Understanding Selenium Biogeochemistry in Engineered Ecosystems: Transformation and Analytical Methods

Rohan Jain, Eric D. van Hullebusch, Markus Lenz and François Farges

Abstract Selenium is used extensively in many industries, and it is necessary for human nutrition. On the other hand, it is also toxic at slightly elevated concentrations. With the advent of industrialisation, selenium concentrations in the environment due to anthropogenic activities have increased. Treatment of selenium-laden wastewaters and bioremediation are of increasing importance for counteracting contamination. Developing an effective treatment process requires the identification of all the selenium chemical species and their concentrations in engineered settings. This chapter collates the available techniques for identifying and quantifying various selenium species in gas, liquid, and solid phases, including X-ray absorption spectroscopy, electron microscopy, and liquid/gas chromatography. This chapter also throws light on isotopic fractionation and sequential extraction methods used to study the behaviour of selenium. Prior to the discussion

R. Jain
Department of Chemistry and Bioengineering, Tampere University of Technology,
P.O. Box 541, Tampere, Finland

E.D. van Hullebusch
Université Paris-Est, Laboratoire Géomatériaux et Environnement (LGE),
EA 4508, UPEM, 77454 Marne-La-Vallée, France

E.D. van Hullebusch (✉)
Department of Environmental Engineering and Water Technology, IHE Delft Institute
for Water Education, P.O. Box 3015, 2601 DA Delft, The Netherlands
e-mail: e.vanHullebusch@un-ihe.org; Eric.vanHullebusch@u-pem.fr

M. Lenz
Institute for Ecopreneurship, School of Life Sciences, University of Applied Sciences
and Arts Northwestern Switzerland (FHNW), Gruendenstrasse 40, 4132 Muttenz,
Switzerland

M. Lenz
Sub-Department of Environmental Technology, Wageningen University,
6700 EV Wageningen, The Netherlands

F. Farges
Institute de Minéralogie, de Physique des Matériaux et de Cosmochimie, Sorbonne
Universités, Muséum National d'Histoire Naturelle, UMR CNRS 7590,
UPMC Univ Paris 06, IRD UMR 206, 75005 Paris, France

of analytical methods, this chapter discusses selenium mineralogy and biochemistry. Finally, the chapter concludes by discussing potential future analytical techniques that will further improve our understanding of selenium biogeochemistry in engineered bioprocesses.

Keywords Elemental speciation · Bioremediation · Trace elements · Redox labile elements

1 Introduction

Selenium (Se) was discovered in 1817 by the Swedish chemists Jöns Jakob Berzelius (1779–1848) and Johan Gottlieb Gahn (1745–1818). It was then isolated from a reddish precipitate that occurred in black waste resulting from the production of sulphuric acid at the Grispholm factory in Sweden. Se is a chalcophile element that belongs to group 16 of the periodic table; thus, the properties of Se closely resemble those of sulphur. Consequently, Se is primarily found in ores along with sulphur minerals, such as FeS_2 (pyrite), $CuFeS_2$ (chalcopyrite), and $(Zn, Fe)S$ (sphalerite) (Lenz and Lens 2009 and references therein). Se is unevenly distributed in the Earth's crust (Dhillon and Dhillon 2003). Se content in soils is generally in the low $\mu g\ kg^{-1}$ range, and soils with a Se concentration above 0.1–0.5 $mg\ kg^{-1}$ are considered seleniferous (Dhillon and Dhillon 2003). Locally, Se soil content can be considerably higher due to anthropogenic/geogenic sources.

Se is primarily (>90%) extracted as a by-product of copper mining (Butterman and Brown 2004). Thus, the production of Se at times does not follow demand, and prices can vary drastically (Lenz and Lens 2009 and references therein). For example, in 2005, Se prices spiked to 110,000 USD per ton, an increase from less than 10,000 USD per ton in 2001. The demand for Se is driven by its various applications in the glass, semiconductor, pigment, photovoltaic, and chemical industries.

Se is known as a "dual-edged" sword due to its essential role in human nutrition and its detrimental effects on human health (Qin et al. 2013; Rayman 2000). There is only a tenfold difference between the recommended dietary allowance of Se and the tolerable upper intake level for humans (Macfarquhar et al. 2011). In the aqueous environment, even moderate Se concentrations (>5–10 $\mu g\ L^{-1}$) may result in the death of fish and in deformation of birds (Hamilton 2004); this is due to Se's tendency for bioaccumulation and biomagnification (Presser and Luoma 2010). Like the responses to similar elements, physiological responses to Se exposure are governed by its speciation and bioavailability (Wu 2004).

Since the advent of industrialisation, there has been an increase in Se emissions into the environment due to anthropogenic activities (Wen and Carignan 2007). The major anthropogenic activities that contribute to Se emission are coal and oil combustion, metal smelting, and agriculture (Nriagu and Pacyna 1988). These activities result in the generation of Se-laden wastewaters, such as those of coal

mines (0.4–1500 µg L^{-1}) and gold mines (170–33,000 µg L^{-1}), flue gas desulphurisation process water (1.0–10,000 µg L^{-1}), and agricultural drainage water (140–1400 µg L^{-1}) (Tan et al. 2016 and references therein). These Se-laden wastewaters should be treated before discharge due to their adverse effects on the environment. Furthermore, due to the importance of Se as a technological element, these wastewaters also represent a secondary source for the recovery of Se (Buchs et al. 2013).

Treatment of Se-laden wastewaters by biological methods is a promising technique for its removal and recovery from wastewaters (Lenz and Lens 2009; Tan et al. 2016; Nancharaiah and Lens 2015a). One of the most important factors in the design of a successful treatment process is the identification of different Se species present in engineering systems. This is also true for understanding Se's behaviour in the environment.

The challenges in the identification of Se species in engineered and environmental systems are different. In engineered systems, Se speciation may be dominated by the presence of labile and uncommon Se species (nanoparticles, quantum dots) (Mal et al. 2016a; Mal et al. 2016b; Lenz et al. 2008b) due to the extreme physical–chemical conditions (pH, salts, redox conditions, temperature, pressure, high Se concentrations, presence of chemicals). However, low Se concentrations in the natural ecosystem represent other challenges in terms of detection sensitivity.

Prior to describing the analytical methods for Se speciation in engineered systems, this chapter focuses on Se environmental chemistry, including mineralogy, and on discussing the different Se species present in engineered systems and in the environment. Finally, this chapter concludes with future perspectives regarding how different techniques can further improve our understanding of Se dynamics and transformation pathways in engineered ecosystems. It also sheds lights on the gaps in our analytical abilities to elucidate Se speciation.

2 Biogeochemistry of Se

2.1 Se Mineralogy

Se is somewhat more heavily concentrated in the Earth's crust than in its deeper shells (mantle and core); this is possibly related to an asteroidic enrichment about four billion years ago (Malisa 2001). In the crust, Se is being concentrated thanks to hydrothermal processes that agglomerate Se disseminated within primary sulphides within deep-seated magmatic rocks, especially basaltic rocks. Volcanic eruptions (basaltic) then contribute to the release of Se into the atmosphere, while the weathering of the basaltic lava flows disperses Se into surface waters and subsequent soils (Malisa 2001; Fordyce 2007). In addition, the clay fraction of soils and sediments is able to uptake significant quantities of this aqueous Se (Fernández-Martínez and Charlet 2009). These processes partially explain why

sedimentary rocks tend to show higher concentrations of Se than their magmatic counterparts (usually below 0.1 mg kg^{-1}). For instance, in organic-rich geological materials (such as coal and crude oil), sedimentary phosphates, and black shales, the Se concentration can peak to about 20, 300 and 600 mg kg^{-1}, respectively (Fordyce 2007).

In nature, 407 Se-bearing minerals are currently known to occur, whereas 259 are described as unique species by the International Mineralogical Association (see www.mindat.org for details about the 10th Strunz-Nickel mineral classification). These minerals are primarily distributed among classes I ('elements', which includes only native Se), II ('sulphides', which includes 182 selenides), IV ('oxides', including 49 selenites), and VI ('sulphates', including four selenates). Only one mineral phase appears organic but has not yet been fully identified (see http://www.mindat.org/min-47537.html; see Witzke et al. 2015). This mineral occurs within coal deposits exposed to spontaneous combustion (either related to lighting, pyrite oxidation or human activities and also called "coal seam fires") and is sometimes associated with a reddish form of Se-bearing native sulphur (Witzke et al. 2015). More generally, hydrocarbons, such as oil and coal, constitute a major reservoir of Se in a form that is yet unknown. Most likely, many new organic Se-bearing phases remain to be discovered.

2.2 Prevalent Se Species in Engineered Systems

Se pools are often distinguished according to their valence states: (−II), (−I), (0), (+IV), and (+VI) (Fernández-Martínez and Charlet 2009) (Table 1). Se can also be divided into inorganic and organic forms, the latter typically being Se amino acids, peptides, or proteins; Se sugars; and alkylated volatile selenides. On the other hand, selenate (VI), selenite (IV), elemental Se (0), and metal selenides (−I, −II) are commonly referred to as inorganic forms (Fernández-Martínez and Charlet 2009).

2.3 Microbial Transformation of Se in Engineered Systems

The transformation of various species of Se is often catalysed by micro-organisms, especially in engineered settings (Nancharaiah and Lens 2015b, Chap. 1). The microbial transformation of Se affects both the mobility and the bioavailability of Se (Buchs et al. 2013; Vriens et al. 2014b). This transformation of Se can be divided into assimilatory and dissimilatory reduction, alkylation, dealkylation, and oxidation reactions (Fig. 1).

Microbial activity transforms Se species and may even change their physical state (solid, dissolved, gaseous; see Table 2). For example, the alkylation of dissolved selenate or selenite leads to the formation of volatile dimethyl selenide and dimethyl diselenide (Lenz et al. 2008a). Similarly, biological reduction of dissolved

Table 1 Examples of different Se species that have been studied by means of X-ray absorption fine structure (XAFS) (see below) (Lenz et al. 2008b)

Species	Chemical formula	Origin	Crystallinity	Space group
Red-α-monoclinic selenium, Se(0)	Se	Synthetic	Monoclinic	P2/n
Amorphous selenium, Se(0)	Se	Biogenic	Amorphous	–
Grey trigonal selenium, Se(0)	Se	New Mexico (USA)*	Trigonal	P321
Penroseite, Se(−I)	(Ni, Co, Cu)Se$_2$	Bolivia*	Isometric diploidal	Pa3
Krutaite, Se(−I)	CuSe$_2$	Bolivia*	Isometric diploidal	Pa3
Achavalite, Se(−II)	FeSe	Synthetic**	Dihexagonal dipyramidal	P6/mmc
Klockmannite, Se(−II)	CuSe	Synthetic**	Dihexagonal dipyramidal	P6/mmc
Selenocysteine, SeC	HSeCH$_2$CHNH$_2$COOH	Synthetic**	Amorphous	–
Ferroselite, Se(−I)	FeSe$_2$	Utah (USA)*	Orthorhombic–dipyramidal	Pnmm
Sodium selenide, Se(−II)	Na$_2$Se	Synthetic**	Cubic	Pm3 m
Stilleite, Se(−II)	ZnSe	Synthetic**	Cubic	F43 m
Berzelianite, Se(−II)	Cu$_2$Se	Czech Republic*	Cubic	F43 m
Sodium selenite, Se(IV)	Na$_2$SeO$_3$	Synthetic	Monoclinic	P2/c
Sodium selenate, Se(VI)	Na$_2$SeO$_4$	Synthetic	Orthorhombic	Fddd

Further XAFS data are available (Bingham et al. 2011; Mitchell et al. 2013)

* Minerals are also found in many different sites other than the one mentioned
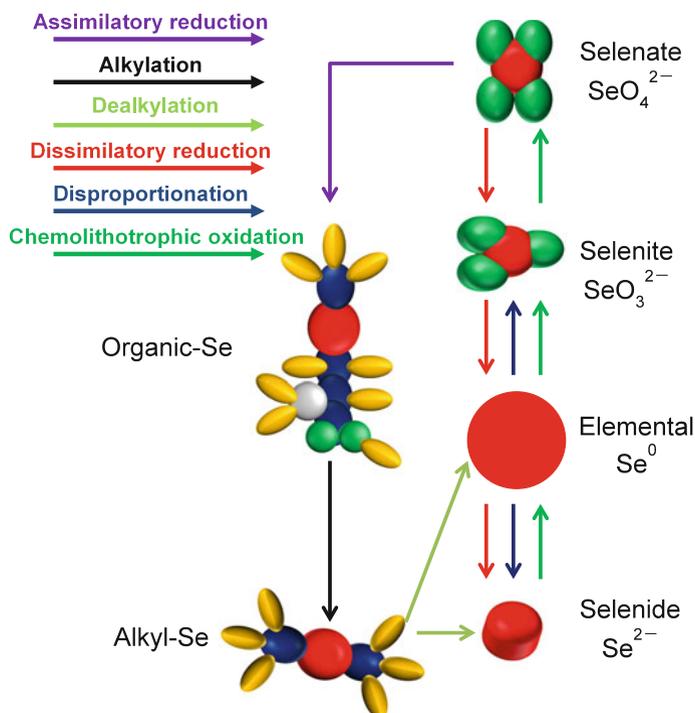
** Natural minerals are also found

Fig. 1 Microbial transformation of Se in nature and in bioreactors

selenate or selenite to solid elemental Se is frequently explored in bioremediation (Oremland et al. 2004). Solid elemental Se usually remains in the form of nanoparticles in colloidal suspension (Buchs et al. 2013; Jain et al. 2015b). This colloidal character is due to the presence of extracellular polymeric substances (Jain et al. 2015a) and/or proteins (Lenz et al. 2011; Buchs et al. 2013; Dobias et al. 2011; Debieux et al. 2011) on the surface of the nanoparticles, which provide colloidal stability. Microbial activity can lead to the reduction of Se oxyanions to selenide. The dissolved selenide reacts with cations, such as Cd and Zn, to form metal selenides (Mal et al. 2016a; Fellowes et al. 2013).

One major anthropogenic source of Se may be the release of Se-rich wastewater, such as flue gas desulphurisation waters or agricultural drainage wastewaters (Lin et al. 2002; Wu 2004; Tan et al. 2016; Akiho et al. 2010; Higgins et al. 2008). Wastewaters containing Se must be treated to certain parts per billion level before discharge due to their inherent potential for bioaccumulation and biomagnification, which has toxic effects on food chain members (Hamilton 2003). Many different bioreactor configurations have been applied for the treatment of Se-containing wastewater (Tan et al. 2016). For detailed information regarding the types of bioreactors that could be used for the treatment of Se-laden wastewater, the readers may refer to Chapter "Industrial Selenium Pollution: Sources and Biological

Table 2 Main selenium chemical species (aqueous or gaseous) present in the engineered settings (adapted from Fernández-Martínez and Charlet 2009)

Species	Chemical formula	Comments
Inorganic species		
Selenate, Se(VI)	H_2SeO_4, $HSeO_4^-$, SeO_4^{2-}	Most oxidised form of selenium, predominant species in soils, sediments and water, highly soluble in water
Selenite, Se(IV)	H_2SeO_3, $HSeO_3^-$, SeO_3^{2-}	Thermodynamically favoured in mildly oxidising, acidic environments (e.g. oil refinery wastewaters), selenite is highly soluble in water
Selenium dioxide, Se(IV)	SeO_2	selenium dioxide is present as gas in volcanic eruptions and combustion processes
Elemental selenium, Se(0)	Se^0	Can be formed as colloidal amorphous spherical nanoparticles upon microbial reduction of selenate and selenite
Selenides, Se(−II)	H_2Se, Me_xSe_y	Volatile selenide formed upon microbial reduction of selenium oxyanions is unstable in terms that it reacts with metals (Me) such as Cd, Zn to form insoluble metal selenides (Me_xSe_y)
Organic species		
Dimethyl selenide, DMSe	$(CH_3)_2Se$	Volatile compound formed upon microbial methylation process
Dimethyl diselenide, DMDSe	$(CH_3)_2Se_2$	
Dimethylselenium sulphide, DMSeS	$(CH_3)_2SeS$	
Dimethylselenium disulphide, DMSeDS	$(CH_3)_2SeS_2$	
Se Amino acids: Selenocysteine, SeCys, Selenomethionine, SeMet	$HSeCH_2CHNH_2COOH$, CH_3Se $(CH_2)_2CHNH_2COOH$	Main selenium species in the organic tissues
Selenoproteins	–	Proteins containing SeCys or SeMet such as glutathione peroxidases, thioredoxin reductases
Trimethylselenonium, TMSe	$(CH_3)_3Se^+$	Urinary metabolite
Selenocyanate	$SeCN^-$	Formed by algal transformation in wastewaters from petroleum refineries

Treatment Technologies" of this book. Most biological treatment processes involve microbial reduction of selenate/selenite to elemental Se, followed by retention or removal of elemental Se from the discharged waters. Furthermore, some systems make use of the algal and bacterial processes (Green et al. 2003), of higher plants alone (Bañuelos 2001; Bañuelos et al. 1997), in combination with bacteria (Huang et al. 2012), or of all the latter (Huang et al. 2013).

The colloidal biogenic elemental Se nanoparticles formed in bioreactors after Se oxyanion reduction can adsorb cations (Jain et al. 2016; Jain et al. 2015a). Because biogenic elemental Se nanoparticles are known to have negative ζ-potential and a number of cations are present in bioreactors (both aerobic and anaerobic), a less negative ζ-potential of the biogenic elemental Se upon interaction with cations is observed. Thus, the interaction of biogenic elemental Se and cations results in increased settleability of Se nanoparticles, which are loaded with cations in the bioreactors.

However, selenate/selenite is often not only reduced to elemental Se but even further reduced to selenide (Herbel et al. 2003). Selenide is only stable towards oxidation and precipitation in highly reducing conditions and in the absence of metals, respectively (Mal et al. 2016a). Formed metal selenides are highly insoluble and thus may strictly limit dissolved Se concentrations. However, because their size can range from 5 to 400 nm, metal selenides remaining as a colloidal suspension may be released with the effluent to the environment (Fig. 2). A similar phenomenon is also known for elemental Se nanoparticles where they are released with the effluent to the environment (Jain et al. 2015c; Lenz et al. 2008a). The reduction of selenate/selenite under both aerobic and anaerobic conditions in ambient temperature conditions usually leads to the formation of spherical-shaped, amorphous elemental Se nanoparticles. However, when the reduction of selenate is carried out at thermophilic conditions, the produced elemental Se is in the form of nanowires (Jain 2015; Dessì et al. 2016), with a median diameter and length of 25 and 570 nm, respectively.

The aerobic reduction of selenate to elemental Se is not widely reported. However, there are many pure cultures, as well as mixed cultures, that have reported the reduction of selenite to elemental Se (more details on the aerobic reduction of Se oxyanions are given in Chapter "Bioprocess Approaches for the Removal of Selenium from Industrial Waste and Wastewater by *Pseudomonas stutzeri* NT-I" of this book). The produced elemental Se nanoparticles can be present in the aqueous phase as a colloidal suspension and in the biomass. Intracellular formation of Se nanoparticles has been reported upon aerobic reduction of selenite by activated sludge (Jain et al. 2015c).

Another important transformation of selenate and selenite in bioreactors (as well as in natural environments) is conversion to alkylated Se compounds, most prevalently dimethyl selenide and dimethyl diselenide. This transformation is reported in both anaerobic and aerobic systems. Anaerobic granular sludge and *Pseudomonas stutzeri* NT1-reducing selenate under anaerobic and aerobic conditions, respectively, have been reported to form alkylated Se compounds that remain dissolved in the aqueous phase before volatilisation (Lenz et al. 2008b; Kagami et al. 2013; Kuroda et al. 2011).
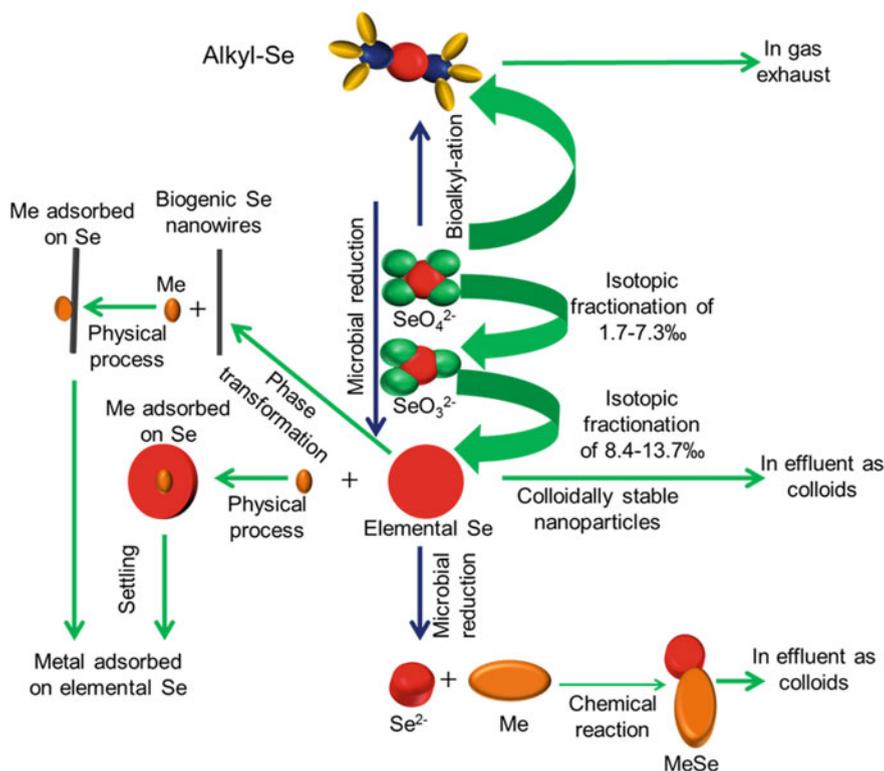
Fig. 2 Se cycle in bioreactors

2.4 The Se Cycle in Nature

Geogenic Se or primary Se, which is present in rocks and minerals as metal selenide or metal selenate, can weather and leach in the form of selenate/selenite (Presser 1994) (Fig. 3). Selenate can be reduced to form elemental Se deposited in sediments (Zhang et al. 2003). Selenate/selenite present in bodies of water can also be taken up by plants and be methylated and released into the atmosphere as alkylated selenide (Vriens et al. 2014a). Volcanic eruptions and untreated incineration flue gas result in the release of Se into the atmosphere as hydrogen selenide and Se dioxide. The subsequent solubilisation of Se dioxide in the atmosphere then results in selenite/selenate falling with the rain (Wen and Carignan 2007). An average atmospheric Se concentration could not be provided due to Selenium's variable natural and anthropogenic emission sources, in addition to the significant differences in atmospheric reactivity (i.e. residence time) among Se chemical species. There are at least three species of Se that should be examined separately according to Wen and Carignan (2007): (1) volatile organic Se (dimethyl selenide [DMSe], dimethyl diselenide [DMDSe], methane selenol [MeSeH], dimethyl Se sulphide, [DMSeS], etc.);
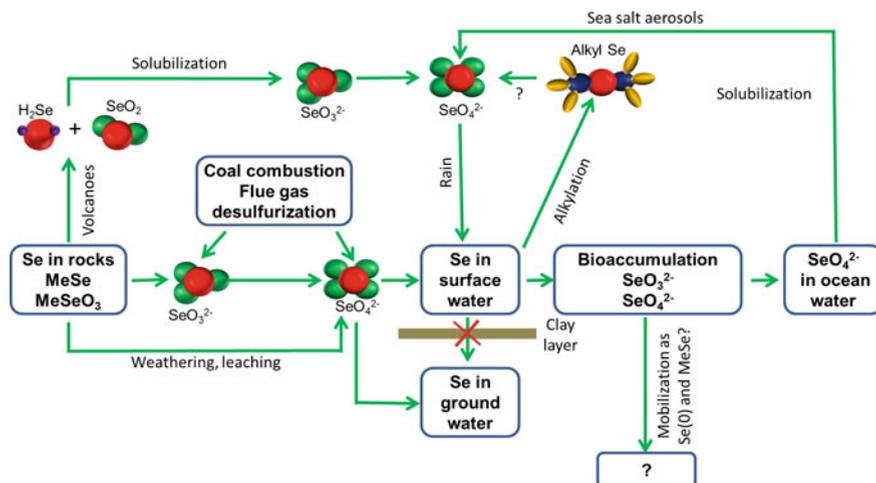
Fig. 3 Se cycle in nature (adapted from Winkel et al. 2012)

(2) volatile inorganic Se (element Se [Se0], hydrogen selenide, [H_2Se], Se dioxide [SeO_2]); and (3) particulate Se. Another important transformation of Se is its assimilation into selenoproteins in living organisms. Decomposition of organisms, in turn, results in the release of Se back into the environment.

3 Analytical Methods for Determining Concentration and Speciation of Se

Environmental and engineered systems represent a different challenge from the analytical point of view. Environmental systems (unless contaminated) are characterised by low Se concentrations in the solid ($\sim$ 0.05 mg kg^{-1} crustal abundance, Fernández-Martínez and Charlet [2009]), liquid (surface waters usually <1 µg L^{-1}), and gas phases ($\sim$few ng m^{-3}) (Mosher et al. 1987).

These low concentrations require the most sensitive detection systems (usually mass spectrometry [MS]) and often require preconcentration methods (see Sect. 3.1.3). In contrast, engineered systems are primarily in place to treat elevated concentrations of Se. However, the matrix itself can be a challenge for analytics (i.e. due to high salt or organic matter concentrations). Furthermore, species different from the oxyanions commonly encountered in natural systems may occur due to high Se concentrations and/or extreme aqueous chemistry (pH, T, pressure, sulphur presence, etc.) (Petrov et al. 2012) and may even be deliberately produced (i.e. Se nanoparticles, quantum dots) (Fellowes et al. 2013).

Se analytical methods can be broadly classified into three types: total Se quantification, fractionation, and species-specific methods.

3.1 Quantification of Total Se

Today, the most commonly used method for the determination of total Se concentrations in the liquid phase is arguably inductively coupled plasma mass spectroscopy (ICP-MS). ICP-MS is known to have detection limits of a few ng L^{-1}; thus, it is sufficiently sensitive for many environmental samples. To quantify Se in the solid phase, either destructive (acid digestion followed by, e.g., ICP-MS) or non-destructive (X-ray fluorescence [XRF]) can be used. However, the high limits of detection severely limit the application of XRF in environmental samples.

Chemical species are specific forms of an element with a defined isotopic composition, oxidation state, and/or complex or molecular structure (Templeton et al. 2000). Speciation analysis in turn is the analytical activity of identifying and/or measuring the quantities of individual chemical species, thus applying techniques with sufficient separation power (Caroli 1996; Cornelis et al. 2003). For Se, these techniques are often liquid chromatography or gas chromatography based. In contrast, fractionation is based on separation procedures with insufficient separation power to differentiate between individual species. Although less detailed, fractionation (e.g. sequential extraction) can give important information about potentially exchangeable and/or bioavailable pools of Se. Table 3 lists the specific techniques that can be used to identify and quantify different Se species.

3.1.1 *Synchrotron* X-Ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) is a powerful, non-destructive, and direct tool for Se speciation in different complex matrixes, including biofilms, natural minerals, and wet pastes (Farges and Wilke 2015). X-ray absorption near edge structure (XANES) provides information on the oxidation state of Se species, whereas extended X-ray absorption fine structure (EXAFS) provides information on the microenvironment of the probed atom (Se), including information about neighbouring atoms, bond types, and coordination chemistry. Because the energy must be tunable with a high resolution, a synchrotron is required to generate these X-rays.

Commonly, the positions of the main edge and/or the first inflection points in the XANES spectra are used to determine oxidation state and speciation. Generally, there is indeed a trend of more oxidised species showing the latter features at higher energies (see, e.g. series elemental Se -> selenite -> selenate, Fig. 4). However, in complex samples containing several Se species and in particular selenides, this relation does not hold true, neither for Se nor for its neighbouring element sulphur (van Hullebusch et al. 2009) (Fig. 5). Therefore, in complex samples and samples in which EXAFS cannot be recorded in sufficient quality (low concentrations, instability), linear combination fitting using a sufficiently large set of reference compounds should be used to determine Se speciation.

Table 3 Techniques for analysis of Se species in various phases

Technique	Comments	Result
Solid-phase analysis		
X-ray diffraction (XRD)	Bulk technique; samples need to be crystalline; mostly, samples need to be in powder and homogenous, qualitative and quantitative	Phase determination Chemical speciation
X-ray photoelectron spectroscopy (XPS)	Surface technique Samples can be amorphous or crystalline Samples can be wet paste or powder Qualitative	Oxidation state of Se Chemical speciation
(μ)X-ray fluorescence spectroscopy (XRF)	Bulk or spatially resolved technique Samples can be powder or pellets Quantitative	Analysis of total Se
(μ)X-ray absorption spectroscopy	Bulk or spatially resolved technique Samples can be amorphous or crystalline Samples can be wet paste or powder Qualitative and quantitative	Oxidation state of Se Chemical speciation
Raman spectroscopy	Bulk technique Samples can be amorphous or crystalline Samples need to be powder or liquid Qualitative	Oxidation state of Se Chemical speciation
Infrared spectroscopy	Bulk technique Samples can be amorphous or crystalline Samples need to be powder Qualitative and quantitative	Oxidation state of Se Chemical speciation
Scanning electron microscopy–energy-dispersive X-ray spectroscopy	Surface technique Samples can be amorphous or crystalline Samples need to be compatible to high vacuum Qualitative and quantitative at high concentration	Elemental analysis Shape identification Localisation
Transmission electron microscopy–selected area electron diffraction	Layer technique Samples can be amorphous or crystalline Samples need to be compatible to high vacuum and thin Qualitative	Elemental analysis Size determination Localisation Chemical speciation Phase determination

Table 3 (continued)

Technique	Comments	Result
Liquid-phase analysis		
Liquid chromatography coupled with inductively coupled plasma mass spectrometry (LC-ICP-MS)	Detection range of few ng L^{-1} Quantitative	Single selenium species including selenium oxyanions and organo-selenium species
Ion chromatography (IC)–conductivity detection	Detection range of 0.1 mg L^{-1} Quantitative	Ionic species only (selenate, selenite)
Inductively coupled plasma mass spectrometry (ICP-MS)	Detection range of few ng L^{-1} Quantitative	Total selenium determination
Atomic adsorption spectroscopy (AAS)-graphite furnace	Detection range of 10.0 µg L^{-1} Quantitative	Total selenium determination
Gas-phase analysis		
Gas chromatograph mass spectroscopy (GC-MS)	Detection range of 10.0 µg L^{-1} Quantitative	Volatile selenium species determination
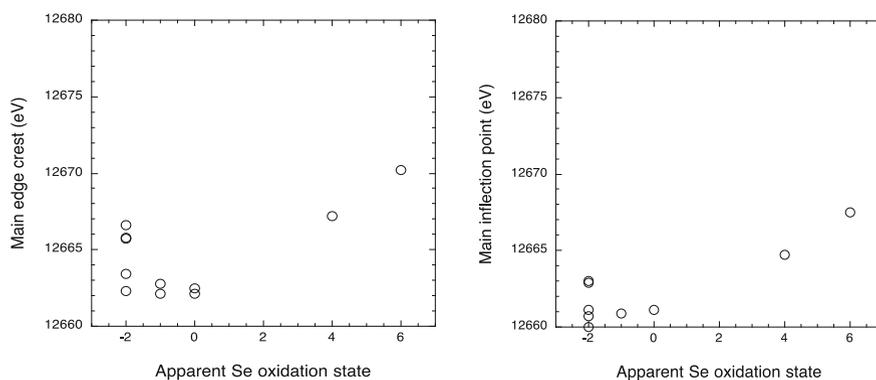
Fig. 4 Se K-edge XANES main edge crest (*left*) and first inflection point (*right*) energy versus the oxidation state model compounds used (data compiled from Lenz et al. 2008b)

3.1.2 Electron Microscopy

Electron microscopy can be used to visualise the shape and size of samples. Regarding elemental Se, the shape can indicate the prevalent allotrope (Fig. 6). However, special care must be employed to avoid the use of electron beams that are too energetic; these might induce unwanted phase transformation. Furthermore, scanning electron microscopy (SEM) coupled with energy-dispersive X-ray analysis (EDX) can be used to localise Se in complex matrixes, such as activated sludge (Jain et al. 2015c) (Fig. 7a–d). Hydrated samples require either drying (which may
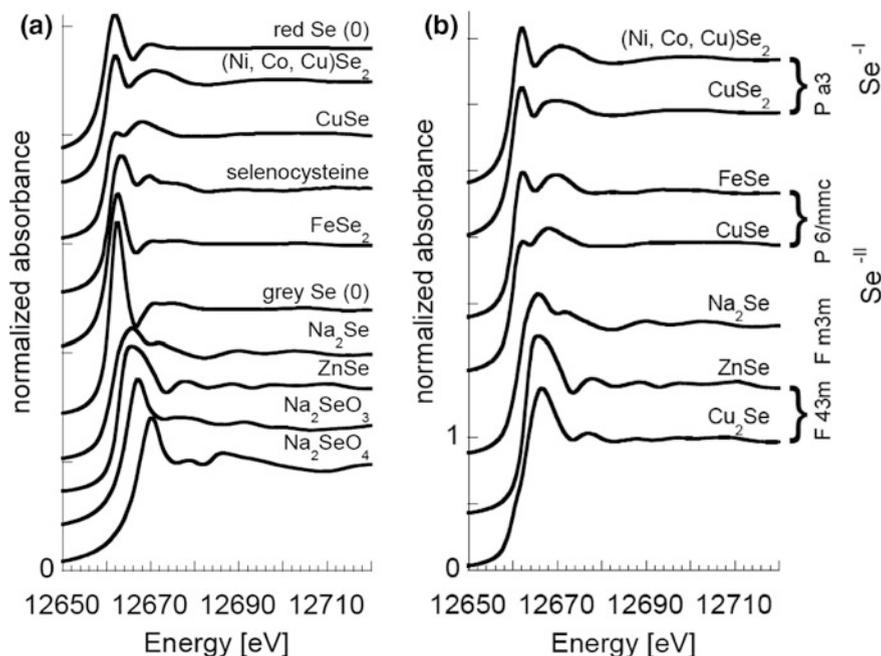
Fig. 5 Normalised Se K-edge XANES spectra for different model compounds. The figure has been adapted from Lenz et al. (2008b) after permission

cause artefacts) or the use of a reduced vacuum (so-called environmental scanning electron microscopy [ESEM]). Transmission electron microscopy (TEM) requires preparation of samples on a grid, as well as high vacuum conditions for drying biological samples.

The use of TEM and 3D reconstruction software can conclusively prove the intracellular localisation of Se (Espinosa-Ortiz et al. 2015 [Fig. 7e]). It is important to identify the localisation of elemental Se nanoparticles, not only to understand their fate in the environment but also to devise strategies for their effective recovery. TEM coupled with selected area electron diffraction (SAED) can be used to identify the allotropes of elemental Se (Gates et al. 2002).

The adsorption of metals on elemental Se nanoparticles and the reaction of metals with selenide to form metal selenide take places in bioreactors (Fig. 2). However, it is challenging to distinguish between these two simultaneous interactions. Techniques such as X-ray photoelectron spectroscopy (XPS) cannot resolve this in some cases because the energies of other compounds, such as Me-oxides or Me-hydroxides, are too close, and selected area measurements are difficult to carry out (Jain et al. 2015a). The combination of TEM with SAED can to some extent resolve this challenge. If the metal selenide is crystalline, the SAED can distinguish between metal adsorbed onto elemental Se and metal selenide by means of electron
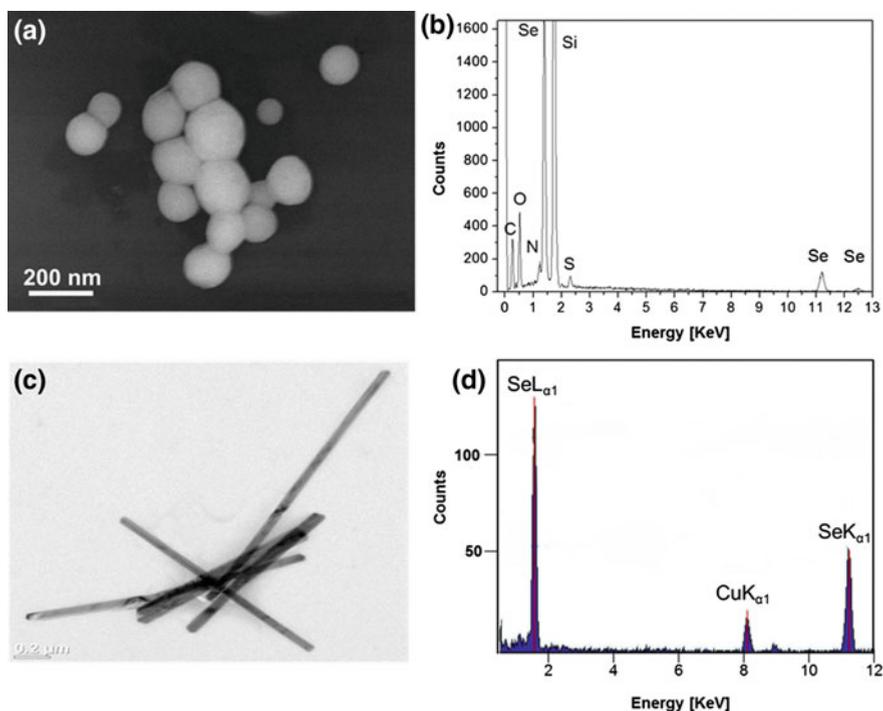
Fig. 6 **a** SEM image of purified biogenic elemental Se nanoparticles and **b** its corresponding EDX spectra. **c** TEM of the chemogenic elemental Se nanowires and **d** their corresponding EDX spectra. The images have been reproduced from Jain et al. (2015a), after permission

diffraction. In addition, the narrower electron beam is useful in identifying a smaller crystalline section in the samples.

3.1.3 Chromatographic Separation for Speciation

As outlined previously, Se (bio)transformations can lead to a diversity of species with anionic, neutral, zwitterionic, or cationic character that are dissolved or gaseous, inorganic or organic (Table 3). Therefore, all variants of liquid chromatography (LC) and gas chromatography (GC) have been applied in species determination. The challenge of necessarily low limits of detection is primarily solved by combining the separation ability of chromatography with highly sensitive ICP-MS, referred to as hyphenation. Exemplarily, we list here some recent hyphenation approaches. The prevalent Se oxyanions are routinely separated by anion-exchange chromatography (Lenz 2008). For engineered systems, simple conductivity detection may be sufficient, with typical limits of detection of somewhat below 1 ppm. Combining an online preconcentration step with ion chromatography combined with ICP-MS
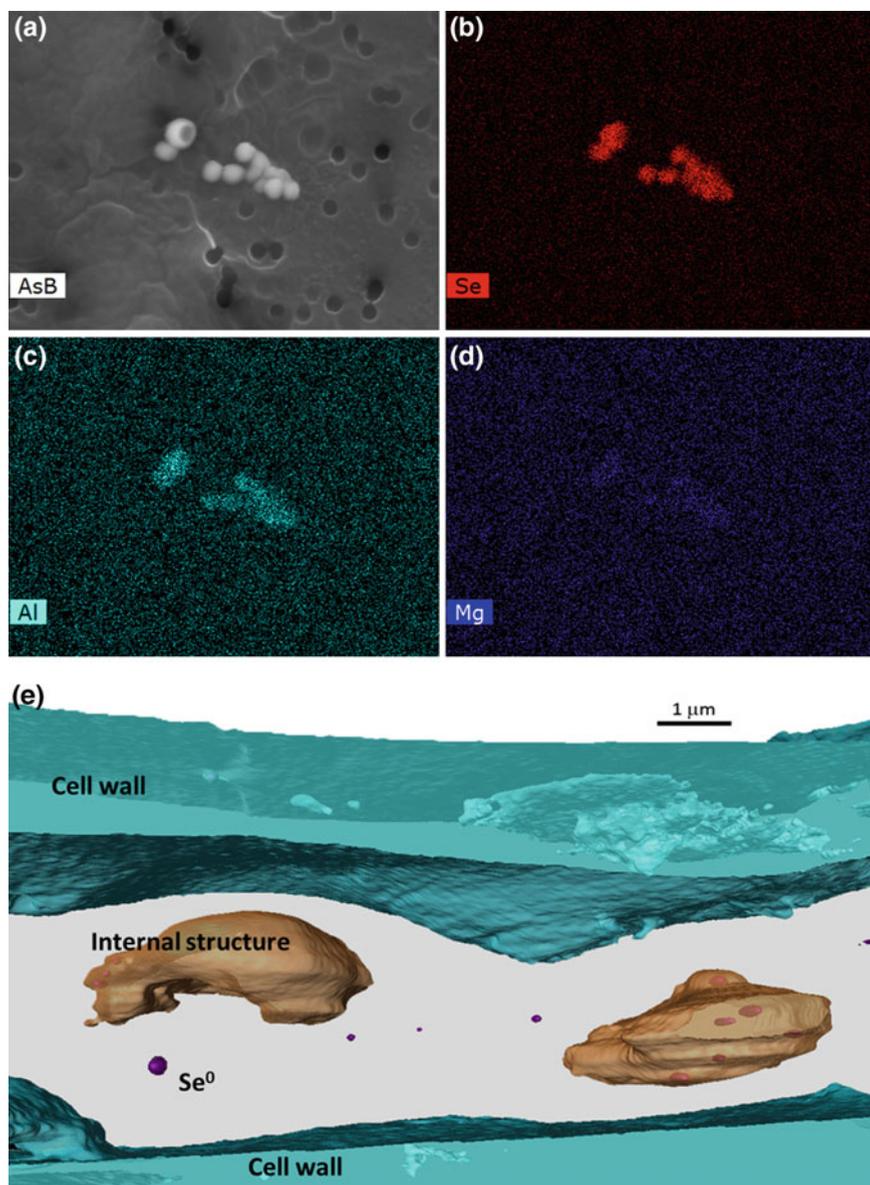
Fig. 7 **a** SEM image of biogenic elemental Se nanomaterial trapped inside activated sludge and EDX analysis corresponding to spatial distribution of **b** Se, **c** Al, and **d** Mg. **e** 3D reconstruction of trapped elemental Se nanomaterial inside the *Phanerochaete chrysosporium* by means of TEM images and 3D tomography software. The figures are reproduced from Jain et al. (2015c) and Espinosa-Ortiz et al. (2015), with permission

(IC-ICP-MS) allowed picogram L^{-1} limit of detection in the study of Se-depleted volcanic ashes (Lenz et al. 2012). A combination of cation and anion-exchange chromatography was used to separate a total of 12 Se species—including Se amino acids and their derivatives, as well as cationic selenonium species—and applied to the analysis of yeast and algae (Larsen et al. 2001). In addition, speciation of Se extracted from yeast by different methods may be characterised by different types of LC, including size-exclusion, anion-exchange, and reversed-phase chromatography with ICP-MS detection (Casiot et al. 1999). However, Casiot et al. (1999) reported that the extraction methods greatly influence the Se speciation, showing the fragility of Se species during sample preparation.

The alkylated Se species, DMSe and DMDSe, are volatile under ambient conditions. In addition, due to their low concentrations, their quantification is challenging in non-contaminated environments. One of the methods for field measurement of these volatile species is trapping them in concentrated HNO_3, in which DMSe is oxidised to dimethyl selenoxide (DMSeO) and DMDSe is transformed to methylseleninic acid (MSe) (Winkel et al. 2010). Both DMSeO and MSe are much less volatile than their respective parent products. The detection of DMSeO and MSe can be carried out via high-performance liquid chromatography coupled with ICP-MS (HPLC-ICP-MS).

Another method for measuring of DMSe and DMDSe is direct immersion solid-phase microextraction gas-chromatography mass spectrometry (DI-SPME-GC-MS) (Lenz et al. 2008a). In this method, SPME fibres are used to adsorb the dissolved compounds before they are volatilised from the fibre, separated and detected by MS. An improvement of this method by automatisation reduces artefacts of manual sample handling and has been used to detect two Se species (DMSe and DMDSe) from a mixture of 10 different Se and sulphur species in different aqueous media (Vriens et al. 2015) simultaneously.

These are only few examples in the dynamic field of Se speciation, and we refer the reader to the extensive annual review series "Atomic Spectroscopy Update" (Journal of Analytical Atomic Spectrometry).

3.2 Tools for Studying Se (Bio) Transformations

3.2.1 Se Isotopes and Their Fractionation

Se has, in total, nine isotopes, out of which six are stable. Se stable isotopes can support the understanding of the biogeochemical processes occurring in engineered ecosystems, as well as in the environment. If the reaction rates differ for the different isotopes, Se isotope fractionation is observed during conversion from one species to another. For instance, Se oxyanion reduction, either microbial or abiotic, involves an enrichment of lighter isotopes in the reaction products and a complementary enrichment of the heavier isotopes in the remaining unreduced Se (Herbel et al. 2000; Ellis et al. 2003; Johnson 2004). This is the prevailing cause of Se

isotope ratio variation in the environment, and isotope ratio shifts are thus useful as indicators of reductive processes occurring. It should be noted that all the possible Se transformation reactions must be studied isotopically to allow unequivocal interpretation of data from natural and engineered environments.

According to Table 4, sorption and precipitation reactions induce little or no Se isotopic fractionation. In contrast, selenite (Se IV) chemical reduction with pyrite, green rust, or ZVI induces Se isotopic fractionation. The range of $\varepsilon^{82/76}$Se values

Table 4 Expected Se fractionation depending on the occurring processes

Se transformation processes	Comments	Effective fractionation $\varepsilon^{82/76}$Se (‰)	References
Selenium sorption and isotope fractionation: Iron (III) oxides (2-line ferrihydrite, goethite, and haematite) versus iron (II) sulphides (mackinawite and pyrite)	Sorption reactions induces little or no Se isotopic fractionation. However Se reduction induces such change	Reductive sorption of Se(IV) to pyrite −9.7‰ Sorption to iron (III) oxides <1‰	Mitchell et al. (2013)
Selenium fractionation during reduction by Fe (II)-Fe (III) hydroxide-sulphate (green rust)		Se(VI) reduction by green rust (−11.1‰)	Johnson and Bullen (2003)
Selenium fractionation during selenate reduction by granular zerovalent iron (G-ZVI)	Se(VI) is reduced into the following compounds: Se (IV), $Fe_2(SeO_3)_3$, FeSe, $FeSe_2$, and Se(0)	The reduction of Se(VI) reduction by G-ZVI gives -4.3‰ within the $CaCO_3$-saturated water and −3.0‰ in ultrapure water	Shrimpton et al. (2015)
Bacterial respiratory reduction of selenium oxyanions	Pure culture experiments with *Sulfurospirillum barnesii* and *Bacillus arsenicoselenatis*	Se(VI) reduction to Se (IV) : from −4 to −5‰ Se(IV) reduction to Se (0): from -6 to -9‰	Herbel et al. (2000)
Selenium fractionation by natural microbial consortia	Natural microbial consortia	Reduction of Se(VI) to Se(IV) yielded a fractionation of −2.6 to −3.1‰ Reduction of Se(IV) to Se(0) yields a fractionation of −5.5 to −5.7‰	Ellis et al. (2003)
Biomethylation of Se	Isotope fractionation of selenium during fungal biomethylation by *Alternaria alternata*	Se(VI) biomethylation at pH4: −3.00 ± 0.26‰ and pH7: −2.72 ± 0.41‰ Se(IV) biomethylation ∼ −8.24‰	Schilling et al. (2011)
Biomethylation of Se	Algal methylation	Se(VI) biomethylation to methlyselenide: <1.1‰	Johnson et al. (1999)

obtained for reductive sorption to iron sulphides or green rust overlaps with those reported for microbial Se reduction. Thus, although Se isotopic signatures in engineered systems may record reduction processes, they may not allow one to distinguish between the abiotic and biotic reduction pathways of Se.

3.2.2 Sequential Extraction Procedures for Fractionation

Sequential extraction procedures (SEPs) are straightforward tools to identify pools of Se in operationally defined fractions. For instance, Wright et al. (2003) carried out optimisation of SEP for Se from synthetic and environmental samples. However, it should be noted that SEPs may suffer from incomplete extraction of targeted pools and/or co-extraction of further pools; thus, results should be interpreted with care. This fact was further confirmed by Lenz et al. (2008b), who achieved direct determination of Se speciation by use of XANES spectroscopy of an anaerobic biofilm, which measured 57% less elemental Se than the SEP.

4 Future Perspectives

The conversion of waste into resources is vital to sustainable development. Se is a scarce resource, with no independent primary mining sources. Hence, its recovery from wastewater may become increasingly important. The microbial reduction of Se oxyanions to elemental Se nanoparticles is an interesting phenomenon that may be explored within the framework of resource recovery (Jain et al. 2014). For recovery and reuse, it would be preferential to produce pure particles of defined shape and size. However, the biogenic Se nanoparticles produced hitherto have showed polydispersity, which is not yet understood. For instance, conventional SEM and TEM do not have the resolution to understand the initial stages of formation. In contrast, cryo-electron microscopy (2 Dimension cryoTEM and cryo-electron tomography) has a resolution of 0.5 nm and may allow the observation of prenucleating clusters (Pouget et al. 2009). This can ultimately shed light on the causes of polydispersity of biogenic Se nanoparticles.

Another analytical approach combining X-ray fluorescence imaging (XFI) and scanning transmission X-ray microscopy (STXM) has been recently implemented by Yang et al. (2016) for the study of multispecies biofilms involved in the bioreduction of Se oxyanions. These complementary synchrotron techniques require minimal sample preparation and have been applied simultaneously to the same biofilm areas. On a microscale, XFI visualises the distribution of Se and endogenous metals, whereas Se K-edge XAS analysis indicates the presence of elemental Se(0). On a nanoscale, carbon K-edge STXM reveals the distributions of microbial cells, extracellular polymeric substances (EPSs), and lipids, along with the presence of highly localised Se(0) using the Se LIII edge. STXM can thus provide highly informative maps of biological macromolecules and morphology

information at a high resolution (~ 30 nm). By implementing this combined analytical approach, Yang et al. (2016) reveal that the elemental Se nanoparticles were closely associated with the microbial cells and the EPS component of the biofilm.

Identification of species in the liquid phase using hyphenated techniques with ICP-MS hitherto relies on the availability of defined standards with retention times matching the unknown Se species. Preliminary studies have used powerful mass spectroscopic combinations, such as liquid chromatography coupled with ICP-MS (LC-ICP-MS) and liquid chromatography electrospray ionisation quadrupole time-of-flight-mass spectrometry (LC-ESI-Q-TOF-MS) (Anan et al. 2015 and references therein). The latter approach may overcome the need for defined standards because it allows standardless identification of unknown compounds (due to the high mass resolving power). However, due to limitations in ionisation, use of this approach may be limited to samples with higher Se concentrations.

For natural, non-impacted systems, low Se concentrations will continue to pose a challenge for analytical chemistry. Although total Se concentrations can probably be measured in most environments (see above), the species-specific analysis that prevails in original speciation may be hard to achieve. If well-defined reference compounds with matching retention times are not available, hyphenated LC-ICP-MS can still be used to quantify (yet not identify) unknown Se compounds (as shown, e.g., with Se-depleted volcanic ashes and flue gas desulphurisation waters) (Lenz et al. 2012; Petrov et al. 2012). Thus, it is doubtful that the sensitivity of most complementary MS techniques is sufficient for the identification of unknown peaks at ultra-traces (few ng L^{-1}). Furthermore, there is no means of verifying that the original species are preserved within samples (e.g. by using certified reference materials). At concentrations in the ng L^{-1} range, traces of oxygen (during sampling, sample preparation, and analysis) would be sufficient to fully oxidise low-concentrated analytes.

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