtaining high quality data. The application of flow manifolds, coupled with the use of high purity reagents and a meticulous approach to cleaning of all laboratory ware, are essential prerequisites for minimising the blank signal and hence achieving the desired limit of detection (LOD).

Transition metals can often be determined simultaneously using e.g. ICP-MS or ICP-OES detection and the key analytical performance data for selected papers are summarised in Table 1. It is also possible to determine individual elements using e.g. ~~flame atomic absorption spectrometry (~~FAAS or ETAAS and performance data for selected papers are similarly summarised in Table 2. Particularly noteworthy features from these papers are considered in more detail below.

The most important component of the flow manifold for these methods is the on-line SPE micro/mini-column. The chemistry of the SPE phase used for on-line preconcentration and matrix removal, i.e. the nature of the support material and the attached chelating ligand or sorptive material, and the design of the column, e.g. column dimensions, shape and fabrication material, and the elution mode (e.g., the use of back-flushing elution) are important considerations. The most common ligands are iminoacetate based chelates ((iminodiacetic acid (IDA), nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA)), quinolinol based chelates ((8-hydroxyquinoline (8HQ)) and dithiocarbamate based chelates. Nobias-chelate PA1 is a chelating resin that has both, EDTA and IDA~~ethylenediaminetriacetic acid and iminodiacetic~~

~~acid~~ chelating groups immobilized on a hydrophilic methacrylate polymer. It is popular because it is commercially available, functions over a relatively wide pH range and has a high affinity for several transition metals[9]. This paper reported an enrichment factor (also called a preconcentration factor) of ~200 for Co, Cu, Fe, Mn, Ni and Zn with a 9 mL sample volume, which allowed excellent detection limits to be achieved. As a general comment it is recommended that all papers using on-line SPE state the method used to calculate the enrichment factor and the experimental details used to obtain the data. Toyopearl AF-Chelate 650 is another popular polymeric resin incorporating ~~iminodiacetate~~ IDA chelating groups that has been used to estimate the uncertainties associated with on-line preconcentration and ICP-MS detection of trace metals in seawater[18]. A schematic diagram of the FI manifold used for this work is shown in Fig. 2.

It is also possible to react the transition metal with the ligand on-line and then use a reversed-phase material such as octadecyl-chemically modified silica for trapping the neutral chelate. In an interesting example, ~~Giakasikli~~ Giakisikli and Anthemidis[19] formed a cadmium complex with diethyldithiocarbamate (DDTC) on-line and then preconcentrated the complex on octadecylsilane functionalized maghemite magnetic particles. The complex was then eluted with isobutyl methyl ketone.

Proprietary resins include 1,5-bis (2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide (PSTH) which was immobilized on aminopropyl-controlled pore glass and incorporated within the injection valve of a simple flow manifold[20]. However, enrichment factors were relatively low, ranging from 2.2 – 6.8 for a range of transition metals. Another proprietary resin utilised a natural product (chitosan) as the support material and ~~ethylenediamine-N,N,N'-triacetate~~EDTA as the immobilised chelating ligand[21], achieving enrichment factors of 14 – 35 for a range of transition (and rare earth) metals for a sample volume of only 5 mL. A conventional mini-column (4 cm length x 2 mm i.d.) was incorporated within a 6-port switching valve as part of a fully automated system.

Unconventional advanced sorbents exploiting nanotechnology, based on the large surface area of nanomaterials, have also been adapted for metal assays in natural waters. For example, multi-walled carbon nanotubes (MWCNTs) have been used for preconcentration, with ligands such as *L*-tyrosine immobilised on the walls of the tubes to enhance interaction with transition metals via cation-π interactions ~~(e.g.~~ [22]. An enrichment factor of 180 was reported for Co using FAAS detection.

Recent developments in microchip fabrication have been used to design compact, on-line miniaturized preconcentration devices. One example is the use of dipole–ion interactions between the highly electronegative C–Cl moieties of 2,2'-azobisisobutyronitrile, which was cross-linked to the channel interior of a poly(methyl methacrylate) fabricated chip, and the positive charges on the transition metal ions in the sample[23]. Using this approach, detection limits ranging from 1.6 – 42 ng L^{-1} were achieved for Co, Cu, Mn, Ni and Pb in river water[24].

Within the last decade, magnetic SPE based on magnetic nanosorbents has ~~gained great~~received considerable interest for matrix separation/preconcentration~~ in general~~. The principle involves magnetisable materials used as sorbents and their attraction by~~to~~ a magnetic field for the isolation of target analytes after extraction from the sample matrix. A ~~very~~ recent review article reports~~about~~ ~~numerous~~several applications based on magnetic nanoparticles (MNPs) for SPE of a suite of ~~heavy~~trace metals in water~~, soil, food, fuel, herbal and~~ and other ~~biological samples~~matrices using inorganic nanoparticles such as silica-coated MNPs, magnetic alumina and titania or magnetic layered double oxides, and organic sorbents including magnetic carbon materials (graphene/graphene oxide), magnetic carbon nanotubes and nitrides and magnetic organic polymers or ionic liquids~~, respectively~~. T~~hough t~~hese extraction procedures are mostly performed in batch mode but the authors explicitly emphasise the ~~high efficiency, simplicity, safety, inexpensiveness and the~~ possibility ~~for~~of automation[25]. An on-line method based on ~~iron~~magnetite-based MNPs as sorbent coupled to ICP-MS for the ~~analysis~~determination of Mn, Co, Cu, Zn and Pb in water (and ~~aqueous biological~~other ~~samples~~matrices) ~~has been~~was first reported in 2009~~ for the first time~~ [26]. Effective separation of matrix constituents and excellent recovery for the CASS-2 CRM ~~could be~~was achieved~~,~~; however, the resulting LODs were not significantly lower compared to direct analysis as only 20 µl sample volume ~~has been~~was processed.

It is essential that robust quality assurance procedures are used to ensure that the results are fit for purpose. For water quality management it is important that results are sufficiently accurate to monitor environmental threshold levels such as the EU maximum admissible concentration values. This requires the use of appropriate (matrix matched) certified reference materials (CRMs) or waters with consensus values such as those produced by the GEOTRACES programme[27]. All publications should report at least one (preferably more) CRM/consensus value for each element, including appropriate statistical assessment of the results. Unfortunately, this is not the case in many reports compiled in Tables 1 and 2 (indicated by °) for which CRMs of matrices other than waters, including biological matrices (e.g., urine or seafood tissues) or environmental solids (e.g. sediments and soils) have been inappropriately selected. For elucidating environmental processes, a key requirement is to be able to statistically distinguish changes in recorded data from analytical uncertainty. Thus, a rigorous assessment of all uncertainties in the sampling and analysis steps should be undertaken[18].

3.2 Rare earth elements

In this section, on-line matrix separation and preconcentration methods based on solid phase extraction for the quantification of rare earth elements (REEs) are discussed. The group of REEs comprises the 15 lanthanoids as well as Sc and Y. They can be further divided into light REEs (Sc, La, Ce, Pr, Nd, Sm, Eu) and heavy REEs (Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). They are not regulated with respect to threshold levels and maximum admissible concentrations in water but there is a growing interest in knowing their concentrations in the aquatic environment. They have been confirmed as critical raw materials by the European Commission in 2014[28] due to their significant economic importance as they are widely used in numerous applications such as the automotive industry and nuclear, oil and green technologies[29]. This, however, increases the emission of REEs into the aquatic environment, resulting in anthropogenic anomalies, e.g. Gd due to its intense use in Gd-based magnetic resonance imaging contrast agents. The assessment of anthropogenic contamination requires a knowledge of naturally occurring concentrations of REEs, which are generally in the low ng L^{-1} range in seawater and fresh water and are found in varying concentrations, depending on the surrounding bedrock geochemistry, in groundwater. Hence, direct measurement with state-of-the-art atomic spectrometry techniques is not sensitive enough, particularly if the sample has to be diluted to decrease the total dissolved solid concentration, as required when ICP-MS is applied, to obtain accurate data. Only a handful of methods dealing with the determination of REEs using an on-line approach have been published in the last decade. It is important to stress (again) that the use of an automated flow-manifold is advantageous due to the increased efficiency and the lower risk of contamination and other accidental errors. Table 3 summarizes key analytical performance data of selected publications reporting the determination of REEs in lake water, river water, coastal water and open ocean seawater by ICP-OES and ICP-(SF)MS. All of these methods use on-line SPE mini- or micro-columns incorporating in-house fabricated chelating resins based on the natural polymer chitosan and functionalized with either EDTA~~ethylenediamine-N,N,N-triacetate-~~type chitosan ~~(EDTriA-type chitosan)~~[21] or N-(2-hydroxyethyl)glycine as chelating moieties[30]~~ or N-(2-hydroxyethyl)glycine[19] as chelating moieties~~. These resins were used in a fully automated manifold coupled to ICP-OES for the extraction of REEs including Sc and Y from river waters at a pH of 5 with recoveries, assessed from spike experiments, in the range of 90 – 110%[21, 30]. Preconcentration factors were estimated by comparison of peak heights obtained by processing a standard solution with the preconcentration system and conventional nebulization. High preconcentration factors, in the range of 83 – 120 (EDT~~ri~~A-type chitosan) and 83 – 102 (N-(2-hydroxyethyl)glycine-type chitosan) were obtained, except for Y and Sc which were ≤ 30, by processing a sample volume of 20 mL. Due to the operation of the manifold in a "multi-mode" with three synchronized collection systems, up to 12 samples h^{-1} could be analysed for a suite of metals. However, LODs of ≥ 0.002 ng mL^{-1} are relatively high compared with other methods surveyed in this review (see Table 3), which might be attributed to the use of ICP-OES as the detection system.

Resins with IDA and EDT$_3$A chelating groups (also referred to as polyaminopolycarboxylic acid groups – PAPC) packed in a chelating column and sold as Nobias PB1M were used by Zhu *et al.* for the determination of REEs in coastal seawater[31], lake water[32] and seawater[33] in an on-line SI manifold directly coupled to ICP-(SF)MS. Initially, 10 mL of seawater were processed within 6 min and a preconcentration factor of 9.6 was obtained, leading to LODs in the range of 0.005 – 0.09 pg mL^{-1}. Recoveries were determined based on spiked sample solutions and the trueness of the method was estimated by comparing published and measured values obtained by the repetitive analysis of CRM NASS-5[31].

Even faster analysis could be performed with an automatic column changing system as reported by the same authors[32]. Elution and measurement of one sample, including the time required for column changing, was performed in 3 min but sample loading was carried out off-line. They compared Nobias PB1M with InterSep ME1, a chelating resin with only IDA moieties. For both resins, a pH of 5.0 was optimal for adsorption and similar recoveries, ranging from 97 – 103%, and precision (RSDs of the peak areas) were obtained with identical elution conditions.

Far lower LODs, ranging from 0.0008 – 0.004 pg mL^{-1}, could be obtained using an automatic pH-adjustment system for SPE of REEs on Nobias-PB1M from seawater by preconcentrating 50 mL of sample[33]. As sample pH is crucial for the sorption efficiency of the target metals and each sample manipulation step (i.e. a manual pH adjustment) increases the risk of contamination, the main focus of this work[33] was the development of a device for automated and contactless pH-adjustment and monitoring, involving the addition of a quantity of aqueous ammonia solution into the sample via a nebuliser, which was controlled by an electromagnetic valve while the transmitted light at 550 nm (the pH indicator was methyl red) was spectrophotometrically monitored. The system has been used to pH adjust sample volumes of 20 to 100 mL within < 5 min per sample prior to REEs determination using the automatic column changing system described above[32]. Blank values measured were significantly lower compared with those obtained by applying "conventional" pH-adjustment with glass- or all-plastic pH electrodes, leading to improved LODs. Spike recovery experiments with two concentration levels were performed to validate the method but CRMs were not analysed.

The use of the commercially available seaFAST^{TM} system (Elemental Scientific Inc.), coupled to ICP-QMS, has been reported by Hathorne *et al.*[34] LODs in the range of 2 – 302 ppq, determined from a 2% HNO_3 solution, were reported by pre-concentrating 7 mL of seawater on the commercially available chelating resin Nobias PA1, which has similar chelating moieties to Nobias PB1M. The system allows automated in-line buffering of the sample and is equipped with trace metal clean-up columns in the up-take capillaries, which deliver buffer solution and carrier. This resulted in extremely low background signals and hence low signal/noise ratios for most REEs. By adjusting the pH value of the samples loaded onto the column to pH 6.0, yields in the range of 94 – 102% were obtained. Yields were estimated by comparing time resolved peaks of a matrix matched (NaCl) standard solution containing 5 ng L^{-1} of REEs after preconcentration with signals obtained from standards diluted in the eluent by bypassing the column. The authors state the susceptibility to errors during the determination of column yields (absolute recoveries) if there is any inconsistency in the acid strengths of eluted and directly analysed standards, which leads to the conclusion that the accurate determination of column recovery is not easy. Trueness of the reported method was appropriately assessed by standard additions of deep Atlantic seawater samples, isotope dilution analysis (for Nd) and by measuring reference samples such as NASS-5 as well as 1:10 diluted VIDAC18 reference mine waste water and SCREE and PPREE reference acid mine waters produced by the United States Geological Survey (USGS), and diluted in different matrices with an appropriate content of NaCl to mimic seawater matrixes.

In addition to commercially available chelating resins, a graphene oxide-TiO_2 composite was synthesized as a novel and inexpensive type of carbon-based nanomaterial and packed into a micro-column for the online preconcentration and ICP-OES detection of La, Ce, Eu, Dy and Yb (additionally Cu and Pb)[35]. High adsorption capacity, fast sorption kinetics, and stability over a wide pH range have been reported due to the unique characteristics of the material, e.g. the large surface area and various oxygen containing groups which offer binding sites for metal ions such as heavy metals and REEs. Adsorption kinetics have been well studied in this work and the adsorption capacity obtained was indicated to be comparable with related SPE materials. Preconcentration factors of 10 could be obtained, yielding LODs in the range of 0.13 – 2.64 ng mL^{-1}. They are, however, orders of magnitude higher compared with those obtained using the chelating resins described above, in particular those obtained using ED~~3~~TA/IDA functionalized resins, and significantly higher than those obtained with chitosan based chelating resins[21, 30], even though the detection system in this case was also ICP-OES, and thus the graphene oxide-TiO_2 composite is not a viable low-cost alternative for the preconcentration of REEs from natural water samples.

It is worth stressing that the accurate quantification of REEs by atomic spectrometric detection techniques in hampered by an exhaustive list of spectral interferences. Emission wavelengths ~~as~~

~~observed~~ in ICP-OES~~/(AES)~~ are interfered by overlapping and partially overlapping spectral lines, and molecular- and background interferences. Various techniques are available to overcome these interferences, particularly the careful selection of interference-free emission wavelengths when ICP-OES~~/(AES)~~ detection is performed [21, 30]. A more detailed discussion ~~about~~ of interferences and ways to overcome them is described in He *et al.*, 2017[36].

Spectral interferences~~observed~~ in ICP-MS include numerous isobaric, as well as polyatomic interferences. Although some of the metals belonging to the group of REEs have 6 or 7 isotopes (e.g. Nd, Sm, Gd, Dy, Er, Yb), most of them have~~are~~ isobaric~~ally~~ interferences (e.g. ^{152}Sm, ^{154}Sm, ^{156}Dy, ^{158}Dy and ^{160}Dy on the respective Gd isotope). Polyatomic interferences are, in particular, lower mass oxides and hydroxides which interfere on higher mass REEs (e.g. $^{139}La^{16}O^+$ on $^{155}Gd^+$ and $^{141}Pr^{16}O^+$ on $^{157}Gd^+$ – the only two Gd isotopes with no isobaric interferences). ICP-QMS equipped with an octopole reaction/collision cell with He as collision gas has been used to overcome oxide and polyatomic interferences[33, 124], however, as stated in Zhu end Zheng (2018)[124], the formation of lighter $REEO^+$ is inevitable. ICP-SFMS operated in the “high-resolution mode” ($m/\Delta m > 10000$) could separate some of these polyatomic interferences but~~, however~~ with a significant loss in sensitivity, and hence, detection capability. Therefore, this possibility ~~and has~~ has~~not~~ been scarcely applied (e.g., ~~in the studies published in reference [27 and 28],~~ the “low-resolution mode” has been used in the studies published by Zhu *et al.* (2009 and 2010)[31 and 32]). A prerequisite is to minimize ~~the~~ oxide formation rate by monitoring the CeO^+/Ce^+ and UO^+/U^+ ratios~~, respectively~~, and the interference ratio of MO^+/M^+ when mathematical interference correction is ~~going to be~~ performed, as applied by[31, 32, 33]. Desolvation units such as the CETAC Aridus™ II or the APEX membrane desolvaters (Elemental Scientific Inc. Omaha, Nebraska) can significantly reduce the oxide formation rate down to ~~>~~ < 0.05~~%,~~ %; however, these devices have not been used in this context (for more detailed information the reader is referred to Fisher and Kara (2016)~~-~~[37] and references therein~~ cited publications~~.

3.3 Precious metals

In this section, on-line matrix separation and preconcentration methods based on solid phase extraction for the quantification of precious metals are discussed (see Table 3 for details of selected methods). The determination of precious metals, including the platinum group elements (PGEs) Ru, Rh, Pd, Os, Ir and Pt, as well as Ag and Au, in natural waters is still in its infancy. Naturally occurring concentrations are in the sub-ng L^{-1} - pg L^{-1} range, thus requiring powerful extraction and preconcentration methods. However, the interest in the determination of, in particular, PGE concentrations in the aquatic environment is steadily increasing because of anthropogenic emissions resulting from their use in industrial, chemical, electrical and pharmaceutical applications and in catalytic converters for cars[38, 30]. Silver has also been used in a wide variety of chemistry, electronics, medicine and other industrial fields and is highly toxic to marine organisms due to bio-accumulation[39]. Time consuming as well as potentially harmful methods based on liquid-liquid extraction using ammonium 1-pyrrolidinedithiocarbamate/diethylammonium diethyldithiocarbamate (APDC/DDDC) and co-precipitation and flotation techniques are being replaced by methods based on SPE using chelating sorbents, prior to detection by atomic spectrometry. Due to the characteristic of these metals to mainly occur as anionic chloro-complexes in the aqueous phase, as facilitated by the chloride content in seawater[40, ~~–~~41], (strong) anion exchangers have traditionally been used. However, few publications report the automation and online separation/preconcentration of precious metals from natural waters. More than 10 years ago, a method was published for the determination of Pt using a chelating ion exchange resin (silica gel modified with 1,5-bis(di-2-pyridyl)methylene thiocarbohydrazide - DPTH-gel) in an on-line flow system coupled to ETAAS[42]. Since this publication is not within the timeframe ~~for references~~herein selected, it will not be discussed further; nevertheless, it is worth mentioning that the LOD obtained by this method is not sufficiently low for monitoring naturally occurring concentrations of these metals. An improved method, based on the extraction of Pt, Pd and Ir on 1.5-bis(2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass (PSTH-cpg) in an on-line mode coupled to ICP-MS [43], could achieve LODs in the low ng L^{-1} range with a sample volume of only 3.3 mL (details are given in Table 3). However, the concentrations of the target analytes could still not be quantified in unspiked seawater and river water samples, ~~Since this publication is not within the timeframe for references, it will not be discussed further; nevertheless, it is worth mentioning that the LOD obtained by this method is not sufficiently low for monitoring naturally occurring concentrations of these metals,~~ clearly indicating that the sample volume processed by the on-line flow system does not provide adequate preconcentration factors for the determination of PGEs in natural waters.

As a viable alternative to commercial strong anion exchangers, polyaniline (PANI) has been evaluated for the on-line preconcentration of Pd from natural waters including ground water, lake water and seawater as a low cost and easy to synthesize alternative to other sorbents[44]. The extraction mechanism is based on anion exchange and preconcentration factors of 125 have been reported by applying a sample volume of 250 mL, thus resulting in LODs of 0.0004 – 0-003 ng mL^{-1} (LODs given for individual Pd isotopes) with ICP-MS detection. These however are still not sufficiently low for monitoring natural Pd concentrations. It should be mentioned here that ~~recently,~~ chemical vapour generation of these elements for ~~the~~ introduction into atomic spectrometric sources has been tested and evaluated (please see On-line sample preparation techniques based on cold vapour- and hydride generation techniques for matrix separation and preconcentration of metals and metal species in natural waters. 4 and Table 5).

Several methods were published for the automatic on-line preconcentration and matrix separation of Ag from seawater more than 10 years ago e.g.[45, 46] using the strong anion exchanger Dowex®1x8 with trimethylbenzylammonium functional groups immobilized on a styrene-divinylbenzene gel but only one method has been published recently for the analysis of estuarine samples[47] using the same sorbent. This resin is very popular for the extraction of Ag chloro-complexes as it has a high adsorption capacity. With a sample consumption of only 7.5 mL, a LOD of 0.06 ng kg^{-1} was obtained. This LOD is comparable with those obtained by the two previous methods[45, 46]. The advantage of the latter method, however, is the lower sample volume required (7.5 mL vs 12 mL) and the low column volume of only 18 µL. Validation was performed with SLEW-3 and CASS-4 certified reference materials. These are not certified for Ag but the authors demonstrated the trueness and good precision of the method by comparing these values with previously reported concentrations.

3.4 Actinides

In this section, on-line matrix separation and preconcentration methods based on solid phase extraction for the quantification of actinides (Th, U) are discussed (see Table 3 for details of selected methods). The actinide elements encompass Ac, Th, Pa, U and the transuranic elements, whereas U and Th are the most abundant actinides naturally occurring in all environmental compartments[48]. Additionally, anthropogenic sources of these radionuclides and their synthetic isotopes (^{232}U, ^{233}U, ^{236}U and ^{229}Th) include technological applications (metallurgy, ceramic and nuclear industries), phosphorous mineral fertilizers and pesticides, uranium mining and milling, coal combustion, fuel processing, nuclear power plants and nuclear tests[49, 50]. Due to the high chemical and radiological toxicity of their soluble compounds, permissible limits of U in drinking water are regulated by the Word Health Organisation (WHO; 30 µg L^{-1}) [51], Environmental protection Agency (EPA; 30 µg L^{-1}) [52] and the Atomic Energy Regulatory Board (AERB; 60 µg L^{-1}) [53]. In the last revision of the Drinking Water Directive of the European Commission (EC)[54], U was included in the list of parameters of naturally occurring but harmful substances to be monitored. In addition, environmental quality standards for freshwater have been elaborated by some member states, ranging from 0.015-25 µg L^{-1} [55] within the EU Water Framework Directive. The WHO also set guidance levels for radionuclides in drinking water, i.e. 10 Bq L^{-1} for ^{238}U (81 µg L^{-1}) and 1 Bq for ^{232}Th (246 µg L^{-1}) [51]. Thus, concentrations in the (aquatic) environment need to be monitored. Various methods, mostly employing SPE on actinide specific resins such as TEVA, UTEVA, TRU and DGA resins, based on flow analysis in combination with atomic spectrometric detection, have been reported for the determination of actinides in natural waters e.g. [56, 57, 58, 59]. They were, however, operated with off-line detection, mostly by applying two or more different resins to cover a wider range of analytes and perform in-line extraction chromatographic separation and hence are not within the scope of this manuscript.

One method has been published for the simultaneous determination of U and Th at environmentally relevant concentrations in various water matrices based on a fully automated lab-on-valve FI system coupled to ICP-QMS[60]. The performance characteristics are outlined in Table 3. Extraction and simultaneous elution, i.e. no separation involved, was based on SPE using the UTEVA chromatographic resin functionalised with dipentyl pentylphosphate (DP[PP]) moieties (also called diamyl amylphosphate (DAAP). The authors estimated a resin durability of 150 injections (up to 8 mL sample volume) and reported recoveries of >95%, determined by analyte-spike recovery experiments, and clearly pointed out the low cost of the method as only 30 mg of resin were packed on-line in the column. They also reported the suppressive effect of high concentrations of phosphate due to the formation of a non-extractable charge neutral complex with Th^{4+} cations. Addition of Al^{3+} counteracts this due to the formation of Al^{3+}-phosphate complexes which inhibits Th-phosphate complexation. It should, however, be mentioned that method validation has not been properly performed with matrix certified reference materials; instead the authors ~~have~~ used a BCR-320R sediment ~~CRM~~material.

3.5 Metal speciation

There are many publications on the use of ICP-MS and ICP-OES, as well as AAS, combining on-line sample preparation with elemental speciation analysis of metal(loid)s in natural waters[61]. Arsenic is the most commonly studied metal, followed by Cr and, to a lesser extent, Hg, Sb, Fe, Se and V. In general, elemental speciation involves the differentiation between oxidation states or organic/inorganic elemental fractions. Historically, research and development on elemental speciation analysis was mainly curiosity driven; however, biogeochemical, biological and toxicological effects as well as bioavailability of the elements ~~is~~are highly depend~~ing~~ent on their chemical form~~and/their atio~~. Nonetheless, legal institutions and governmental ~~bodies~~agencies such as WHO, US EPA and EC (e.g. via the EU Water Framework Directive[62]) still define environmental quality standards and limits only for the total elemental concentrations, including all (toxic) compounds.~~whereas nowadays legal institutions and governmental bodies such as WHO, US EPA and EC (e.g. via the Water Framework Directive) define limits not only on total~~

~~elemental concentrations but also on elemental species (oxidation states) or organic molecules containing certain elements, which is a major driver for research on elemental speciation analysis.~~ On-line SPE is mainly used for separation of elemental species or fractions of interest in combination with atomic spectrometric detection and only very few studies deal with the on-line combination of SPE with liquid chromatographic separation. The key analytical performance data for selected papers using on-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the speciation of metals in natural waters are summarised in Table 4.

Commented [PW1]: This seems repetitive and contradictory. Needs some deletion.

Commented [s2R2]: I agree...this is confusing. Müssen wir diskutieren....

Commented [I3]: As far as I know, no guidelines define quality standards for the individual species yet...

Chromium speciation with SPE was performed on-line in several studies using either ETAAS[63, 64, 65] or ICP-MS[66, 67, 68, 69] as the detection technique. In general, these studies achieved LODs in the low ng L^{-1} range and trueness was, in most cases, demonstrated using CRMs. In 2008, Hu *et al.*[68] reported a useful method for the simultaneous speciation of inorganic As(III)/As(V) and Cr(III)/Cr(VI) in natural waters. They used mesoporous Al_2O_3, which was prepared by sol-gel technology, as a capillary micro-extraction coating material. The column retained AsO_4^{3-} and $Cr_2O_7^{2-}$/CrO_4^{-} under acidic condition while cationic As(III) and Cr(III) were not retained. Elution of the retained species was performed under alkaline conditions. They reported LODs of 0.7 and 18 ng L^{-1} for As(V) and Cr(VI), and 3.4 and 74 ng L^{-1} for As(III) and Cr(III), respectively. Evidently, such differential approaches can also be performed on-line with ETAAS. Zou *et al.*[65] combined a *C. vulgaris* cell (green microalgae) mini-column in sequential combination with an anion exchange resin mini-column for the retention of Cr(III) and Cr(VI), respectively. Utilizing a SI system, Cr(III) and Cr(VI) were eluted by 0.04 mol L^{-1} and 1.0 mol L^{-1} nitric acid, respectively, and quantified on-line with ETAAS. LODs were 0.02 µg L^{-1} for Cr(III) and 0.03 µg L^{-1} for Cr(VI), which unfortunately does not meet the California Public Health Goal set to 0.02 µg L^{-1} for Cr(VI).

Selenium speciation is of great interest as the toxicity, bioavailability, and essential nature of this element is highly depending on its chemical form. Huang *et al.*[70] published a double column method combining nanometre-sized Al_2O_3 and mesoporous TiO_2 which was chemically modified by dimercaptosuccinic acid. A schematic diagram of the flow manifold used for this work is shown in Fig. 3. The inorganic selenium species Se(IV) and Se(VI) were selectively adsorbed by Al_2O_3 while the organic Se species, i.e. the seleno-amino acids selenocysteine and selenomethionine, which were not retained on the first column, were retained on the chemically modified, mesoporous TiO_2. Sequential elution enabled the selective and sensitive determination of the four species (LODs were in the range of 45 - 210 ng L^{-1}) in lake water.

Vanadium, like Se, is one of the major essential elements, but also has toxic properties depending on both the concentration and oxidation state. Xiong *et al.* [71] speciated V(IV) and V(V) on a conical micro-column packed with cetyltrimethylammonium bromide-modified alkyl silica.

The species showed different pH dependent retention behaviour: V(V) was quantitatively retained in the pH range 2.0 – 7.0, while V(IV) was not retained at pH 2.0 - 3.5 but quantitatively retained at pH 5.0 - 7.0. V(IV) was quantified by subtracting V(V) from total V. The LOD for V(V) was 0.03 µg L^{-1}.

It can be concluded that FI in combination with elemental speciation analysis is mature in terms of the technical developments, which have been achieved over many decades. The situation regarding CRMs certified for elemental species is still not well developed, as for many matrices no reliable materials are available. Regarding validation, the authors of this work wish to emphasise that in order to assure comparability of different studies in terms of LODs and LOQs and in terms of their applicability to control legal limits, improvements towards setting a harmonized procedure are much needed. Evidently there are several ways to calculate these values for transient signals, but most of the time the procedures are not fully described or completely missing. Accordingly, we propose adoption of the well elaborated procedure outlined in the EURACHEM guide "The Fitness for Purpose of Analytical Methods"[72] for calculating LODs and LOQs for methods which use peak areas for calibration and quantification purposes.

4 On-line sample preparation techniques based on cold vapour- and hydride generation techniques for matrix separation and preconcentration of metals and metal species in natural waters.

Cold vapour generation (CVG) and hydride generation (HG) techniques have been used in on-line flow systems to separate the analyte from the matrix, in some instances in combination with sorptive preconcentration using chelating sorbents. A precondition, however, is the formation of volatile species upon reaction with reducing agents such as sodium borohydride in an acidic environment. The classical elements determined by HG are Ge, Sn, As, Bi, Sb, Se and Te after chemical transformation into their gaseous hydrides, whereas e.g. Hg and Cd are determined by CVG after volatile species are generated. It should be mentioned that for the reduction of inorganic Hg, tin chloride can also be used. Through gas/liquid phase separation by an argon gas carrier stream, the volatile hydrides/elements are transported into the plasma or graphite furnace. Matrix separation is based on the fact that non-volatile interfering elements such as major ions do not form hydrides, and thus remain in the liquid phase and are drained off to waste. Hydride analyte transport efficiencies up to 100%, leading to higher signal/noise ratios, and hence lower LODs, in comparison with conventional liquid sample introduction, are reported[73]. HG/CVG is an important sample introduction technique when coupled on-line to atomic spectrometric detectors[73] but careful optimization of the hydride generation process is required, e.g. the concentration of the reducing agent because too high a concentration of $NaBH_4$ may lead to foaming and the production of droplets as well as the generation of excessive hydrogen gas. These factors result in plasma instability[74], especially when coupled to ICP-based detectors.

Methods employing CV and HG techniques for the matrix separation and preconcentration of metals in natural waters are summarized in Table 5.

Only a limited number of papers have been published within the last decade reporting the determination of As[75], Cd[76] and Hg[77] in natural waters after HG and CV generation with $NaBH_4$ without preconcentration on chelating sorbents. For example, for the quantification of Hg, the CV technique, even without preconcentration, LODs are reported to improve by a factor of 24 when CV-ICP-QMS is used compared with solution nebulization based ICP-QMS due to reduced signal suppression from matrix effects[77].

Nevertheless, also in combination with CV and HG techniques, matrix effects with a negative effect on the accuracy and sensitivity of these methods have been observed. To overcome matrix interferences arising from e. g. Ca, Mg, K and Na, as well as various transition metals (Cu, Fe, Ni, Co) present in natural waters at high(er) concentrations, SPE based on ion-exchange has been applied prior to HG/CV generation in various applications (see Table 5). The challenge here is to find the optimum acid concentration for both the elution of the retained metal species from the preconcentration column (stronger acids usually enhance recovery) and efficient hydride generation as this process is strongly dependent on the pH and acid strength. For example, Sb, Bi and Sn were preconcentrated from seawater on ~~1,5-bis(di-2-pyridyl)methylene thiocarbonohydrazide~~DPTH bonded to silica gel (DPTH-gel) packed in a mini-column prior to HG-ICP-QMS analysis[78]~~[65]~~. As hydride generation efficiency depends on the oxidation state of the elements, *L*-cysteine was used as a pre-reducing and masking agent. Increased signal intensities could be obtained for Sn, whereas those for Sb and Bi were not affected by *L*-cysteine addition. Enrichment factors of 2.5 – 8.6 were achieved with a sample volume of 4.8 mL. Limits of detection were in the sub µg L^{-1} range and sufficiently low for the determination of these elements in diluted CRMs and real seawater samples. A similar approach has been applied to~~for~~ the determination of these elements and, in addition, ~~for~~ Hg from seawater and river water[13]~~[66]~~**Error! Bookmark not defined.**~~[79]~~. DPTH was functionalized on mesoporous silica, packed in a mini-column and ~~the~~ elution was performed with HCl (plus thiourea for Hg) while in [78] ~~the former paper~~[74]~~[65]~~ HNO_3 alone was used instead. A comparison between these two methods showed similar performance for Sb, Bi and Sn with respect to trueness (estimated from TMDA 54.4 and

TM 24.3 fortified lake water CRMs), precision, relative recovery and the detection capability of ICP-QMS vs ETAAS.

Sánchez-Trujillo *et al.*[80] addressed a problem associated with simultaneous multi-element determinations for Pb, Cd and Hg using CVG-ICP-QMS, i.e., different optimal conditions are required for individual elements. Catalysts such as thiourea and Co were used for more efficient reaction of Cd, and hexacyanoferrate (III) was proposed as an oxidizing reagent for the conversion of Pb(II) to Pb(IV) ([80] and therein cited publications). The elimination of interferences on the determination of other elements requires the use of appropriate sorbent materials, oxidizing agents and catalysers. In fact, two mini-columns packed with DPTH-gel were incorporated in the flow manifold in parallel, *viz.*, in the injection loop of two rotary valves, and loaded with sample adjusted to pH 5.0. Elution with thiourea in HNO_3 was performed, and whereas the eluted metals from the first column were mixed with a reducing agent consisting of $NaBH_4$ and $K_3Fe(CN)_6$ for the generation of PbH_4 (and Hg^0 vapour), those eluted from the second column were mixed solely with $NaBH_4$ for Cd^0 and Hg^0 vapour generation. Hence, the most efficient vapour generation conditions for each element were obtained. Enrichment factors in the range of 14.4 – 27.3 were obtained and LODs were in in the low ng L^{-1} range. However, these are at least 3 times higher than those obtained by HG/CVG methods developed for the single element determination of e.g. Hg[77], Cd[76] and Pb[81] (see Table 5), probably due to the addition of reagents for pH adjustment, oxidation and improved elution efficiency contributing to the blank signal.

Noble metals are not traditionally analysed by CVG due to the unknown identity and formation efficiency of their hydrides and volatile species but recent studies have shown its suitability for the determination of Pt, Pd, Ir[82], and ~~in addition to these~~also Os, Rh, Ag and Au ~~Au, Ag, Pd, Pt, Ir, Rh and Os determinations using NaBH4 as the reducing agent~~83, 84. using $NaBH_4$ as the reducing agent. The target analytes were preconcentrated using SPE on DPTH-gel82 packed in a mini-column and MSPE on DPTH immobilized on iron oxide magnetic nanoparticles (DPTH-MNPs)83 and DP~~HT~~TH immobilized on magnetic graphene oxide (DPTH-GO)[84], which were retained in a knotted reactor by an external magnetic field, with the analytes eluted with thiourea in HCl or HNO_3 prior to online ICP-OES detection. Detailed methodological information is given in Table 5. Since chemical vapours of noble metals are unstable, rapid transition and separation from the liquid phase into the gas phase and introduction into the detection system is required, thus making this procedure very sophisticated. The spray chamber has been used as a gas-liquid separator in these studies. By mixing the analytes with the reducing reagent via a T-junction just before the nebulizer ~~showed an achievement in~~ the formation of volatile species is improved but ~~lower~~ efficiencies were lower compared ~~to~~with "conventional" SPE without CVG[82] ~~were detected~~. *In situ* CVG ~~by~~ using a commercially available multi-mode sample introduction (MMSI) system for CVG and liquid nebulization, which also served as gas/liquid separator, was a pre-requisite for the applicability of this approach for efficient vapour generation. ~~After preconcentration of these metals onto DPTH immobilized on iron oxide magnetic nanoparticles, which were retained in a knotted reactor by an external magnetic field, and elution with thiourea/HCl, the eluate was directed into a multi-mode sample introduction (MMSI) system for CVG and liquid nebulization. This MMSI also served as the gas/liquid phase separator. *In situ* CVG was a pre-requisite for the applicability of this approach as noble metal hydrides are unstable and require rapid separation from the liquid phase. ~~It was shown that hydride formation in the presence of $NaBH_4$ was appropriate for Ag, Pt, Pd and Os whilst Au, Ir and Rh signals did not improve compared with non-CVG results, hence requiring the use of compromised conditions[83]. A ~~prefered~~preferred or missing formation rate of noble metal volatile species has not been reported by García-Mesa (2019)~~in reference~~ [84]. Widely ranging ~~. E~~enrichment factors – depending on the applied method and the analytes – ~~a~~were reported and LODs w~~ere in the range of ≤20 for Pd, Os, Au, Ir and Rh, 144 for Pt and 206 for Ag. The LODs were in the ran~~ere in the low µg L^{-1} and sub-µg L^{-1} ranges, ~~ge of 0.03 µg L^{-1} (Ag) and 100 µg L^{-1} (Rh), ~~i.e. not sufficiently low for the determination of ambient noble metal concentrations in natural waters.

Sample introduction techniques based on ~~cold vapour~~CV and ~~hydride generation~~HG have also been used in this context with elemental speciation analysis. Details of selected methods are summarized in Table 6. Two studies have addressed the separation of inorganic mercury and methyl mercury. Krishna *et al.* [85] developed a speciation approach for the two fractions employing efficient preconcentration of natural water samples (pH 7) on a polyaniline microcolumn and subsequent selective elution of MeHg and iHg using 2% HCl and a mixture of HCl–thiourea (2% HCl + 0.02% thiourea) respectively. This successful combination of preconcentration, speciation and CVG-ICP-MS (all on-line) enabled quantification of the two species in the high ng L^{-1} range. Sánchez-Trujillo *et al.* [86] published a similar concept using on-line CVG-ICP-MS after on-line enrichment/speciation of the two Hg-fractions on mesoporous silica functionalized with 1,5-bis(2-pyridyl) methylene thiocarbohydrazide. Selective elution of CH_3Hg^+ and Hg^{2+} was obtained with 0.2% HCl and 0.1% thiourea in 0.5% HCl, respectively. Total mercury (calculated as the sum of the two fractions) was determined in LGC 6016 (Estuarine Water) and was in good agreement with the results obtained by the same group in an earlier study[80]. The LODs in this work were lower than those obtained in the earlier study using the polyaniline material, which can be explained mainly by the use of a next generation ICP-MS detection system. In a similar approach to that used in many other studies, method LODs in the two above mentioned studies were calculated from background noise, its standard deviation and the height

Commented [l4]: UMSCHREIBEN

of a measured standard solution. It is noteworthy that this method allows relative inter-comparison of different methods but is not capable to give reliable LODs or LOQs, as quantification is routinely performed via peak integration (peak area), whereas in these cases LODs/LOQs are calculated via peak height.

~~Hydride generation~~HG was used in ~~two further~~ studies on the speciation of different oxidation states of ~~arsenic~~As[87, 88] and ~~antimony[65]~~Sb[74]. ~~The~~ One ~~work~~ report concerning ~~arsenic~~ As used a differential approach by passing natural water sample through a strong anion exchanger cartridge, on which As(V) was selectively retained, whereas As(III) passed through the column and was detected via HG AAS[87]. The concentration of As(V) was then determined by subtracting the As(III) concentration from the total As concentration of the sample. LODs were of the order of 0.5 µg L^{-1}. The authors discussed the limitations of their work regarding organic As species (which would also pass through the column and lead to false positive As(III) results) and present a method that is fast and reliable and suitable for the analysis of low salinity natural waters for As(III). A very recent study has been published by Montoro-~~-~~Leal *et al.*[88] using functionalized Fe_3O_4 magnetic nanoparticles packed in two knotted reactors for inorganic As speciation in environmental waters following a similar differential approach. However, speciation was based on different reduction conditions; thus, different concentrations of borohydride were used. This method showed a high sample throughput and very low detection limits of 2.7 and 3.2 ng L^{-1} for As(III) and total inorganic As and has been validated for the determination of As ~~also~~ in highly saline samples such as seawater. For the speciation of inorganic ~~antimony~~Sb, selective sorption materials were used in a FI approach with sequential elution and on-line HG-ICP-MS detection[74]. Accuracy was demonstrated for the sum of the quantified Sb species by the analysis of the CRMs SLRS-5 River Water and TMDA-54.4 Fortified Lake Water. It should be mentioned that, due to the lack of species-specific CRMs, it is difficult to assess method accuracy with regard to the target species. In such cases inter-comparison with independent methods available in-house, or inter-comparison with other competent laboratories is mandatory for method validation/verification in terms of trueness.

5 On-line sample preparation techniques based on liquid-liquid-micro extraction ~~and cloud point extraction~~ techniques for matrix separation and preconcentration of metals in natural waters.

There are a limited number of published papers dealing with liquid-phase microextraction (LPME) in flow systems for trace element analysis in surface waters as compared with those using SPE[10]~~[89]~~. This is attributed to operational difficulties in achieving (i) reliable dispersion of the aqueous and organic phases across the conduits of flow platforms, (ii) quantitative

Commented [I5]: MANUEL and PAUL: we only cited 1 publication about CPE (2009 Li) but we did not add the information to Table 7 (as far as I remember, no one of us could access the paper). Should we just delete CPE and only focus on LLME studies? (please see comment of Referee 3 Section 5, page 17) separation under the flow regime of the analyte-containing organic phase after extraction and (iii) high enrichment factors on account of the limited organic to liquid-phase ratios in miniaturized systems. Moreover, metal species usually need to be derivatized prior to ~~liquid-phase extraction~~LPME[90] ~~or reacted with an appropriate surfactant for cloud-point extraction (CPE)[91]~~, in contrast to SPE for which there is a plethora of commercially available sorbents with a wide range of chelating moieties for direct extraction and preconcentration at the appropriate pH. The key analytical performance data for selected papers ~~using liquid-liquid micro-extraction (LLME) and cloud point extraction~~~~CPE~~LPME ~~techniques~~ approaches for the matrix separation and preconcentration of metals in natural waters are summarised in Table 7.

Some of the FI-based papers on LPME for trace metal determinations merely report semi-automatic methods. The flow platform is used for automation of the detection step after batch LPE[92], or phase separation by modification of the ionic strength or temperature and retrieval of the metal-containing phase for detection[93].

Computer-controlled flow methodologies using programmable flow, such as sequential injection analysis and its variants[94, 95, 96], have been designed for the miniaturization of ~~liquid-phase extraction~~LPME schemes, endowing these methods with green chemical credentials whilst also ameliorating extraction efficiencies and enrichment factors. For example, Anthemidis and co-workers have developed a number of appealing ~~intriguing~~ ~~liquid-phase microextraction (~~LPME variants, such as dynamic single-drop LPME[95, 96], countercurrent LPME[90] and dispersive LPME (DLPME)[97, 98, 99, 100] that were fully automated as a front-end to ~~flame~~ FAAS or ETAAS~~electrothermal AAS~~ for direct on-line injection of the metal-enriched organic phase. In those articles dealing with DLPME[97, 98, 99, 100], the aqueous sample, organic solvent containing the chelating reagent and dispersing solvent were merged on-line to generate droplets of the organic phase for efficient extraction of the neutral chelates followed by on-line trapping of the metal containing organic droplets into reversed-phase materials packed in flow-through micro-columns. A schematic diagram of a flow manifold integrating in-line DLPME as a front end to ETAAS is shown in Fig. 4.

The main issue observed by a number of FI/SI systems incorporating LPE/LPME, alike SPE, is that method validation is performed with overly simplistic CRMs (e.g. lyophilised solutions[94]) or entirely different matrices (e.g., sediments and mussel tissues) that do not properly simulate the composition of the target matrices (river water, seawater) analysed in those papers[100, 90, 96]. Moreover, FI/SI-based LPME methods sometimes use environmentally unfriendly solvents, and on-line coupling to standard ICP instrumentation is more complicated as compared ~~to~~with SPE ~~counterparts~~ because of potential incompatibility of the extracting medium (back-extraction is usually recommended instead), thus making multi-elemental analysis troublesome.

6 Conclusions and perspectives

~~Flow injection~~FI has become a mature approach for metal determination and non-chromatographic speciation analysis, but still constitutes a viable platform and vehicle for on-line implementation of in-house and commercially available sorptive (nano)materials prior to atomic spectrometric detection systems for trace and ultra-trace analysis. ~~Out of the several~~When comparing theon-line sample preparation approaches discussed herein ~~overviewed~~ (i.e., LPME, SPE, CV/HG), SPE is by far the most attractive ~~approach that~~because it offers superior performance in terms of versatility, reliability and enrichment capability for trace elements in freshwater systems. The analytical detection techniques have not greatly evolved in terms of sensitivity and instrumental detection limits over the last 10 years and thus efficient sorbent phases and ligands for element preconcentration and clean-up analysis of natural waters are still required. It should however be noted that some of the analytical methods reported in the literature that include enrichment protocols are not sensitive enough for the analysis of natural waters and thus spike concentration levels that are not environmentally relevant of natural waters are used for method validation instead. Likewise, inappropriate reference materials, such as biological materials, sediments and wastewaters, have been selected for evaluation of the trueness of methods applied to natural waters. It is therefore recommended that QC/QA tools and uncertainty measurements should be adopted in fully validated protocols using FI approaches.

The last two decades have also witnessed the advent of novel miniaturized and portable devices based on mesofluidic Lab-on-Valve and microfluidic Lab-on-chip platforms, yet application to continuous on-line monitoring is still in its infancy.

Acknowledgement

Manuel Miró acknowledges financial support from the Spanish State Research Agency (AEI) and Ministry of Science, Innovation and Universities (MCIU) through projects CTM2017-84763-C3-3-R (MCIU/AEI/FEDER, EU) and CTM2017-90890-REDT (MCIU/AEI/FEDER, EU).

Table 1: Multi-element on-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the determination of the total metal concentration of transition metals and metalloids in natural waters. (All units as in the original publication)

Analyte	**Matrix**	**Solid phase**	**Detection technique**	**Sample treatment/ Elution**	**Figures of merit**				**Validation**	**Sample volume**	**Enrichment factor**	**Sample throughput**	**Ref**
					DL	**Linear range**	**Precision**	**Relative Recovery**					
Mn, Co, Ni, Cu, Pb	River water	PMMA microchip (treated with saturated NaOH)	ICP-MS	pH 6 (NH_4Ac)/ 0.5% HNO_3	Mn: 2.62 ng L^{-1} Co: 1.69 ng L^{-1} Ni: 42.54 ng L^{-1} Cu: 13.85 ng L^{-1} Pb: 1.64 ng L^{-1}	Up to 5 μg L^{-1}	2.9-3.6% (n=3)	83-110%	NIST 1640a trace elements in natural water	20 μL	≥2	19.35 h^{-1}	24
Zn, Cu, Cd, Cr, V, As	River water, lake water (*well water)	MWCNTs-silica	ICP-OES	pH 8.5/ 2 M HCl	Zn: 0.27 μg L^{-1} Cu: 0.11 μg L^{-1} Cd: 0.45 μg L^{-1} Cr: 0.91 μg L^{-1} V: 0.55 μg L^{-1} As: 0.67 μg L^{-1}	LOD–100 μg L^{-1}	3.1-8.6% at 10 μg L^{-1} (n=7)	82-115%	GSBZ50009-88, GSBZ 50029-94 environmental waters	6 mL	10	n.a.	101
Co, Fe, Pb, V	Seawater	Toyopearl AF-Chelate-650	ICP-MS	pH 5 (NH_4Ac)/ 1 M HNO_3	0.021-0.34 nmol L^{-1}	n.a.	4-23%	76.111%	NASS-5 seawater, GEOTRACES reference samples	7.5 mL	10-15	8.25 min/ sample	18
Mn, Co, Ni, Cu, Cd, Pb	River water	PMMA	ICP-MS	pH 8 (maleate buffer)/ 0.5% HNO_3	Mn: 20.6 ng L^{-1} Co: 5.44 ng L^{-1} Ni: 11.86 ng L^{-1} Cu: 4.90 ng L^{-1} Cd: 16.11 ng L^{-1} Pb: 3.48 ng L^{-1}	0.05-100 μg L^{-1}	< 9% CV (long term)	82-118%	NIST 1643a artificial saline water	50 μL	n.a.	13.33 h^{-1}	23
Mn, Fe, Co, Ni, Cu, Zn	Seawater	Nobias PA 1	ICP-SFMS	pH 5.7, pH 7.0 $(AcNH_4)$/ 1.6 M HNO_3	Mn: 0.002 Co: 0.00029 Fe: 0.014 Ni: 0.013 Cu: 0.003 Zn: 0.016 nmol kg^{-1}	n.a.	1-3% for Ross seawater (long term)	96-107%	GEOTRACES reference samples	9 mL	200	8.75 min/ sample	9

Cd, Co, Cu, Ni, Pb, Zn	Oceanic waters	IDA	ICP-MS	pH 6.0 (AcNH$_4$)/ 0.8 M HNO$_3$	Co: 3.2 pM Ni: 23 pM Cu: 46 pM Zn: 71 pM Cd: 2.7 pM Pb: 1.5 pM	up to: Co: 0.89 nM Ni: 24 nM Cu: 9.6 nM Zn: 20 nM Cd: 2.8 nM Pb: 0.59 nM	3.4-8.6% for SAFe D2	92-102%	NASS-5 seawater, GEOTRACES reference sample (SAFe)	7 mL	10	6 min/ sample	[102]
Co, Cr, Ni, Cd, Mn, Zn, Cu, Pb	Seawater	PTSH-cpg resin	ICP-MS	pH 8.0±0.5 (borate/ boric acid buffer)/ 5% (m/m) HNO$_3$	Co: 0.002 µg L^{-1} Cr: 0.057 µg L^{-1} Ni: 0.117 µg L^{-1} Cd: 0.004 µg L^{-1} Mn: 0.21 µg L^{-1} Zn: 0.260 µg L^{-1} Cu: 0.030 µg L^{-1} Pb: 0.020 µg L^{-1}	DL-60 µg L^{-1}	< 5% (at twice the DL, n=10)	82-111%	SLEW 3 and LGC6016 estuarine water, CASS-5 coastal seawater, SLRS-5 river water, TMDA-54.4 fortified lake water	2.1 mL	2.2-6.8	8.6 h^{-1}	[20]
Cd, Pb, Cu	River water, lake water, (*urine)	SCX Bond Elut® Plexa™ PCX	FAAS	pH 2 (HNO$_3$)/ 1 mol L^{-1} HCl	Cd: 0.1 µg L^{-1} Pb: 1.8 µg L^{-1} Cu: 0.5 µg L^{-1}	Cd: 0.4-20 µg L^{-1} Pb: 7.5-450 µg L^{-1} Cu: 1.8-100 µg L^{-1}	Cd: 2.9% at 2 µg L^{-1} Pb: 3.1% at 30 µg L^{-1} Cu: 2.7% at 10 µg L^{-1} (n=10)	95-99%	NIST CRM 1643e trace elements in water, (°BCR 278-R trace elements in mussel tissue)	2 mL	90-95	30 h^{-1}	[103]
V, Cr, Cu, As, Pb	River water and tap water (*amongst others)	S-CS-MWCNTs	ICP-MS	pH 7 (HNO$_3$, NH$_3$ H$_2$O)/ 0.5 mol L^{-1} HNO$_3$	V: 0.002 µg L^{-1}, Cr: 0.0038 µg L^{-1} Cu: 0.0035 µg L^{-1} As: 0.0013 µg L^{-1} Pb: 0.0036 µg L^{-1}	0.005-10 µg L^{-1}	V: 3.8% Cr: 1.4% Cu: 3.1% As: 4.6% Pb: 1.6% at 1 µg L^{-1} (n=11)	91-105%	GBW08607 riverine water, (°GBW10024 scallop)	20 mL	V. 111 Cr: 95 Cu: 60 As: 52 Pb: 128	n.a.	[104]
Cd, Co, Ni	Seawater	8-HQ	ICP-MS	AcNH$_4$ buffer/ 1 M HNO$_3$	Cd: 0.008 ng mL^{-1} Co: 0.006 ng mL^{-1} Ni: 0.009 ng mL^{-1}	Cd and Co: 0-0.5 ng mL^{-1} Ni: 0.1-1.0 ng mL^{-1}	Cd: 2.47% Co: 2.09% Ni: 3.03% at 0.25 ng mL^{-1} (n=3)	99-110%	CASS-2 coastal seawater, SLEW-1 estuarine water	40 µL	n.a.	n.a.	[105]
Cd, Pb	Coastal seawater, river water, (*tap water)	OASIS HLB	FAAS	O~~o~~n-line complex formation with DDTP/ Methanol	Cd: 0.09 µg L^{-1} Pb: 0.9 µg L^{-1}	Cd: 0.3-12.0 µg L^{-1} Pb: 3.1-200 µg L^{-1}	Cd: 2.9% at 4 µg L^{-1} Pb: 2.6% at 20 µg L^{-1}	95-99%	NIST CRM 1643e trace elements in water	12 mL	Cd: 155 Pb: 180	24 h^{-1}	[106]

Cu, Mn, Ni	River- and lake water	Alumina hollow fibre	ICP-OES	pH 8.5 (NH_4NO_3)/ 2.5 mol L^{-1} HCl	Cu: 0.88 ng mL^{-1} Mn: 0.61 ng mL^{-1} Ni: 0.38 ng mL^{-1}	Up to 200 ng mL^{-1}	6.2-7.9% at 10 ng mL^{-1} (n=7)	87-110%	GSBZ50009-88 environ-mental water	3 mL	10	5 h^{-1}	107
V, Cu, Pb, Cr	River- and lake water	Modified meso-porous TiO_2	ICP-OES	pH 6.5 (NH_4Cl/ NH_3 H_2O)/ 1 M HNO_3	V: 0.09 µg L^{-1} Cu: 0.23 µg L^{-1} Pb: 50 µg L^{-1} Cr: 0.15µg L^{-1}	0.3-50 µg L^{-1}	V: 1.7% Cu: 3.9% Pb: 4.6% Cr: 2.9% at 5 µg L^{-1} (n=7)	89-107%	GSBZ50009-88 environ-mental water	6 mL	20	10 h^{-1}	108
Co, Cr, Cd, Mn, Zn, Ni	Seawater, river water	DPTH-gel	ICP-MS	pH 8.6 (boric acid/Na tetra-borate)/ 2% (m/m) HNO_3	0.004-0.530 µg L^{-1}	DL-60 µg L^{-1}	0.3-4% at double the conc. used for Dl of the analytes (n=5)	93-110%	SLEW-3 estuarine water, NASS-5 seawater, SLRS-4 river water, TMDA-54.4 fortified water	5 mL	2.3-32.9	10 h^{-1}	109
V, Cu, Pb, Cd, Hg	Lake- and river water	Chitosan modified ordered mesoporous silica	ICP-OES	pH 6.5 (NH_4Cl/NH_3 H_2O)/ 1 M HCl	V: 0.33 ng mL^{-1} Cu: 0.30 ng mL^{-1} Pb: 0.96 ng mL^{-1} Cd: 0.05 ng mL^{-1} Hg: 0.93 ng mL^{-1}	n.a.	V: 2.8% Cu: 6.7% Pb: 1.8% Cd: 4.0% Hg: 5.3% at 10 ng mL^{-1} (n=7)	> 90%	GSBZ50009-88 environ-mental water sample	6 mL	20	10 h^{-1}	110
Cd, Co, Cu, Mn, Ni, Pb, V, Zn	River water	EDTriA-type chitosan	ICP-OES	pH 5 ($AcNH_4$)/ 1.5 M HNO_3	0.002-0.15 ng mL^{-1}	n.a.	< 10%	90-110%	SRLS-4 river water	5 mL	14-35	28 h^{-1}	30
Cd, Co, Cu, Mn, Ni, Pb, V, Zn	River water	Glycine-type chitosan	ICP-OES	pH 5 ($AcNH_4$)/ 1.5 M HNO_3	0.004-0.17 ng mL^{-1}	n.a.	< 10%	90-110%	SRLS-4 river water	5 mL	14-106	27 h^{-1}	21
Mn, Co, Cu, Zn, Pb	(*CRMs)	Fe-based MNPs-PAA	ICP-MS	pH 9 ($AcNH_4$)/ 1% HNO_3	0.04-0.06 µg L^{-1} Cu and Zn: 0.6 µg L^{-1}	0.5-50 µg L^{-1}	4% at 5 µg L^{-1} (n=3)	96-109%	CASS-2 nearshore seawater, (°RSM 2670a trace elements in urine)	20 µL	n.a.	5 min/sample	26
~~Sb, Hg~~	~~Seawater, mineral water (*spiked tap water)~~	~~Functional-ized magnetic graphene oxide~~	~~ICP-OES~~	~~pH 3.0 (glycin-HCl)/2% (wt/vol) thiourea in~~	~~Sb: 1.5 µg L^{-1}~~ ~~Hg: 0.05 µg L^{-1}~~	~~Sb: 9.0-5000 µg L^{-1}~~ ~~Hg: 0.2-1000 µg L^{-1}~~	~~Sb: 4.5%~~ ~~Hg: 1.6% at 25 µg L^{-1} (n=11)~~	~~Sb: 93-117%~~ ~~Hg: 93-105%~~	~~TMDA 54.4 fortified lake water~~	~~16.8 mL~~	~~Sb: 9~~ ~~Hg: 3~~	~~13 h^{-1}~~	~~111~~

Commented [l6]: 2019 Garcia Mesa gehört zu CVG/HG section

~~4% (wt/wt) HNO_3~~

Abbreviations:
8-HQ: 8-hydroxyquinoline (8-quinolinol)
cpg: controlled pore glass
DPTH gel: 1-(di-2-pyridyl)methylene thiocarbonohydrazide bonded to silica gel
EDTriA-type chitosan: ethylenediamine N,N,N'-triacetate-type chitosan
IDA: iminodiacetate
MNPs-PAA: magnetic nanoparticles with polyacrylic acid
MWCNTs: multi-walled carbon nanotubes
OASIS HLB: poly(divinylbenzene-N-vinylpyrrolidone) co-polymeric beads
PCX: polymeric cation exchanger
PMMA: poly(methyl methacrylate)
S-CS-MWCNTs: Schiff base-chitosan grafted multiwalled carbon nanotubes
SCX: strong cation exchanger

Table 2: Single-element on-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the determination of the total metal concentration of transition metals and metalloids in natural waters. (All units as in the original publication)

Analyte	**Matrix**	**Solid phase**	**Detection technique**	**Sample treatment/Elution**	**Figures of merit**				**Validation**	**Sample volume**	**Enrichment factor**	**Sample throughput**	**Ref**
					DL	**Linear range**	**Precision**	**Relative Recovery**					
Co	Underground water, (*tap water)	Fe_3O_4 nanoparticles	ETAAS	None/ Ethanol	6 ng L^{-1}	0.01-5μg L^{-1}	2.8% at 0.5 μg L^{-1} (n=11)	96-99%	(°GBW 07303 stream sediment, GBW10017 powdered milk)	2 mL	30	18 h^{-1}	112
Co	(*Only CRM)	*L*-tyrosine functionalized MWCNTs	FAAS	pH 7.0 ($AcNH_4$)/ 10% (v/v) HNO_3	50 ng L^{-1}	DL-250 μg L^{-1}	2.7-3.4% at 10 μg L^{-1} (n=10)	102%	QC METAL LL2 metals in natural waters	10 mL	180	>600 s/ sample	22~~113~~
Cu	Coastal and estuarine water	TMA	ICP-OES	pH 5.5 ($AcNH_4$)/ 2% (v/v) HNO_3	0.4 μg L^{-1}	0-50 μg L^{-1}	3.2% at 5.0 μg L^{-1}	91-103%	(°CRM22 fish otoliths, SRM 1400 bone ash)	10 mL	5	n.a.	114
As	(*Cave water, tap water)	Live HeLa cells immobilized on Sephadex G-50 beads	GFAAS	pH 3.0 (phosphate buffer)/ 2 M HNO_3	0.05 μg L^{-1}	0.15-2.5 μg L^{-1}	1.7% at 1.25 μg L^{-1} and 3.4% 0.5 μg L^{-1} (n=9)	97-98%	SRLS-4 river water	450 μL	11	13 h^{-1}	115
Cd	Ground-, river- and coastal seawater	SiMAG-Octadecyl	ETAAS	pH 2.0±0.2 (HNO_3); on-line addition of DDTC/ IBMK	3 ng L^{-1}	9-350 ng L^{-1}	3.9% at 50 ng L^{-1} (n=11)	94-98%	NIST CRM 1643e trace elements in water	5 mL	19	8 h^{-1}	19
Cd	Mineral water, (*tap water, synthetic seawater)	3-MPTMS-MWCNTs	FAAS	pH 7.5 (phosphate buffer)/ 1 M HCl	0.15 μg L^{-1}	1-60 μg L^{-1}	4.04% at 1 μg L^{-1} and 2.34% at 55.0 μg L^{-1} (n=10)	92-110%	NIST SRM 1643e trace elements in natural waters, (°NIST SRM 1573a tomato leaves)	20 mL	31.5	14 h^{-1}	116

Commented [l7]: Lisa check Ref (cross ref 20 2009 Pacheco)

Cd	Spring water, rain water, snow water	Fe-based MWNTs	ETAAS	pH 6.0 (NaOH)/ 0.002 mol L^{-1} H_3PO_4 and 0.1 mol L^{-1} HN_4NO_3	1.3 ng L^{-1}	0.003-0.2 µg L^{-1}	2.2% at 0.1 µg L^{-1} (n=11)	97-105%	GBW08608 trace elements in water, (°GBW07404 soil)	1000 µL	31.2	12 h^{-1}	117
Cd	Spring water, rain water, seawater, (*tap water)	*S. cerevisiae* cell-loaded cytopore® beads	GFAAS	pH 6-7 (0.1 mol L^{-1} NaOH)/ 0.8 mol L^{-1} HNO_3	1.1 ng L^{-1}	5-100 ng L^{-1}	3.3% at 50 ng L^{-1} (n=11)	69-102%	(°GBW 07404 soil)	1 mL	30	20 h^{-1}	118
Cd	Mineral water, lake water, (*tap water)	Histidine functionalized MWCNTs	FAAS	pH 8.50 (ammoniacal buffer)/ 0.8 M HNO_3	0.20 µg L^{-1}	2-140 µg L^{-1}	3.11% at 40 µg L^{-1} (n=10)	96-104%	(°Tort 2 Lobster Hepato-pancreas)	15 mL	17.7	16 h^{-1}	119
Cd	River water, spring water, ground water, (*tap water)	Salen/Cd(II) complex imprinted polymer	FAAS	pH 6.8 (Britton-Robinson buffer)/ 1% HNO_3	0.11 µg L^{-1}	1-10 µg L^{-1}	6.3% at 1 µg L^{-1} (n=5)	92-107%	ES-H-2 ground water, (°EU-H-3 waste water)	16 mL	117	20 h^{-1}	120
Pb	Mineral water, (*tap water, synthetic seawater amongst other samples)	IIHC	TS-FFAAS	pH 6.46 (phosphate buffer)/ 0.5 mol L^{-1} HNO_3	0.75 µg L^{-1}	2.5-65.0 µg L^{-1}	5% at 10.0 µg L^{-1} and 3.6% at 60.0 µg L^{-1} (n=10)	93-110%	(°DORM-3 fish protein, MESS-3 and PACS-2 marine sediments)	20 mL	128	n.a.	121
Pb	Ground water, river water, coastal seawater	PEEK	FAAS	On-line complex formation with 0.5% (m/v) DDPA in water/ IBMK	0.32 µg L^{-1}	3.6-300 µg L^{-1}	2.2% at 50 µg L^{-1} (n=11)	95-97%	NIST CRM 1643e trace elements in water, (°IAEA-433 marine sediment, BCR 278-R trace elements in mussel tissue)	22 mL	110	20 h^{-1}	122
Pb	Seawater, (*tap water)	Filamentous fungal biomass-loaded TiO_2 NPs	FAAS	pH 4.0 (HNO_3)/ 1 M HCl	0.78 µg L^{-1}	2.5-10 µg L^{-1}	9.1-1.8% at 2.5-100 µg L^{-1} (n=5)	96-104%	NASS-5 seawater	250 mL	868	n.a.	123

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Abbreviations:

IIHC	ion imprinted polyvinylimidazole-silica hybrid copolymer
MPTMS	mercaptopropyltrimethoxysilane
MWCNTs	multi-walled carbon nanotubes
NP	nanoparticle
PEEK	polyether ether ketone
SiMAG	silica maghemite
TMA	2-thiozylmethycrylamide
WCNT	wall coated nanotubes

Table 3: On-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the determination of the total metal concentration of rare earth elements, precious metals and actinides in natural waters. (All units as in the original publication)

Analyte	Matrix	Solid phase	Detection technique	Sample treatment /Elution	Figures of merit				Validation	Sample volume	Enrichment factor	Sample throughput	Ref
					DL	Linear range	Precision	Relative Recovery					
Rare earth elements													
REEs (incl. Y)	Seawater	Toyopearl AF Chelate 650M®	ICP-MS	pH 5.5±0.2 ($AcNH_4$)/ 0.8 M HNO_3	0.002 ng kg^{-1} (Tm)- 0.078 ng kg^{-1}(Ce)	Up to 200 ng kg^{-1} Tm: 100 ng kg^{-1}	Y6% (n=5)	93-106%	CASS-4, SLEW-3 coastal seawaters	6 mL	n.a.	11 h^{-1}	124
La, Ce, Eu, Dy, Yb	Lake water, river water, seawater	GO-TiO_2	ICP-OES	pH 5 / 1 M HNO_3	0.13-2.64 ng mL^{-1}	0.5-1000 ng mL^{-1}	3.2-8.6% at 10 ng mL^{-1} (n=7)	> 90%	(°GBW07301a stream sediment)	7 mL	10	12 h^{-1}	35
REEs	Seawater	SDCC (Nobias PB 1 M)	ICP-MS	pH 6 ($AcNH_4$)/ 2 M HNO_3	0.00008-0.04 pg mL^{-1}	n.a.	< 3.3% for seawater (n=4)	97-100%	Previous results	50 mL	n.a.	n.a.	33
REEs (incl. Y)	Seawater	Nobias PA 1	ICP-MS	pH 6 ($AcNH_4$)/ 1.5 M HNO_3 + 0.4% acetic acid	1-36 ppq	0.1-10 ppt	< 15-23% for 2000 m seawater sample (n=50)	94-102%	NASS-5 seawater, (°VIDAC18 Portuguese mineral water (1:10 diluted))	7 mL	15	15 min/~~sample~~ sample	34
REEs	Lake water	SDCC (Nobias PB 1 M) and InterSEP ME1	ICP-SFMS	pH 5 ($AcNH_4$)/ 2 M HNO_3	0.013-0.15 pg mL^{-1}	n.a.	1.03%	96-104%	NMIJ 7201-1 river water	10 mL	n.a.	3 min/ sample	32
REEs (incl. Sc and Y)	River water	EDTriA-type chitosan	ICP-OES	pH 5 ($AcNH_4$)/ 2 M HNO_3	0.002-0.095 ng mL^{-1}	n.a.	< 10% at 1 ng mL^{-1}	> 95%	SRLS-4 river water	20 mL	83-120	12 h^{-1}	21
REEs (incl. Sc and Y)	River water	Chitosan based chelating resin	ICP-OES	pH 5 ($AcNH_4$)/ 1.5 M HNO_3	0.002-0.25 ng mL^{-1}	n.a.	< 10%	90-110%	SRLS-4 river water	20 mL	21-102	11 h^{-1}	30~~19~~
REEs	Coastal seawater	SDCC (PAPC)	ICP-SFMS	pH 5 ($AcNH_4$)/ 2 M HNO_3	0.005 -0.09 pg mL^{-1}	n.a.	<10%	93-99%	NASS-5 seawater	10 mL	9.6	6 min/ sample	31

Precious metals													
~~Ag, Au, Ir, Os, Pd, Pt~~	~~Seawater, mineral water (*spiked tap water)~~	~~Functionalized magnetic graphene oxide~~	~~ICP-OES~~	~~pH 3.0 (glycin-HCl)/2% (wt/vol) thiourea in 4% (wt/wt) HNO_3~~	~~Ag: 0.5 µgL^{-1}~~ ~~Au: 0.6 µgL^{-1}~~ ~~Ir: 0.2 µgL^{-1}~~ ~~Os: 1.2 µgL^{-1}~~ ~~Pd: 2.6 µgL^{-1}~~ ~~Pt: 0.4 µgL^{-1}~~	~~Ag: 3.0-5000 µgL^{-1}~~ ~~Au: 4.8-3500µgL^{-1}~~ ~~Ir: 6.5-400 µgL^{-1}~~ ~~Os: 7.7-400 µgL^{-1}~~ ~~Pd: 8.3-5000 µgL^{-1}~~ ~~Pt:2.8-5000 µgL^{-1}~~	~~Ag: 3.2%~~ ~~Au: 2.6%~~ ~~Ir: 3.1%~~ ~~Os: 3.8%~~ ~~Pd: 4.0%~~ ~~Pt: 3.8% at 25 µgL^{-1} (n=11)~~	~~Ag: 90-106%~~ ~~Au: 90-104%~~ ~~Ir: 93-113%~~ ~~Os: 90-104%~~ ~~Pd: 95-106%~~ ~~Pt: 86-106%~~	~~TMDA 54.4 fortified lake water~~	~~16.8 mL~~	~~Ag: 22~~ ~~Au: 29~~ ~~Ir: 9~~ ~~Os: 33~~ ~~Pd: 6~~ ~~Pt: 28~~	~~13 h^{-1}~~	~~99~~
Ag	Estuarine - and seawater	Dowex AG1X	ICP-MS	None/ 2.5 M HNO_3	0.06 ng kg^{-1}	LD-1000 ng kg^{-1}	< 3% (n=5)	99-102%	SLEW-3 estuarine water, CASS-4 coastal seawater	7.5 mL	n.a.	7 h^{-1}	47
Pd	Groundwater, lake water, seawater	Polyaniline	ICP-OES, ICP-MS	No acidification/ 3% HCl + 0.06% thiourea	0.0004 ng mL^{-1}	100 (ICP-OES)/0.22 (ICP-MS) ng mL^{-1}	< 3%	> 99%	Standard additions	250 mL	125	n.a.	44
Pt, Pd, Ir	(*spiked seawater and river water samples)	PSTH-cpg	ICP-MS	pH: 3.2/ 0.03% (m/v) thiourea in 3.2% (v/v) HNO_3	Pt: 78.5 ng L^{-1} Pd: 55.5 ng L^{-1} Ir: 0.1 ng L^{-1}	Up to 600 ng L^{-1}	3% (n=10)	93-107%	(°NIST-2557 autocatalyst)	3.3 mL	Pt: 18 Pd: 2.3 Ir: 43	10 h^{-1}	43
Actinides													
Th, U	Seawater, well water, mineral water, fresh water, (*tap water)	UTEVA	ICP-MS	Acidified to 3M HNO_3/ 0.05 M $H_2C_2O_4$/ 0.01 M HNO_3	Th: 0.4 ng L^{-1} U: 2.8 ng L^{-1}	0-200 µg L^{-1}	1.7% at 2.5 ng L^{-1} (n=5)	> 90%	(°BCR-320R channel sediment)	8 mL	13	9 h^{-1}	60

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Note: Only additional sample treatment other than filtration and preservation with acid is mentioned here.
Abbreviations:

Commented [l8]: Information given in 2019 Garcia Meas belongs to the CVG/HG Table.

Commented [l9]: Lisa: check this reference – okay – aber gehört zu CVG/HG section (2019 Garcia Mesa)

3-MPTMS: 3-mercaptopropyltrimethoxysilane
AC-TBAH: tetrabutylammonium hydroxide-modified activated carbon
AF-MMPs: amine-functionalized magnetite microspheres
APS: 3-aminopropyltriethoxysilane
Bromo-PADAP: 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol
CNTs: carbon nanotubes
CTAB: cetyltrimethylammonium bromide
DDTC: diethyldithiocarbamate
DPTH gel: 1-(di-2-pyridyl)methylene thiocarbonohydrazide bonded to silica gel
EDTriA-type chitosan: ethylenediamine N,N,N'-triacetate-type chitosan
GO-TiO$_2$: graphene oxide titanium dioxide
IIHC: ion imprinted polyvinylimidazol-silica hybrid copolymer
MNPs-PAA: magnetic nanoparticles with polyacrylic acid
MWCNTs: multi-walled carbon nanotubes
OASIS HLB: poly(divinylbenzene-N-vinylpyrrolidone) co-polymeric beads
PAPC: divinylbenzene-methacrylate copolymeric resin containing polyaminopolycarboxylic acid groups = ethylendiaminetriacetic acid and iminodiacetic acid groups
PDDA: poly(diallyldimethylammonium chloride
PMMA: poly(methyl methacrylate)
PSTH-cpg: 1.5-bis(2-pyridyl)3-sulphophenyl methylene thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass
Salen/Cd(II) complex: (cadmium(II) 2,2'-{ethane-1,2-diylbis[nitrilo(E)methylylidene]} diphenolate)
S-CS-MWCNTs: Schiff base-chitosan grafted multiwalled carbon nanotubes

Table 4: On-line sample preparation (matrix separation/preconcentration) based on solid phase extraction for the speciation of metals in natural waters. (All units as in the original publication)

Analyte	Matrix	Solid phase	Sample treatment/ Elution	Detection technique	Figures of merit				Validation	Sample volume	Enrichment factor	Sample throughput	Ref
					DL	Linear range	Precision	Relative Recovery					
Fe(II)/ Fe(III)	Ground water, River water, seawater (*tap water)	Non-functionalized acrylate resin	Fe(II): pH 5 (evacuation by air); Fe(III): pH 4 (evacuation by water)	ICP-MS	Fe(II): 1 ng L^{-1} Fe(III): 1-2 ng L^{-1}	5-5000 ng L^{-1}	n.a.	Total Fe: 97-115% Fe(III): 89-110% Fe(II): 89-108%	SLEW-3, 1640a, 1643e trace metals in natural waters	1 mL	Fe(III) pH 4: 10.1 Fe (II)pH 5: 13.3 Fe(III) pH 5: 20.9	7.5 h^{-1}	125
V(V)/ V(IV)	Seawater, fresh water	CTAB-modified alkyl silica	pH 2.5 and 6.0/ 1 M HNO_3	ICP-OES	V(V): 0.03 µg L^{-1}	0.1-500 µg L^{-1}	V(V): 4.3% total V: 4.0% at 5 µg L^{-1} (n=9)	>90%	GSBZ50029-94 environmental water	3 mL	27.9	24 h^{-1}	71
Cr(III)/ Cr(VI)	Seawater (surface coastal)	Amberlite IRA 910, DPTH-gel	pH 5.5 (NaAc)/ 2 M HNO_3	ICP-MS	0.03 µg L^{-1}/ 0.009 µg L^{-1}	DL-60 µg L^{-1}	2.6%/ 3.2% at 0.3 µg L^{-1} (n=10)	98-113%	SLEW-3, LGC6016 estuarine waters, TMDA-54.4 fortified lake water (1:100)	4 mL	2.4/3.7	7.5 h^{-1}	66~~126~~
Cr(VI)	Snow water, spring water, river water	PDDA-MWNTs	pH 6/ 0.1 M ammonium nitrate	ETAAS	0.016 µg L^{-1}	0.05-1.5 µg L^{-1}	3.9% at 0.5 µg L^{-1} (n=11)	100%	GBW08608 trace elements in water	1000 µL	8.6	9 h^{-1}	64
Cr(III)/ Cr(VI)	Mineral water, lake water, (*waste water)	SWCNTs	pH 3 (HNO_3, CH_3COONa)/ 1.2 M HNO_3	ICP-MS	0.01 ng mL^{-1}/ 0.024 ng mL^{-1}	0.1-100 ng mL^{-1}	<2.1%/ 4.0% at 1 ng mL^{-1} (n=9)	>90%	spiking experiments	20 mL	63	n.a.	67~~127~~

Cr(VI)	Mineral water, river water (*effluent water)	Functionalized mesoporous silica (APS)	pH 2 (HCl)/ 0.1 M $NH_2OH·HCl$ in 1 M HCl	ETAAS	1.2 ng L^{-1}	n.a.	2.5 % at 0.50 µg L^{-1} (n=10)	100%	Recovery studies; total conc.: SRM 1643e trace elements in water	2 mL	27	21 h^{-1}	63
Cr(III)/ Cr(VI)	Lake water, mineral water (*tap water)	Mesoporous Al_2O_3	pH 4.0 (NH_3 H_2O/HNO_3)/ 0.01 M NaOH	ICP-MS	3.4 ng L^{-1}/ 74 ng L^{-1}	n.a.	2.8%/ 3.9% at 1 ng mL^{-1} (n=7)	>90%	GSBZ50027-94, GSBZ50004-88 environmental waters	0.5 mL	5	8 h^{-1}	68
Cr(III)/ Cr(VI)	River water (* tap water)	*C. Vulgaris*/ 717 anion exchanger	pH 6/ 0.04 M/1.0 M HNO_3	ETAAS	0.02 µg L^{-1}/ 0.03 µg L^{-1}	0.1-2.5 µg L^{-1}/ 0.12-2.0 µg L^{-1}	1.9%/ 2.5% at 1.0 µg L^{-1} (n=11)	100%/99 %	GBW08608 trace elements in water	600 µL	10.5/ 11.6	n.a.	65
As(III)/ As(V)	Lake water, mineral water, (*tap water)	Mesoporous Al_2O_3	pH 4.0 (NH_3 H_2O/HNO_3)/ 0.01 M NaOH	ICP-MS	0.7 ng L^{-1}/ 18 ng L^{-1}	n.a.	3.1%/ 4.0% at 1 ng mL^{-1} (n=7)	>90%	GSBZ50027-94, GSBZ50004-88 environmental waters	0.5 mL	5	8 h^{-1}	68
As(III)/ As(V)	River water, lake water, well water, rain water	(CTAB)-modified alkyl silica sorbent	None/ 1 M HNO_3	ICP-OES	As(V): 0.15 µg L^{-1}	0.5-1000 µg L^{-1}	As(V): 4.0% at 5.0 µg L^{-1} (n=9)	n.a.	BW3209 (0602), BW3210 (0602), GSBZ 50031-94 (203706) environmental waters	3 mL	26.7	24 h^{-1}	128
Se(IV)/ Se(VI)	River water, lake water, well water, rain water	(CTAB)-modified alkyl silica sorbent	None/1 M HNO_3	ICP-OES	Se(VI): 0.10 µg L^{-1}	0.5-1000 µg L^{-1}	Se(VI): 3.6% at 5 µg L^{-1} (n=9)	n.a.	BW3209 (0602), BW3210 (0602), GSBZ 50031-94 (203706) environmental waters	3 mL	27.6	24 h^{-1}	128
Se(IV)/ Se(VI), SeCys/ Se-Met	Lake water, (*biological samples)	Nanometre sized Al_2O_3/ mesoporous TiO_2	pH 3.5/pH 6/ 0.2 M NaOH	ICP-MS	45-210 ng L^{-1}	n.a.	7.0-9.7% at 0.8 ng mL^{-1} (n=7), 3.6-5.8% at 5 ng mL^{-1} (n=7)	n.a.		4 mL	1-5	5 h^{-1}	70

*Matrices in brackets indicated with a * are not within the scope of this review.*
n.a.: not available.

Note: Only additional sample treatment other than filtration and preservation with acid is mentioned here.
Abbreviations:
3-MPTMS: 3-mercaptopropyltrimethoxysilane
AC-TBAH: tetrabutylammonium hydroxide-modified activated carbon

AF-MMPs: Amine-functionalized magnetite microspheres
APS: 3-aminopropyltriethoxy silane
CTAB: cetyltrimethylammonium bromide
DDTC: diethyldithiocarbamate
DPTH-gel: 1-(di-2-pyridyl)methylene thiocarbonohydrazide bonded to silica gel
EDTriA-type chitosan: ethylenediamine N,N,N'-triacetate-type chitosan
~~GO-TiO_2: Graphene-oxide-titanium dioxide~~
MWCNTs: multi-walled carbon nanotubes
PAPC: divinylbenzene-methacrylate copolymeric resin containing polyaminopolycarboxylic acid groups = ethylendiaminetriacetic acid and iminodiacetic acid groups
PDDA: poly(diallyldimethylammonium) chloride
PMMA: poly(methyl)-methacrylate
PSTH-cpg: 1.5-bis(2-pyridyl)3-sulphophenyl methylene thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass
S-CS-MWCNTs: Schiff base-chitosan-grafted multiwalled carbon nanotubes
SSDC: syringe driven chelating column (packed with divinylbenzene-methacrylate co-polymeric resin containing polyaminopolycarboxylic acid groups (PAPC) = ethylendiaminetriacetic acid and iminodiacetic acid groups
SWCNTs: micro-column packed single-walled carbon nanotubes
TAR: 4-(2-thiazolylazo)resorcinol
TMA: 2-thiozylmethycrylamide
UTEVA: Uranium and TEtraValent Actinides - diamyl amylphosphonate (DAAP) functionalized

Table 5: Methods employing cold vapour generation (CVG) and hydride generation (HG) techniques for the matrix separation and preconcentration of metals in natural waters. (All units as in the original publication)

Analyte	**Matrix**	**Solid phase**	**Detection technique**	**Sample treatment/ Elution/Reduction**	**Figures of merit**				**Validation**	**Sample volume**	**Enrich-ment factor**	**Sample through-put**	**Ref**
					DL	**Linear range**	**Precision**	**Relative Recovery**					
Hg	Natural water samples	Dithizone chelate	AFS	~~Sample~~ pH: 4.0~~;~~/ 1.5 mol L^{-1} HCl/ ~~Reduction:~~ 1.5% (m/v) $NaBH_4$ in 0.5% (w/v) NaOH~~; Elution: 1.5 molL^{-1} HCl~~	0.02 µg L^{-1}	0.06-3.0 µg L^{-1}	5.2% (n=7) at 0.5 µg L^{-1}	90-105%	Standard addition/ recovery experiments	50 mL	29	5 h^{-1}	129
Pt, Pd, Os, Ir, Rh, Ag, Au	Spiked seawater (*tap water, environmental samples)	DPTH-MNPs	ICP-OES	Water samples: pH 1 (HCl); (*acid digests: pH 0.9 (NaOH)/ 2.5% thiourea (w/v) in 6% (w/w) HCl/ 2.1% (w/v) $NaBH_4$ in 0.1% (w/v) NaOH)	Pd: 1.5 µg L^{-1} Ag: 0.03 µg L^{-1} Os:0.65 µg L^{-1} Au: 0.62 µg L^{-1} Ir: 0.57 µg L^{-1} Pt: 0.63 µg L^{-1} Rh: 100 µg L^{-1}	n.a.	2.6-8.5% at 0.74-14.7 µg L^{-1}	92-108%	TMDA 54.4 fortified lake water, SRM 1643e trace elements in fresh water (°NIST 2557 autocatalyst)	12 mL	Pd: 20 Ag: 206 Os: 9 Au: 18 Ir: 17 Pt: 144 Rh: 3	17 h^{-1}	83
Ag, Au, Ir, Os, Pd, Pt, Sb, Hg	Seawater, mineral water (*spiked tab water	Function-alized magnetic graphene oxide	ICP-OES	pH 3.0 (0.2 M glycin/HCl)/ 2% (wt/vol) thiourea in 4% (wt/vol) HNO_3/ 2.6% (wt/vol) $NaBH_4$ in 0.2% (wt/vol) NaOH	Ag: 0.5 µg L^{-1} Au: 0.6 µg L^{-1} Ir: 0.2 µg L^{-1} Os: 1.2 µg L^{-1} Pd: 2.6 µg L^{-1} Pt: 0.4 µg L^{-1} Sb: 1.5 µg L^{-1} Hg: 0.05 µg L^{-1}1	Ag: 3.0-5000 Au: 4.8-3500 Ir: 6.5-400 Os: 7.7-400 Pd: 8.3-5000 Pt:2.8-5000 Sb: 9.0-5000 Hg: 0.2-1000 µg L^{-1}	Ag: 3.2% Au: 2.6% Ir: 3.1% Os: 3.8% Pd: 4.0% Pt: 3.8% Sb: 4.5% Hg: 1.6% at 25 µg L^{-1} (n=11)	Ag: 90-106% Au: 90-104% Ir: 93-113% Os: 90-104% Pd: 95-106% Pt: 86-106 Sb: 93-117% Hg: 93-105%	TMDA 54.4 fortified lake water	16.8 mL	Ag: 22 Au: 29 Ir: 9 Os: 33 Pd: 6 Pt: 28 Sb: 9 Hg: 3	13 h^{-1}	84

As, Sb, Hg	Seawater	DPTH-MNPs	HR-CS-ETAAS	pH: 5 (acetic acid/sodium acetate buffer)/ 5.0% (wt/wt) HCl/ 0,1% (wt/vol) $NaBH_4$ in 0.1% (wt/vol) NaOH	As:0.25 µg L^{-1} Sb: 0.003 µg L^{-1} Hg: 0.22 µg L^{-1}	n.a.	2.2-2.9 % (n=11) at As: 8 µg L-^{1}, Sb: 0.2 µg L^{-1}, Hg: 1.5 µg L^{-1}	90.4-110%	TM 24.3 and TMDA 54.4 fortified lake water	12 mL	As: 23.4 Sb: 2.9 Hg: 3.3	16.7 h^{-1}	78~~1~~ ~~6~~
Sb, Bi, Sn, Hg	Seawater, river water	DPTH-silica gel	HR-CS-ETAAS	pH 2.2 (glycine/HCl)/ Sb, Bi, Sn: 3.1% HCl, Hg: 4.6% thiourea/ 0.6% (w/v) $NaBH_4$ in 0.1% (w/v) NaOH	Sb: 0.009 µg L^{-1} Bi: 0.001 µg L^{-1} Sn: 0.18 µg L^{-1} Hg: 0.17 µg L^{-1}	0.025-2.5 µg L^{-1}	1.9-2.4% at 1 µg L^{-1} (n=11)	91-103%	TM 24.3, TMDA 54.4 fortified lake waters	3 mL	Sb: 4 Bi: 18 Sn: 7 Hg: 9	7.5 h^{-1}	~~6917~~ 13
Pt, Pd, Ir	Spiked seawater	DPTH-gel	ICP-OES	pH: 7.5 (borate-boric acid buffer)/0.07% (wt/v) thiourea in 2 mol L^{-1} HCl/0.5% (wt/v) $NaBH_4$ in 0.1% (wt/v) NaOH	Pt: 1.4 µg L^{-1} Pd: 0.5 µg L^{-1} Ir: 0.6 µg L^{-1}	0.05 – 3 mg L^{-1}	Pt: 2.8% Pd: 2.7% Ir: 2.9% (n=10)	94.5-105.8%	(*NIST 2557 autocatalyst)	6.6 mL	Pt: 6.3 Pd: 6.7 Ir: 6.3	11 h^{-1}	82s
Pb, Cd, Hg	Natural waters including seawater	DPTH-silica gel	ICP-MS	pH 5.0 (acetic acid/sodium acetate)/ 1.5% (w/w) thiourea in 1.5% (w/w) HNO_3/ Pb: 1.25% (w/v) $NaBH_4$ + 3% (w/v) $K_3Fe(CN)_6$; Cd and Hg: 1.25% (w/v) $NaBH_4$ in 0.1% (w/v) NaOH	Pb: 9 ng L^{-1} Cd: 17 ng L^{-1} Hg: 12 ng L^{-1}	DL-30.0 µg L^{-1}	2.5-2.9% at 0.5 µg L^{-1} (n=9)	985-105%	TMDA-54.4 fortified lake water, LGC6016 estuary water, CASS-5 seawater	5.4 mL	Pb: 16.4 Cd: 25.1 Hg:27.3	10.4 h^{-1}	80
Sb, Bi, Sn	Seawater	DPTH-silica gel	ICP-MS	pH 3.5 (0.75% cysteine added)/ 4% HNO_3/ 0.5% $NaBH_4$ in 0.1% NaOH	Sb: 0.01 µg L^{-1} Bi: 0.002 µg L^{-1} Sn: 0.142 µg L^{-1}	DL-60.0 µg L^{-1}	1.1-1.5% (n=10)	97-108%	Diluted TMDA-54.5, TM-24.3 natural waters	4.8 mL	Sb: 7.0 Bi: 8.6 Sn: 2.5	12 h^{-1}	78
As	River water, tap water, mineral water, (*waste water)	N~~n~~one	AAS	0.01 mol L^{-1} HCl/ 4.0 mol L^{-1} HCl/ 1.0% (m/v)NaBH4 in 0.1% (m/v) NaOH	0.05 µg L^{-1}	0.15-6.0 µg L^{-1}	3.2% at 2.0 µg L^{-1} (n=10)	96-102%	Reference method based on on-line FI-HG-AAS (FIAS 400)	3 mL	n.a.	9 h^{-1}	75

Sb	River- and seawater	DPTH-silica gel	ETAAS	pH 5.0 (acetic acid/ sodium acetate)/ 2.0% thiourea in 4.0% HNO_3/ 0.5% (w/v) $NaBH_4$ in 0.1% (w/v) NaOH	1 ng L^{-1}	0.025-2.5 µg L^{-1}	0.9% at 1 µg L^{-1} (n=11)	98-108%	TMDA 54.4 fortified lake water, SLRS-5 estuarine water	5 mL	22	20 h^{-1}	[130]
Cd	Seawater, ground water	N~~n~~one	AAS	2 mol L^{-1} HCl/ 0.75% (m/v) thiourea in 0.05 mol L^{-1} HCl/ 6% (w/v) $NaBH_4$ in 0.5% (m/v) NaOH	5.8 ng L^{-1}	19.3 ng L^{-1}-5 µg L^{-1}	1.4-2.9% at 0.25 and 2.5 µg L^{-1}	94-101%	CASS-4 seawater	2 mL	n.a.	87 h^{-1}	[76]
Pb	Seawater, river water	PSTH-cpg	ETAAS	pH 6.0 (NaH_2PO_4/Na_2HPO_4)/ 1% (v/v) HCl/ 2.6% (m/v) $NaBH_4$ + 3% (m/v) ($K_3Fe(CN)_6$) in 0.5% (m/v) NaOH	3.0 ng L^{-1}	n.a.	2.5% at 50 ng L^{-1} (n=10)	97-105%	TMDA 54.4 fortified lake water, LG6016 estuarine water	6.4 mL	20	18 h^{-1}	[81]
Hg	River water	N~~n~~one	ICP-MS, MC-ICP-MS	S~~s~~tabilization ($K_2Cr_2O_7$), isotope dilution/ 0.2% (w/w) $NaBH_4$ in 0.05% (w/w) NaOH	0.25 ng L^{-1}	n.a.	0.6-2.9% for ERM-CA615 (n=3)	n.a.	ERM-CA615 ground water	500 µL	10-50	40 h^{-1}	[77]

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Abbreviations:
cpg: controlled pore glass
DPTH: 1-(di-2-pyridyl)methylene thiocarbonohydrazide
MNP: magnetic nanoparticle
PSTH: 1.5-bis(2-pyridyl)3-sulphophenyl methylene thiocarbonohydrazide

Table 6: Methods employing cold vapour- and hydride generation techniques for the speciation of metals in natural waters. (All units as in the original publication)

Analyte	Matrix	Solid phase	Detection technique	Sample treatment/ elution/reduction	Figures of merit				Validation	Sample volume	Enrichment factor	Sample throughput	Ref
					LOD	Linear range	Precision	Relative Recovery					
As(III)/ As(V))/ total iAs	Seawater, well-water	PSTH-MNPs	ICP-MS	pH 4.0 (acetic acid/sodium acetate)/ 0.1% (m/v) thiourea + 2.8% (m/v) *L*-cysteine in 7% (w/w HNO_3/ As(III): 0.1% (w/v) $NaBH_4$ in 0.5% NaOH As(V): 0.5% (w/v) $NaBH_4$ in 0.5% NaOH	As(III): 2.7 ng L^{-1} iAs: 3.2 ng L^{-1}	As(III): 0.01-50 µg L^{-1} total iAs: 0.03-100 µg L^{-1}	As(III): 2.5% iAs: 2.7% (n=8)	90-110%	SLEW—estuarine water, CASS-5 sea water, TMDA 54.4 fortified lake water, SPS-SW 2 Batch 125 surface water	9.6 mL	As(III): 1.9 total iAs: 2.1	14.4 h^{-1}	88
As(III)/ As(V)/ total iAs	Groundwater	Cl-SAX	AAS	None - neutral sample/ As(III): 3.5 mol L^{-1} HCl/ 0.35% (m/v) $NaBH_4$ in 0.025% NaOH	As(III): 0.5 µg L^{-1} iAs: 0.6 µg L^{-1}	1.7-25 µg L^{-1}	<2% at 5 µg L^{-1} (n=3)	98-106%	NIST 1643e trace elements in water	500 µL	n.a.	60 h^{-1}	87
~~iHg/ MeHg~~	~~Lake water, ground water, seawater, (*tap water, fish tissue)~~	~~PANI~~	~~ICP-MS~~	~~None - neutral sample/ MeHg: 0.5% HCl, iHg: 2% HCl + 0.02% thiourea/ 1% $NaBH_4$~~	~~iHg: 25.2 pg mL^{-1}/ 32.4 pg mL^{-1}~~	~~0.1-10 ng mL^{-1}~~	~~2%/2.5% at 1 ng mL^{-1} (n=10)~~	~~96-102%~~	~~(°ERM-CE463, ERM-CE464, IAEA 350 fish tissues)~~	~~100 µL~~	~~iHg:240; MeHg:120~~	~~10 h^{-1}~~	~~73~~
iHg/ MeHg	Seawater	DPTH-silica gel	ICP-MS	pH 5.0 (acetic acid/sodium acetate)/ MeHg: 0.2% HCl, iHg: 0.5% HCl + 0.1% thiourea/ 0.25% (w/v) $NaBH_4$ in 0.5% (w/v) NaOH	MeHg: 0.011 µg L^{-1} iHg: 0.024 µg L^{-1}	DL-70 µg L^{-1}	MeHg: 2.8% iHg: 2.6% at 2 µg L^{-1} (n=10)	92-107%	LGC 6016 estuarine water, (°SRM 2976 mussel tissue)	4.6 mL	MeHg: 4.7 iHg: 11	7.1 h^{-1}	86
Sb(III)/ Sb(V)	Seawater, river water, lake water	PSTH-cpg/ Amberlite IRA-910	ICP-MS	pH 8.4 (boric acid/borax)/ 0.04% thiourea in 5% HNO_3/ 0.2% (m/v) $NaBH_4$ in 0.05% NaOH	Sb(III): 0.05-80 µg L^{-1} Sb(V): 0.05-80 µg L^{-1}	Sb(III): 0.013 µg L^{-1} Sb(V): 0.021 µg L^{-1}	Sb(III): 4.6% Sb(V): 3.0% (n=10)	97-105%	SLRS-5 river water, TMDA-54.4 lake water	2.2 mL	Sb(III): 5.5 Sb(V): 3.9	9 h^{-1}	74

---

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Note: Only additional sample treatment other than filtration and preservation with acid is mentioned here.
Abbreviations:
Cl-SAX: Silica-based chloride-form strong anion exchange resin
~~DMA: dimethylarsinic acid~~PSTH-MNPs: (Fe_3O_4) magnetic nanoparticles functionalized with [1,5-bis (2-pyridyl) 3-sulfophenylmethylene] thiocarbonohydrazide

PANI: polyaniline
DPTH-silica gel: 1,5-bis(di-2-pyridyl)methylene thiocarbonohydrazide bonded to silica gel
~~MNPs: magnetic nanoparticles~~
PSTH-cpg: [1,5-bis(2-pyridyl)-3-sulfonphenyl methylene]thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass

Commented [I10]: We don't need this abbreviation, do we?

Table 7: Methods employing liquid-liquid-micro-extraction for the matrix separation and preconcentration of metals in natural waters. (All units as in the original publication)

Analyte	Matrix	Detection technique	Sample treatment	Disperser/ complexing solution	Figures of merit				Validation	Sample volume	Enrich-ment factor	Sample through-put	Ref
					DL	Linear range	Precision	Relative Recovery					
Pb	Coastal water, ditch water	FAAS	pH 2 (HNO_3)	DDPA/chloroform	1.5 μg L^{-1}	5.0-280 μg L^{-1}	2.7% at 40.0 μg L^{-1} (n=9)	95-102%	CRM 1643e trace elements in natural water, (°BCR 278-R mussel tissue)	6 mL	130	13 h^{-1}	[90]
Pb	Lake water, coastal water	FAAS	pH 2 (HNO_3)	APDC/chloroform	1.8 μg L^{-1}	6.0-300 μg L^{-1}	2.9% at 50 μg L^{-1} (n=10)	94-98%	CRM 1643e trace elements in natural water, (°BCR 278-R mussel tissue)	10 mL	125	7 h^{-1}	[96]
Tl	River water, lake water, coastal seawater (*tap water)	FAAS	pH 2.0 (HNO_3)	Methanol containing 0.6% (v/v) ([Hmim][PF_6]; Elution: MIBK; Support: PUF micro column	0.86 μg L^{-1}	2.8-120 μg L^{-1}	2.7% at 20 μg L^{-1}	94-98%	SRM 1643e trace elements in natural water, (°SRM 2704 river sediment)	15 mL	290	16 h^{-1}	[100]
U	Ground water, seawater	ICP-OES, ICP-MS	pH 1	APDC/CTAB; extraction into chloroform, back extraction into HNO_3	ICP-OES: 2.0 μg L^{-1} ICP-MS: 30 ng L^{-1}	ICP-OES: 5-200 μg L^{-1}; ICP-MS: 50-5000 ng L^{-1}	ICP-OES: 5% ICP-MS: 4% (n=6)	90-105% at 10 and 5 μg L^{-1}	BCR 403 North Seawater, laser fluorimetry	10 mL	11-25	n.a.	[92]
Ag	River water, seawater, (*waste water)	FAAS	0.1 mol L^{-1} HNO_3	DDTC in 0.3% (m/v) methanol; Elution: MIBK; Support: PEEK-microcolumn	0.15 μg L^{-1}	0.40-20 μg L^{-1}	2.9% at 5 μg L^{-1} (n=10)	96-99%	NIST CRM 1643e trace elements in natural water	16.2 mL	186	12 h^{-1}	[99]
Pb, Cd	Natural waters (river water, coastal seawater)	ETAAS	None	Methanol containing 2% (v/v) xylene a + 0.2% (m/v) APDC; Elution: MIBK; Support: PTFE-tubing	Pb: 10 ng L^{-1} Cd: 2 ng L^{-1}	Pb: 0.04-1.5 μg L^{-1} Cd: 0.006-0.150 μg L^{-1}	Pb: 3.8% at 0.5 μg L^{-1} Cd: 4.1% at 0.03 μg L^{-1}	94-98% (n=3)	NIST CRM 1643e trace elements in natural water	8.1 mL	Pb: 80 Cd: 34	10 h^{-1}	[98]

V	River water, (*tap water)	ETAAS	pH 4.0 (acetic acid/ acetate)	(5-Br-PADAP) + ([C4mim][PF6]) RTIL; Elution: 10% (v/v) HNO_3 (in acetone); Support: Florisil	4.8 ng L^{-1}	DL-15 µg L^{-1}	4.1% at 5 µg L^{-1} (n=10)	96-103% (n=6)	NIST CRM 1643e trace elements in natural water	5 mL	n.a.	6 h^{-1}	93
Cd	Seawater, river water	ETAAS	pH 2.0±0.2 (HNO_3)	DDPA/DIBK	0.01 µg L^{-1}	0.03-0.6 µg L^{-1}	3.9% at 0.1 µg L^{-1} (n=9)	94-98%	NIST CRM 1643e trace elements in natural water	15 mL	10	6 h^{-1}	95
Cu, Pb	River water, coastal water	FAAS	pH 1.4 (HNO_3)	Methanol containing 2% (v/v) xylene ~~a~~ + 0.3% (m/v) DDPA; Elution: MIBK; Support: PTFE-micro column	Cu: 0.04 µg L^{-1} Pb: 0.54 µg L^{-1}	0.16-12.0 µg L^{-1}	Cu: 2.1% at 2.0 µg L^{-1} Pb: 1.9% at 30 µg L^{-1} (n=10)	96-100%	NIST CRM 1643e trace elements in natural water	12 mL	Cu: 560 Pb: 265	12 h^{-1}	97
Cr	Spring water, river water, seawater	ETAAS	pH 3.5 (phthalate buffer)	APDC	0.02 µg L^{-1}	0.5-6 µg L^{-1}	7% (n=6)	90-103%	(°CRM 544 lyophilized solution (no real matrix))	2.5 mL	20	n.a.	94

*Matrices in brackets indicated with a * are not within the scope of this review.*
Reference samples in brackets indicated with a ° are not appropriate for method validation of natural waters.
n.a.: not available.

Note: Only additional sample treatment other than filtration and preservation with acid is mentioned here.
Abbreviations:
APDC: ammonium pyrrolidine dithiocarbamate
([C4mim][PF6])RTIL: 1-butyl-3-methylimidazolium hexafluorosphosphate room temperature ionic liquid
([Hmim][PF6]): 1-hexyl-3-methylimidazolium hexafluorophosphate ionic liquid
(5-Br-PADAP): 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol
CTAB: cetyltrimethyl ammonium bromide
DDPA: ammonium diethyldithiophosphate
DDTC: sodium diethyldithiocarbamate
DIBK: di-isobutyl ketone
MIBK: methyl isobutyl ketone
PUF: polyurethane foam

Figure captions

Figure 1: A conceptual diagram of the combination of on-line FI/SI sample preparation with atomic spectrometric detectors.

Abbreviations: LPME: liquid phase microextraction; SPE: solid phase extraction; HG/CVG-GLS: hydride generation/cold vapour generation-gas liquid separator; PP: peristaltic pump; SP: syringe pump; MPW: multi position valve; HC: holding coil; IV: injection valve; S: sample; R: reagent; E: eluent; W: waste.

Source: adapted from Miró and Hansen (2013)~~reference~~ [10]

Figure 2: A conceptual diagram of the combination of on-line FI/SI sample preparation with atomic spectrometric detectors. Reproduced from [18] (Talanta 133 (2015) 164, authored by Robert Clough, Hagit Sela, Angela Milne, Maeve C. Lohan, Serife Tokalioglu and Paul J. Worsfold), with permission from Elsevier.

Figure 3: FI microcolumn preconcentration/separation system for simultaneous speciation of Se(IV) and Se(VI), selenocysteine and selenomethionine, prior to ICP detection.

Abbreviations: P1/P2: peristaltic pumps; C1/C2: micro columns; V: valves.

a) Separation of inorganic ((Se(IV) and Se(VI)) and organic Se species (Se-Met and Se Cys$_2$) on C1 and C2, respectively. (SeCys$_2$ retained on C2, Se-Met was detected by ICP-MS)
b) Elution of Se-Cys$_2$ from C2 with 0.5 mol L^{-1} NaOH and ICP-MS detection.
c) Elution of inorganic Se from C1 with 0.2 mol L^{-1} NaOH and pH adjustment
d) Separation of inorganic Se species on C2. (Se(IV) retained on C2, Se(VI) was detected by ICP-MS)
e) Elution of Se(IV) with 0.5 mol L^{-1} NaOH and ICP-MS detection.

Source and a more detailed description can be found in [70].

Figure 4: Schematic illustration of a sequential injection system for automatic DLPME of trace elements as a front end to ETAAS.

Abbreviations: S: sample; MeOH (APDC, xylene), extracting solvent composed of 2.0% (v/v) xylene and 0.2% (m/v) APDC in methanol which acts as dispersant; P: peristaltic pump; SP: syringe pump; MV: multi-position valve; V: head valve; HC: holding coil; C: micro-column containing sorbent; CC: confluence connector; DT: delivery tube; GF: graphite furnace of ETAAS. Reprinted from [98] (A.N. Anthemidis, K.-I.G. Ioannou / Analytica Chimica Acta 668 (2010) 35–40, Copyright (2010)), with permission from Elsevier.

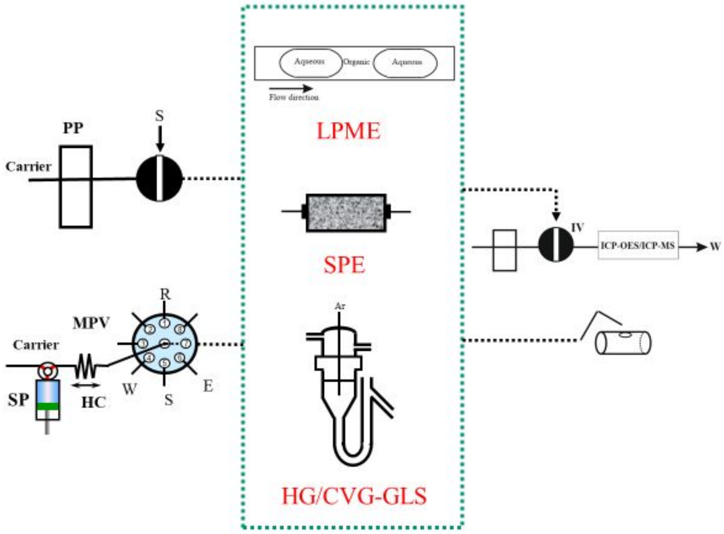
Aqueous
Organic
Aqueous
Flow direction
LPME
PP
S
Carrier
SPE
IV
ICP-OES/ICP-MS
W
R
MPV
Carrier
SP
HC
W
S
E
1
2
3
4
5
6
7
8
Ar
HG/CVG-GLS

Fig. 1

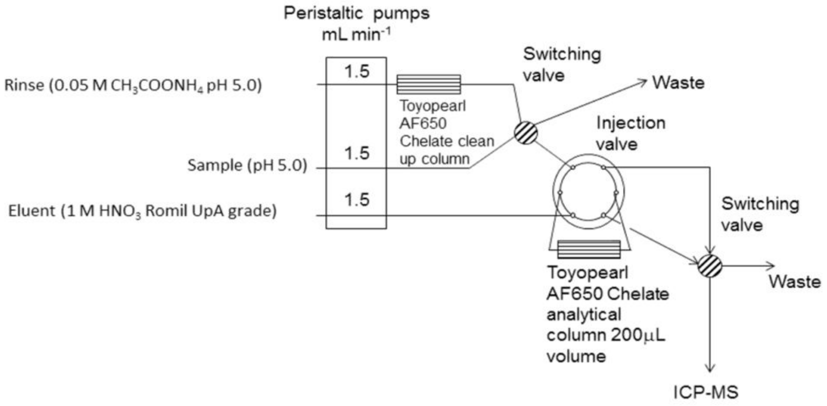
Peristaltic pumps
mL min^{-1}
1.5
1.5
1.5
Rinse (0.05 M CH_3COONH_4 pH 5.0)
Sample (pH 5.0)
Eluent (1 M HNO_3 Romil UpA grade)
Toyopearl AF650 Chelate clean up column
Switching valve
Waste
Injection valve
Switching valve
Waste
Toyopearl AF650 Chelate analytical column 200μL volume
ICP-MS

Fig. 2

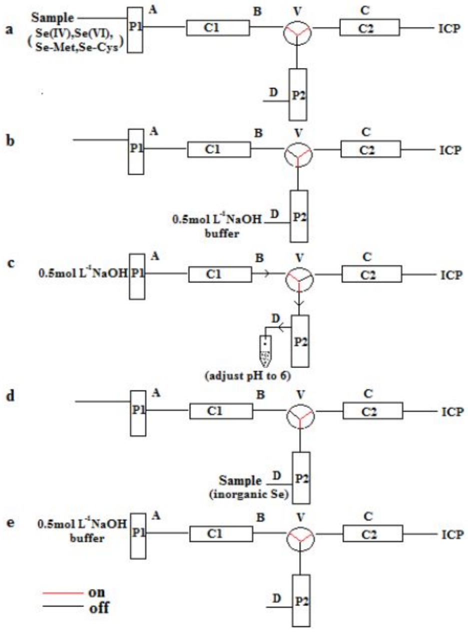
a
Sample
(Se(IV),Se(VI), Se-Met,Se-Cys)
P1
A
C1
B
V
C
C2
ICP
D
P2
b
0.5mol L-1NaOH buffer
c
0.5mol L-1NaOH
(adjust pH to 6)
d
Sample (inorganic Se)
e
0.5mol L-1NaOH buffer
on
off

Fig. 3

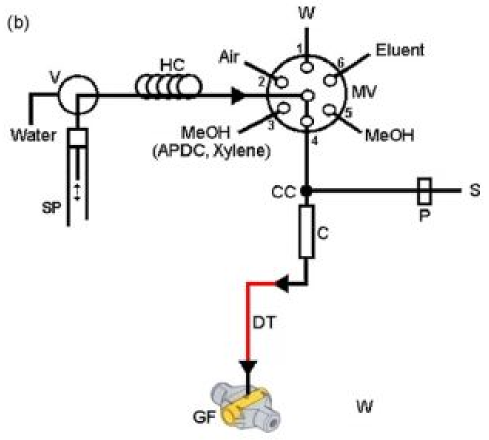
(b)
W
1
Air
Eluent
6
HC
V
2
MV
Water
MeOH
(APDC, Xylene)
3
4
5
MeOH
CC
S
P
SP
C
DT
GF
W

Fig. 4

References

---

[1] J. Gaillardet, J. Viers and B. Dupré, *Treatise on Geochemistry: Second Edition*, Elsevier Inc. 2013, pp. 195-235.

[2] Y. Sohrin and K.W. Bruland, *Trends Anal. Chem.,* 2011, **30**, 1291-1307.

[3] W. H. Schlesinger and E. S. Bernhardt*, Biogeochemistry: An analysis of global change.* Third Edition, Elsevier Inc. 2013.

[4] R. Clough, C. F. Harrington, S. J. Hill, Y. Madrid and J. F. Tyson, *J. Anal. At. Spectrom.,* 2018, **33**, 1103-1149.

[5] B. Buszewksi, W. Piekoszewsky, P. Pomastowski, K. Rafinska, M. Sugajski and T. Kowalkowski, *Recent Advances in Trace Elements*, Wiley Blackwell 2017, pp: 33-60.

[6] S. J. Ussher, E. P. Achterberg and P. J. Worsfold, *Environ. Chem.,* 2004, **1**, 67-80.

[7] P. Lindahl, S. H. Lee, P. Worsfold and M. Keith-Roach, *Mar. Environ. Res.*, 2010, **69**, 73-84.

[8] M. Marcinkowska and D. Baralkiewicz, *Talanta*, 2016, **161**, 177-204.

[9] M. E. Lagerström, M. P. Field, M. Séguret, L. Fischer, S. Hann and R. M. Sherrell, *Mar. Chem.,* 2013, **155**, 71-80.

[10] M. Miró and E. H. Hansen*, Anal. Chim. Acta*, 2013, **782**, 1-11.

[11] P. J. Worsfold, R. Clough, M. C. Lohan, P. Monbet, P. S. Ellis, C. R. Quétel, G. H. Floor and I. D. Mc Kelvie., *Anal. Chim. Acta*, 2013, **803**, 15-40.

[12] A. Cárdenas Valdivia, M.M López Guerrero, E. I. Vereda Alonso, J. M. Cano Pavón and A-Garcia de Torres, *Microchem. J.,* 2018, **138**, 109-115.

[13] M.M. López-Guerrero, M. T. Siles-Cordero, E. Vereda-Alonso, J. M. Cano-Pavón and A. Garcia de Torres, *J. Anal. At. Spectrom*., 2015, **30**, 1169-1178.

[14] A. Leclercq, A. Nonell, J. L. Todolí Torró, C. Bresson, L. Vio, T. Vercouter and F. Chartier, *Anal. Chim. Acta*, 2015, **885**, 33-56.

[15] A. Leclercq, A. Nonell, J. L. Todolí Torró, C. Bresson, L. Vio, T. Vercouter and F. Chartier, *Anal. Chim. Acta*, 2015, **885**, 57-91.

[16] G. R. D. Prabhu and P. L. Urban, *Trends Anal. Chem.,* 2017, **88**, 41–52.

[17] E. H. Hansen and M. Miró, *Flow Injection Analysis-Comprehensive Analytical Chemistry* (S. D. Kolev and I. McKelvie, Eds), Chap. 14, pp. 375-405, Elsevier, The Netherlands, 2008.

[18] R. Clough, H. Sela, A. Milne, M. C. Lohan, S. Tokalioglu and P.J. Worsfold, *Talanta*, 2015, **133**, 162-169.

[19] G. Giakisikli and A. N. Anthemidis, *Talanta*, 2013, **110**, 229-235.

[20] I. Sánchez-Trujillo, E. Vereda-Alonso, A. García de Torres and J.M. Cano-Pavón, *Microchem. J.,* 2012, **101**, 87-94.

---

[21] ~~R.K. Katarina, M. Oshima and S. Motomizu, *Talanta*, 2009, **79**, 1252-1259.~~ R. K. Katarina, M. Oshima and S. Motomizu, *Talanta*, 2009, **78**, 1043-1050.

[22] P. H. Pacheco, P. Smichowski, G. Polla and L. D. Martinez, *Talanta,* 2009, **79**, 249-253.

[23] T. T. Shih, I. H. Hsu, S. N. Chen, P. H. Chen, M. J. Deng, Y. Chen, Y. W. Lin and Y. C. Sun, Analyst, 2015, 140, 600-608.

[24] T. T. Shih, C. C. Hsieh, Y. T. Luo, Y. A. Su, P. H. Chen, Y. C. Chuang, Y. C. Sun, *Anal. Chim. Acta*, 2016, **916**, 24-32.

[25] M. Hemmati, M. Rajabi and A. Asghari, *Microchim. Acta*, 2018. **185**, 160.

[26] P.-L. Lee, Y.-C. Sun and Y.-C. Ling, *J. Anal. At. Spectrom*., 2009, **24**, 320-327.

[27] R. Schlitzer, R. F. Anderson, E. M. Dodas, M. Lohan, W. Geibert, A. Tagliabue, A. Bowie, C. Jeandel, M. T. Maldonado, W. M. Landing, D. Cockwell, C. Abadie, W. Abouchami, E. P. Achterberg, A. Agather, A. Aguliar-Islas, H. M. van Aken, M. Andersen, C. Archer, M. Auro, H. J. de Baar, O. Baars, A. R. Baker, K. Bakker, C. Basak, M. Baskaran, N. R. Bates, D. Bauch, P. van Beek, M. K. Behrens, E. Black, K. Bluhm, L. Bopp, H. Bouman, K. Bowman, J. Bown, P. Boyd, M. Boye, E. A. Boyle, P. Branellec, L. Bridgestock, G. Brissebrat, T. Browning, K. W. Bruland, H. J. Brumsack, M. Brzezinski, C. S. Buck, K. N. Buck, K. Buesseler, A. Bull, E. Butler, P. Cai, P. C. Mor, D. Cardinal, C. Carlson, G. Carrasco, N. Casacuberta, K .L. Casciotti, M. Castrillejo, E. Chamizo, R. Chance, M. A. Charette, J. E. Chaves, H. Cheng, F. Chever, M. Christl, T. M. Church, I. Closset, A. Colman, T. M. Conway, D. Cossa, P. Croot, J. T. Cullen, G. A. Cutter, C. Daniels, F. Dehairs, F. Deng, H. T. Dieu, B. Duggan, G. Dulaquais, C. Dumousseaud, Y. Echegoyen-Sanz, R. L. Edwards, M. Ellwood, E. Fahrbach, J. N. Fitzsimmons, A. Russell Flegal, M. Q. Fleisher, T. van de Flierdt, M. Frank, J. Friedrich, F. Fripiat, H. Fröllje, S. J. G. Galer, T. Gamo, R. S. Ganeshram, J. Garcia-Orellana, E. Garcia-Solsona, M. Gault-Ringold, E. George, L. J. A. Gerringa, M. Gilbert, J. M. Godoy, S. L. Goldstein, S. R. Gonzalez, K. Grissom, C. Hammerschmidt, A. Hartman, C. S. Hassler, E. C. Hathorne, M. Hatta, N. Hawco, C. T. Hayes, L. E. Heimbürger, J. Helgoe, M. Heller, G. M. Henderson, P. B. Henderson, S. van Heuven, P. Ho, T. J. Horner, Y. T. Hsieh, K. F. Huang, M. P. Humphreys, K. Isshiki, J. E. Jacquot, D. J. Janssen, W. J. Jenkins, S. John, E. M. Jones, J. L. Jones, D. C. Kadko, R. Kayser, T. C. Kenna, R. Khondoker, T. Kim, L. Kipp, J. K. Klar, M. Klunder, S. Kretschmer, Y. Kumamoto, P. Laan, M. Labatut, F. Lacan, P. J. Lam, M. Lambelet, C. H. Lamborg, F. A. C. Le Moigne, E. Le Roy, O. J. Lechtenfeld, J. M. Lee, P. Lherminier, S. Little, M. López-Lora, Y. Lu, P. Masque, E. Mawji, C. R. McClain, C. Measures, S. Mehic, J. L. M. Barraqueta, P. van der Merwe, R. Middag, S. Mieruch, A. Milne, T. Minami, J. W. Moffett, G. Moncoiffe, W.S. Moore, P. J. Morris, P. L. Morton, Y. Nakaguchi, N. Nakayama, J. Niedermiller, J. Nishioka, A. Nishiuchi, A. Noble, H. Obata, S. Ober, D.C. Ohnemus, J. van Ooijen, J. O'Sullivan, S. Owens, K. Pahnke, M.

Paul, F. Pavia, L. D. Pena, B. Peters, F. Planchon, H. Planquette, C. Pradoux, V. Puigcorbé, P. Quay, F. Queroue, A. Radic, S. Rauschenberg, M. Rehkämper, R. Rember, T. Remenyi, J. A. Resing, J. Rickli, S. Rigaud, M. J. A. Rijkenberg, S. Rintoul, L. F. Robinson, M. Roca-Martí, V. Rodellas, T. Roeske, J. M. Rolison, M. Rosenberg, S. Roshan, M. M. Rutgers van der Loeff, E. Ryabenko, M. A. Saito, L. A. Salt, V. Sanial, G. Sarthou, C. Schallenberg, U. Schauer, H. Scher, C. Schlosser, B. Schnetger, P. Scott, P. N. Sedwick, I. Semiletov, R. Shelley, R. M. Sherrell, A. M. Shiller, D. M. Sigman, S. K. Singh, H. A. Slagter, E. Slater, W. M. Smethie, H. Snaith, Y. Sohrin, B. Sohst, J. E. Sonke, S. Speich, R. Steinfeldt, G. Stewart, T. Stichel, C. H. Stirling, J. Stutsman, G. J. Swarr, J. H. Swift, A. Thomas, K. Thorne, C. P. Till, R. Till, A. T. Townsend, E. Townsend, R. Tuerena, B. S. Twining, D. Vance, S. Velazquez, C. Venchiarutti, M. Villa-Alfageme, S. M. Vivancos, A. H. L. Voelker, B. Wake, M. J. Warner, R. Watson, E. van Weerlee, M. Alexandra Weigand, Y. Weinstein, D. Weiss, A. Wisotzki, E. M. S. Woodward, J. Wu, Y. Wu, K. Wuttig, N. Wyatt, Y. Xiang, R.C. Xie, Z. Xue, H. Yoshikawa, J. Zhang, P. Zhang, Y. Zhao, L. Zheng, X. Y. Zheng, M. Zieringer, L. A. Zimmer, P. Ziveri, P. Zunino and C. Zurbrick, *Chem. Geol*.,2018, **493**, 210-223.

[28] European Commission. *Critical Raw Materials for the EU. Report of the Ad-hoc Working Group on Defining Critical Raw Materials*. 2014. Ref. Ares (2015)1819503 - 29/04/2015, Brussels.

[29] S. Massari and M. Ruberti*, Resour. Policy*, 2013, **38**, 36-43.

[30] R. K. Katarina, M. Oshima and S. Motomizu, *Talanta*, 2009, **789**, 1252-1~~050~~259.

[31] Y. Zhu, T. Umemura, H. Haraguchi, K. Inagaki and K. Chiba, *Talanta*, 2009, **78**, 891-895.

[32] Y. Zhu, A. Itoh, T. Umemura, H. Haraguchi, K. Inagaki and K. Chiba, *J. Anal. At. Spectrom*., 2010, **25**, 1253-1258.

[33] Y. Zhu, A. Hioki and K. Chiba, *J. Anal. At. Spectrom*., 2013, **28**, 883-889.

[34] E. C. Hathorne, B. Haley, T. Stichel, P. Grasse, M. Zieringer, M. Frank, *Geochem. Geophys. Geosyst.*, 2012, **13**, 1-12.

[35] Y. Zhang, C. Zhong, Q. Zhang, B. Chen, M. He and B. Hu, *RSC Adv*., 2015, ~~**5**,~~**8** 5996-6005.

[36] M. He, B. Hu, B. Chen and Z. Jiang, *Physical Sciences Reviews,* 2017, 20160059.

[37] A. Fisher and D. Kara, *Anal. Chim. Acta*, 2016, *935*, 1-29.

[38] M. M. González-García, F. Sánchez-Rojas, C. Bosch-Ojeda, A. García de Torres and J. M. Cano-Pavón, *Anal. Bioanal. Chem.*, 2003, **375**, 1229-1233.

[39] Ratte H. T, *Environ. Toxicol. Chem.*, 1999, **18**, 89–108.

[40] R. H. Byrne, *Geochem. Trans*., 2002, **3**(2), 11-16.

[41] F. L. Bernardis, R. A. Grant and D. C. Sherrington, *Reac. Funct. Polym*., 2005, **65**, 205-2017.

[42] C. B. Ojeda, F. Sánchez-Rojas, J. M. Cano-Pavón and A. García de Torres*, Anal. Chim. Acta*, 2003, **494**, 97-103.

---

[43] M. L. Alonso Castillo, A. García de Torres, E. Vereda Alonso, M. T. Siles Codero and J. M. Cano Pavón, *Talanta*, 2012, **99**, 853-858.

[44] M. V. Balarama Krishna, M. Ranjit, K. Chandrasekaran, G. Venkateswarlu and D. Karunasagar, *Talanta*, 2009, **79**, 1454-1463.

[45] J. L. Barriada, A. D. Tappin, E. H. Evans and E. P. Achterberg, *Trends Anal. Chem.*, 2007, **26**(8), 809-817.

[46] L. Yang and R. E. Sturgeon, *J. Anal. At. Spectrom.*, 2002, **17**(2), 88-93.

[47] Z. Zhu and A. Zheng, *Spectroscopy,* 2017, **32**, 50-59.

[48] D. A. Atwood, *Radionuclides in the Environment*. John Wiley & Sons, Chichester, 1st edn, 2010.

[49] C. Poinssot. *Radionuclide Behaviour in the Natural Environment: Science, Implications and Lessons for the Nuclear Industry.* Eds.: C. Poinssot and H. Geckeis. Woodhead Publishing Series in Energy, 2012, Cambridge, UK.

[50] Q.-H. Hu, J.-Q. Wang and J.-S. Wang, *J. Environ. Radioact.,* 2010, **101**, 426-437.

[51] World Health Organization, *Guidelines for Drinking-Water Quality*, WHO, Geneva, fourth edition incorporating the first addendum, 2017. https://www.who.int/water_sanitation_health/publications/drinking-water-quality-guidelines-4-including-1st-addendum/en/.

[52] *Uranium Fact sheet, Environmental Protection Agency*, US EPA, 2013; https://www.wqa.org/Portals/0/Technical/Technical%20Fact%20Sheets/2014_Uranium.pdf.

[53] AERB Drinking water specifications in India. Department of Atomic Energy, Govt. of India, 2004; https://www.aerb.gov.in/english/.

[54] T. Laaninen. *Revision of the Drinking Water Directive.* European Union, 2019. http://www.europarl.europa.eu/RegData/etudes/BRIE/2018/625179/EPRS_BRI(2018)625179_EN.pdf.

[55] European environmental quality standards (EQS) variability study. Scientific Report from DCE – Danish Centre for Environment and Energy Nr. 198, 2016; http://dce.au.dk/en/.

[56] Z. Wang, J. Lin, S. Li, Q. Guo, W. Huang, W. Wen, G. Dan and Z. Tan, *J. Radioanal. Nucl. Chem.*, 2018, **315**, 103-110.

[57] A. Habibi, C. Vivien, B. Boulet, C. Cossonnet, R. Gurriaran, M. Gleizes, G. Cote and D. Larivière, *J. Radionanal. Nucl Chem.*, 2016, **310**, 217-227.

[58] A. Habibi, B. Boulet, M. Gleizes, D. Larivière and G. Cote, *Anal Chim Acta*, 2015, **883**, 109-116.

[59] J. X. Qiao, X. L. Hou, P. Steier and R. Golser, *Anal. Chem.*, 2013, **85**, 11026-11033.

[60] J. Avivar, L. Ferrer, M. Casas and V. Cerda, *J. Anal. At. Spectrom.*, 2012, **27**, 327-334.

---

[61] J. R. Bacon, O. T. Butler, W: R. L. Cairns, J. M. Cook, C. M. Davidson, O. Cavoura and R. Mertz-Kraus, *J. Anal. At. Spectrom.*, 2020, **35**(1), 9-53.

[62] Official Journal of the European Union, Directive 2008/105/EC of the European Parliament and of the council of 16 December 2008 (L 348/84).

[63] M. Kim, J. Stripeikis and M. Tudino, *Spectrochim. Acta Part B*, 2009, **64**, 500-505.

[64] X. Zhang, M. Chen, Y. Yu, T. Yang and J. Wang, *Anal. Methods*, 2011, **3**, 457-462.

[65] A. M. Zou, X. Y. Tang, M. L. Chen and J. H. Wang, *Spectrochim. Acta Part B*, 2008, **63**, 607-611.

[66] M. M. López-Guerrero, E. Vereda-Alonso, J. M. Cano-Pavón, M. T. Siles-Cordero and A. García de Torres, J. Anal. *At. Spectrom*., 2012, **27**, 682-688.

[67] S. Chen, L. Zhu, D. Lu, X. Cheng and X. Zhou, *Microchim Acta*, 2010, **196**, 123-128.

[68] W. Hu, F. Zheng and B. Hu, *J. Hazard. Mater*., 2008, **151**, 58-64.

[69] Y. F. Huang, Y. Li, Y. Jiang and X. P. Yan. *J. Anal. At. Spectrom*. 2010, 25, 1467-1474.

[70] C. Huang, B. Hu, M. He and J. Duan, *J. Mass Spectrom*., 2008, **43**, 336-345.

[71] C. Xiong, Y. Qin and B. Hu, *J. Hazard. Mater*., 2010, **178**, 164-170.

[72] B. Magnusson and U. Örnemark (Eds.) *Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics*. (2nd ed. 2014). ISBN 978-91-87461-59-0. Available from http://www.eurachem.org.

[73] G. Ying, L. Rui and Y. Lu, *Chinese Sci. Bul*., 2013, **17**, 1980-1991.

[74] A. Calvo-Fornieles, A. García De Torres, E. Vereda-Alonso, M. T. Siles-Cordero and J. M. Cano-Pavón, *J. Anal. At. Spectrom.*, 2011, **26**, 1619-1626.

[75] A. N. Anthemidis, E. I. Daftsis and N. P. Kalogiouri, *Anal. Methods*, 2014, **6**, 2745-2750.

[76] L. O. B. Silva, L. A. Portugal, E. Palacio, L. Ferrer, V. Cerdà and S. L. C. Ferreira. *J. Anal. At. Spectrom*., 2014, **29**, 2398-2404.

[77] L. Fischer, M. Brunner, T. Prohaska and S. Hann., *J. Anal. At. Spectrom*., 2012, **27**, 1983-1991.

[78] A. Calvo-Fornieles, A. García de Torres, E. I. Vereda-Alonso and J. M. Cano-Pavón, *J. Anal. At. Spectrom*., 2013, **28**, 364-372.

~~[79] M.M. López-Guerrero, M. T. Siles-Cordero, E. Vereda-Alonso, J. M. Cano-Pavón and A. Garcia de Torres, *J. Anal. At. Spectrom*., 2015, **30**, 1169-1178.~~

[80] I. Sánchez-Trujillo, A. García De Torres, E. I. Vereda-Alonso and J. M. Cano-Pavón, *J. Anal. At. Spectrom*., 2013, **28**, 1772-1780.

[81] I. Sánchez-Trujillo, M. L. Alonso-Castillo, J. M. Cano-Pavón, E. I. Vereda-Alonso and A. García de Torres, *Anal. Methods*, 2013, **5**, 2551-2557.

[82] A. Calvo Fornieles, A. García de Torres, E. Vereda Alonso and J. M. Cano Pavón, *Microchem. J.*, 2016, **124**, 82-89.

---

[83] M. M. López-Guerrero, E. Vereda-Alonso, A. García De Torres and J. M. Cano-Pavón, *J. Anal. At. Spectrom*., 2017, **32**, 2281-2291.

[84] J. C. García-Mesa, P. Montoro Leal, M. M. López Guerrero and E. I. Vereda Alonso, *Microchem. J*., 2019, **150**, 104141.

[85] M. V. B. Krishna, K. Chandrasekaran and D. Karunasagar. *Talanta*, 2010, **81**, 462-472.

[86] I. Sánchez-Trujillo, E. Vereda-Alonso, J.M. Cano-Pavón and A. García De Torres, *J. Anal. At. Spectrom*., 2015, **30**, 2429-2440.

[87] M. Sigrist, A. Albertengo, H. Beldoménico and M. Tudino, *J. Hazard. Mater.,* 2011, **188**, 311-318.

[88] P. Montoro Leal, E. Vereda Alonso, M. M. López Guerrere, M. T. Siles Cordero, J. M Cano Pavón, A. García Torres, Talanta, 2018, **184**, 251-259.

[89] ~~M. Miró and E. H. Hansen, *Anal. Chim. Acta*, 2013, **782**, 1-11.~~

[90] C. Mitani and A. N. Anthemidis, *Talanta*, 2015, **133**, 77-81.

[91] ~~Y. Li and B. Hu, *At. Spectrosc*., 2009, **30**, 104-111.~~

[92] K. Chandrasekaran, D. Karunasagar and J. Arunachalam, *Anal. Methods*, 2011, **3**, 2140-2147.

[93] P. Berton, E .M. Martinis and R. G. Wuilloud, *J. Hazard. Mater*., 2010, **176**, 721-728.

[94] F. Pena, I. Lavilla and C. Bendicho, *Spectrochim. Acta Part B*, 2008, **63**, 498-503.

[95] A. N. Anthemidis and I. S. I. Adam, *Anal. Chim. Acta*, 2009, **632**, 216-220.

[96] C. Mitani and A. N. Anthemidis, *Anal. Chim. Acta*, 2013, **771**, 50-55.

[97] A. N. Anthemidis and K. – I. G. Ioannou, *Talanta*, 2009, **80**, 413–421.

[98] A. N. Anthemidis and K. I. G. Ioannou, *Anal. Chim. Acta*, 2010, **668**, 35-40.

[99] A. N. Anthemidis and K. I. G. Ioannou, *Talanta*, 2011, **84**, 1215–1220.

[100] A. N. Anthemidis and K. I. G. Ioannou, *Anal. Bioanal. Chem*., 2012, **404**, 685–691.

[101] H. Peng, N. Zhang, M. He, B. Chen and B. Hu, Int. J. Environ. Anal. Chem., 2016, 96, 212-224.

[102] J. E. O'Sullivan, R .J. Watson and E. C. V. Butler, *Talanta*, 2013, **115**, 999-1010.

[103] A. N. Anthemidis, S. Xidia and G. Giakisikli, *Talanta*, 2012, **97**, 181-186.

[104] B. Dai, M. Cao, G. Fang, B. Liu, X. Dong, M. Pan and S. Wang, *J. Hazard. Mater*., 2012, **219-220**, 103-110.

[105] A. O. AlSuhaimi and T. McCreedy, *Arab. J. Chem*., 2011, **4**, 195-203.

[106] A. N. Anthemidis, G. Giakisikli, S. Xidia, M. Miró, *Microchem. J*., 2011, **98**, 66-71.

[107] C. Cui, M. He and B. Hu, *J. Hazard. Mater*., 2011, **187**, 379-385.

[108] D. Chen, B. Hu, M. He and C. Huang, *Microchem. J*., 2010, **95**, 90-95.

[109] I. Sánchez-Trujillo, E. Vereda-Alonso, M. T. Siles-Cordero, J. M. Cano-Pavón and A. García De Torres, *J. Anal. At. Spectrom*., 2010, **25**, 1063-1071.

---

[110] D. Chen, B. Hu and C. Huang, *Talanta*, 2009, **78**, 491-497.

~~[111] J. C. García-Mesa, P. Montoro-Leal, M. M. López-Guerrero and E. I. Vereda-Alonso, *Microchem. J.*, 2019, **150**, 104141.~~

[112] Y. Wang, X. Luo, J. Tang, X. Hu, Q. Xu and C. Yang, *Anal. Chim. Acta*, 2012, **713**, 92-96.

~~[113] P. H. Pacheco, P. Smichowski, G. Polla and L. D. Martinez, *Talanta*, 2009, **79**, 249-253.~~

[114] V. Yilmaz, Z. Arslan, O. Hazer and H. Yilmaz, *Microchem. J.*, 2014, **114**, 65-72.

[115] X.-W. Chen, A.-M. Zou, M.-L. Chen, J.-H. Wang and P. K. Dasgupta, *Anal. Chem*., 2009, **81**, 1291-1296.

[116] M. Z. Corazza, B. F. Somera, M. G. Segatelli and C. R. T. Tarley, *J. Hazard. Mater*., 2012, **243**, 326-333.

[117] X.-X. Zhang, L.-P. Zhang, T. Yang, L.-M. Shen, M.-L. Chen and J.-H. Wang, *J. Anal. At. Spectrom*., 2012, **27**, 1680-1687.

[118] T. Yang, X.-X. Zhang, M.-L. Chen and J.-H. Wang. *Analyst*, 2012, **137**, 4193-4199.

[119] G. F. Lima, F. M. Oliveira, M. O. Ohara, M. G. Segatelli and C. R. T. Tarley, *Evaluation of histidine functionalized multiwalled carbon nanotubes for improvement in the sensitivity of cadmium ions determination in flow analysis,* In: Carbon Nanotubes - From Research to Applications, Dr. Stefano Bianco (Ed.), In Tech, Croatia, 2011.

[120] M. Gawin, J. Konefal, B. Trzewik, S. Walas, A. Tobiasz, H. Mrowiec and E. Witek, *Talanta*, 2012, **80**, 1305-1310.

[121] C. R. T.Tarley, F. N. Andrade, F. Midori de Oliveira, M. Z.Corazza, L. F. Mendes de Azevedo and M. G. Segatelli, *Anal. Chim. Acta*, 2011, **703**, 145-151.

[122] A. N. Anthemidis, I. S. I. Adam and G. A. Zachariadis, *Talanta*, 2010, **81**, 996-1002.

[123] Y. Bakricioglu, D. Bakircioglu and S. Akman, *J. Hazard. Mater*., 2010, **178**, 1015-1020.

[124] Z. Zhu and A. Zheng, *Molecules*, 2018, **23**, 489.

[125] C. K. Su, Y. T. Chen and Y. C. Sun, *Microchemical J*., 2019, **146**, 835-841.

~~[126] M. M. López-Guerrero, E. Vereda-Alonso, J. M. Cano-Pavón, M. T. Siles-Cordero and A. García De Torres, *J. Anal. At. Spectrom*., 2012, **27**, 682-688.~~

~~[127] S. Chen, L. Zhu, D. Lu, X. Cheng and X. Zhou, *Microchim. Acta*, 2010, **196**, 123-128.~~

[128] C. Xiong, M. He and B. Hu, *Talanta*, 2008, **76**, 772-779.

[129] S. S. Lins, C. F. Virgens, W. N. L. dos Santos, I. H.S. Estevam and S. L. C. Ferreira, *Microchem. J*., 2019, **150**, 104075.

[130] M. M. López-Guerrero, M. T. Siles-Cordero, E. Vereda-Alonso, A. García De Torres and J. M. Cano-Pavón. *Talanta*, 2014, **129**, 1-8.