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Review

Speciation and Fractionation of Less-Studied Technology-Critical Elements (Nb, Ta, Ga, In, Ge, Tl, Te): A Review

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Abstract

Technology-critical elements (TCE) are of great relevance in the development of key emerging technologies, including renewable energy, energy efficiency, electronics and the aerospace industry. A sudden increase in industrial demand in support of an emerging technology or unexpected cutoff from a supply of critical minerals can have a drastic impact on national security and economic health. The growing release of TCEs requires understanding their mobility, reactivity, and chemical transformations in the environment, which are critically dependent on their chemical form. Here we review the speciation of less studied technology-critical elements (LSTCEs): Nb, Ta, Ga, In, Ge, Tl and Te. We discuss the trends in analytical techniques using in TCEs speciation. The development of analytical techniques significantly increases the interest of researchers in these elements and species. In particular, there is still little information in the literature on the speciation of niobium and tantalum.

Keywords: LSTCE, less studied technology-critical elements, speciation, fractionation, TCE

Introduction

Global population growth, wealthier lifestyles, technological change, and government policies have altered the supply and demand patterns of raw materials since the early twentieth century. In particular, the use of multiple materials in single applications to increase product functionality and the push towards low carbon technologies and resource efficiency have increased the demand for many of the so-called technology-critical elements (TCEs), that were not widely used just a few years ago. The global trade networks of goods, in which materials move along the value chain of mining, processing, manufacture, use, disposal, collection, and waste management, have increased in complexity in recent years as multiple countries are involved in the lifecycles of products [1]. As a consequence of their growing use in electronic and industrial products, increasing amounts of TCEs are being released into the environment. Electronic waste is often the source of precious metals belonging to TCEs [2-6].

Currently, little is known about the fate of many of TCE elements. The lack of certain minerals in countries in the European Union (EU) has forced efforts to secure the supply of mineral resources within the EU. Forecasts indicate that demand for critical raw materials

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and "high-tech" metals will grow with the development of innovative technologies. Accordingly, the European COST Action TD1407 scientists and practitioners are interested in TCE, from evaluating their environmental processes to understanding potential threats to human health [7].

TCEs are a rather heterogeneous group and they are not a coherent group of elements from the chemical point of view. Critical elements are those which are expected to play an important role in high-technology, energy supply, green, and defense applications, but their supply and demand is unbalanced. Our level of knowledge concerning the environmental impact of their use is quite variable; while the impact of elements such as Pt or Pd has been known for a long time, almost nothing is known about the environmental behavior of Nb or Ta, for example [8]. Moreover, there is an increasing demand for analytical techniques that are able to measure technology-critical elements, a set of elements increasingly used in technological applications (e.g., Pt-group elements, Nb, Ta, Te, In, Ga, Ge, and Tl). For most of the elements, their environmental and toxicological effects are unknown. Their impact on the biogeochemical cycles and potential biological and human health threats needs to be explored further [9, 10].

The term speciation is often used to define an analytical procedure conducted to determine and identify chemical species and to measure their distribution in a particular sample or matrix. Chemical speciation can also be seen as the process of identification and determination of specific chemical species allowing us to learn about the availability and mobility of metals in the context of understanding their chemical behavior. Speciation defines chemical forms whereas fractionation classifies analytes or analyte groups in a sample with regard to the physical and chemical properties [11, 12]. The fractionation is a process of classification of an analyte or a group of analytes from a certain sample according to or chemical properties. The sequential extraction procedures are the fractionation, not speciation analysis. The most popular fractionation methods are the Bureau of Reference (BCR) or Tessier chemical sequential extractions.

Recently, speciation analysis has played a unique role in the studies of the biogeochemical cycles of chemical compounds, determination of the toxicity and ecotoxicity of selected elements and many others. Conventional methods like AAS (Atomic Absorption Spectrometry) or ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) help to determine total metal and metalloid contents in the sample. The attractive alternatives are hyphenated techniques in which the separation method is coupled with multi-dimensional detectors. The main advantages of these techniques are extremely low detection and quantification limits, insignificant influence of any interference, and high precision and repeatability of the determinations. The data on the speciation of TCEs in the literature are relatively scarce and essentially limited to Ge, Te, Tl, Pt, Pd, Rh, and Gd [13].

Speciation of LSTCE

Thallium Speciation

The toxicity and environmental mobility of Tl are critically dependent on the oxidation state [14]. The toxicity of Tl(I) is 100 times higher than that of Cd and the literature available regarding this is only a tiny fraction of that on Cd. Moreover, there is evidence that Tl(I) can be metabolized to Tl(III) by plankton which is 50,000 times more toxic Tl(I). The acute toxicity of Tl(III) to mammals is greater than that of Hg(II), Cd(II), and Pb(II). Tl(III) is reported to be more abundant in species in sea and lake waters, whereas Tl(I) (analogue of potassium) occurs predominantly in soil and the roots, stems and leaves of plants [15, 16].

Me_2Tl^+ was detected in freshwater at low ng/L levels [17] and accounts for up to 50% of Tl in the ocean [18]. The conversion of Tl to methylated forms is of significant importance because of its toxicity and its environmental mobility. The speciation analysis of Tl refers to the discrimination between the Tl(I) and Tl(III) oxidation states with the question of Me_2Tl^+ being specifically addressed, and the analysis of seawater is further complicated because of the presence of salt. The stability of Tl(I) and Tl(III) depends on the type of sample and the environmental conditions.

Sample acidification was inadequate to maintain the original distribution of Tl(I) and Tl(III); the addition of DTPA (diethylenetriamine pentaacetic acid) was found to have a stabilizing effect. The sample preparation step potentially raises the risk of changes in speciation but a comparison between HPLC-ICP-MS (high performance liquid chromatography-inductively coupled plasma-mass spectrometry) and direct speciation of Tl in a plant by XANES (x-ray absorption near edge structure) [16] showed coherent results. Chemical speciation of Tl can be determined directly by chromatographic separation followed by elemental detection, usually with ICP-MS [19, 20], or using a microcolumn-based method [21, 22]. Electrochemical methods can also be used for the speciation analysis of Tl [23]. However, the most common methods used in thallium speciation are IC-ICP-OES (ion chromatography-inductively coupled plasma-optical emission spectroscopy) and IC-ICP-MS [15]. Table 1 presents examples of LSTCE speciation in the literature.

Speciation of Gallium

In the literature, there is little information about the gallium species. Among the few papers on this subject, several publications should be noted. Due to the harmful effects of Ga(III) for living organisms, research was conducted on the thermodynamic changes and the

preservation of this form of gallium [24, 25]. Gallium is a valuable element in the electronics industry and in the processing of bauxite ores for the recovery of Ga, and a high-level of purification of the raw Ga product is required for electronic applications. Therefore, and effective speciation analysis of this element is necessary. For differentiating chemically important Ga(III) species, the Amberlite XAD-2 polystyrene-divinylbenzene copolymer was chloromethylated using $AlCl_3$ as a catalyst, and later, 5-palmitoyl-8-hydroxyquinoline was covalently bound to this chloromethylated product via Friedel-Crafts reaction, resulting in the synthesis of a Ga-specific resin (Amberlite XAD-2-P·Ox) [26]. The sequential extraction scheme of Tessier et al. [27] for heavy metals was examined for the separation of scandium and gallium [28]. Very sensitive, spectrophotometric methods based on a mixture of the complexes of Sc(III) and Ga(III) with Chrome Azurol S and benzyldodecyldimethylammonium bromide were applied for the determination of scandium and gallium, after their separation by solvent extraction. In contrast, research on the sorption of gallium species on ilites has

Table 1. Examples of LSTCE speciation in the literature.

Element	Species	Type of test sample	Techniques	Literature
Tl	Tl(I), Tl(III)	Plants	IC-ICP-MS	[14]
	Tl(I), Tl(III)	Plants	HPLC-ICP-MS	[15]
	Tl(I), Tl(III)	Plants	IC-ICP-MS, SEC-ICP-MS	[16]
	Tl^+, $(CH_3)_2Tl^+$	River water	LC-MS, IC-ICP-MS	[17]
	$(CH_3)_2Tl^+$	Seawater	PTI–IDMS	[18]
	Tl(I), Tl(III)	River water	HPLC-ICP-MS	[19]
	Tl(I), Tl(III)	Mustard plants	HPLC-ICP-MS	[20]
	Tl(I), Tl(III)	Tap water	CNTs, ETAAS	[21]
	Tl(I), Tl(III)	Soil, green cabbage	Microcolumns, ICP-MS	[22]
	Tl(I)	Plants	DPASV, HMDE, HPLC-ICP-MS	[23]
Ga	Ga(III)	Water	Extraction, ICP-MS	[24]
	Ga(III)	Seawater	Extraction	[25]
	Ga(III)	Water	Cation exchange	[26]
	Ga(III)	Soil	Spectrophotometric methods	[27]
	Ga(III)	Montmorillonite and illite	Ionic exchange and surface complexation	[29]
	Ga(III)	Calcite and goethite	Isotope fractionation	[30]
	Ga(III)	Water	Extraction on ZnO nanowires	[31]
	Ga(III)	Leach liquors	Solvent extraction and ion exchange	[32]
	Radiogallium	$ZnCl_2$/HCl solutions	Membrane-Based Liquid-Liquid Extraction	[33]
	Ga(III)	Aluminum/gallium-based ionic liquids	MALDI-TOF, FT-IR	[34]
	^{68}Ga	Large zeolite particles	PEPT	[35]
Nb and Ta	Nb, Ta	Alkaline media	LLE	[39]
In	In^{3+}, In^0	Clean In, samples of In_2O_3 and $In(OH)_3$	XPS, HREELS, and TPD	[44]
	In(III)	Atmospheric particulate matter	ICP-OES, ICP-MS, fractionation	[45]
	In^{3+}, $In(OH)_4^-$	Aqueous sulfate solution	Nanofiltration	[46]
	Total In, In^{3+}	Solutions	SCP, AGNES	[47]
	In^{3+}, In^{5+}	Catalyst	XRD, EDX	[48]
	InP	Hydra vulgaris	X-Ray Microspectroscopy	[49]
	In^0, In^{3+}	Aqueous solution	AGNES	[50]
	In(III)	Aqueous HCl solution	EXAFS, ^{115}InNMR, extraction	[53]

Table 1. Continued.

Te	Te(IV), Te(VI)	Water samples	DLLM-ETAAS	[55]
	CdTe QDs and Te(IV)	Natural waters	Combining hydride generation with HS-SDME and GFAAS	[56]
	Te(IV)	Waters	Solid-phase extraction, ICP-MS	[57]
	Te(IV), Te(VI)	Water samples	LC-HG-ASF	[59]
	Te(IV), Te(VI)	Refractory environmental samples	HG–AFS	[60]
	Te(IV), Te(VI)	Bioleaching solution	HG-AFS	[61]
	MeTeCysO, Te(IV), Te(VI)	Garlic	ESI-MS-MS, HPLC-ICP-MS	[65]
	Te(IV), Te(VI)	Bedrock, ores	HPLC-ICP-MS	[66]
	Te(IV)	Environmental water samples	DLLM-ETV-ICP-MS	[67]
	Te(IV)	Quantum dots	CZE-ICP-MS	[68]
	Te(IV)	Rats	ICP-MS	[69]
	Te(IV), Te(VI)	Soil, water	HPLC-ICP-MS, XAFS	[70]
	Te radionuclides (^{132}Te and ^{129}Te)	Air, water, soil		[71]
Ge	MMGe, DMGe, TMGe, EGe, DEGe, TEGe	Water, saline matrix	LC-HG-ICP-OES	[73]
	Ge(IV), MMGe, DMGe	Acidic aqueous leachates	LC-ICP-QQQ-MS	[75]

AGNES absence of gradients and nernstian equilibrium stripping; CNTs carbon nanotubes
CZE-ICP-MS capillary zone electrophoresis-inductively coupled plasma-mass spectrometry; DEGe diethyl germanium
DMGe dimethyl germanium; DLLM dispersive liquid-liquid microextraction
DLLME-ETAAS dispersive liquid-liquid microextraction and electrothermal atomic absorption spectrometry
DLLM-ETV-ICP-MS dispersive liquid liquid microextraction-electrothermal vaporization inductively coupled plasma-mass spectrometry
DPASV differential pulse anodic stripping voltammetry
DPASV-HMDE differential pulse anodic stripping-voltammetry using a hanging mercury drop electrode
EDX energy-dispersive X-ray spectroscopy; EGe ethyl germanium; ESI-MS-MS electrospray tandem mass spectrometry
ETAAS electrothermal atomization atomic absorption spectrometry;
FT-IR fourier transform infrared; GFAAS graphite furnace atomic absorption spectrometry
HG-AFS hydride generation coupled to atomic fluorescence spectroscopy
HPLC-ICP-MS high performance liquid chromatography- inductively coupled plasma-mass spectrometry
HS-SDME headspace single drop microextraction;
HREELS high-resolution electron energy loss spectroscopy; InP indium phosphide
ICP-MS inductively coupled plasma-mass spectrometry; LLE liquid liquid extraction
LC-HG-ASF liquid chromatography-hydride generation-atomic fluorescence spectrometry
LC-ICP-QQQ-MS liquid chromatography-inductively coupled plasma-triple quadrupole mass spectrometry
MALDI-TOF matrix-assisted laser-desorption ionization time-of-flight; MMGe monomethyl germanium
PEPT positron emission particle tracking; PTI–IDMS positive thermal-ionization isotope-dilution mass spectrometry
SCP stripping chronopotentiometry; TEGe triethyl germanium; TMGe trimethyl germanium
TPD temperature programmed desorption; XAFS X-ray absorption fine structure spectroscopy
XPS X-ray photoelectron spectroscopy; XRD X-ray diffraction

shown that the sorption of Ga on montmorillonite and illite can be explained by the Ga^{3+} exchange in very acidic conditions (pH < ~3.8) [29]. The hydrated Ga(III) ion is octahedral, coordinated by water molecules, but there is some evidence for $GaCl_4^-$ that conversion to tetrahedral coordination may occur upon replacement of water by a sufficient number of other ligands. In most hydrothermal solutions, the authors predict that hydroxide complexes will be the most important forms of the transport of Ga, although fluoride complexes will be important in environments where fluoride activities are relatively high (e.g., during greisen formation). Gallium isotopic fractionation during its adsorption on calcite and goethite, suggests that the adsorption of Ga by oxides, carbonates, or clay minerals could yield significant Ga isotope fractionation between secondary

minerals and surficial fluids, including seawater [30]. In the literature you can find many articles on the separation of gallium with ions of other metals, most often by extraction methods [26, 31-33], while there are few publications on the speciation of gallium ionic forms [34, 35].

Niobium and Tantalum Speciation

Our knowledge of the environmental behavior and the fate of any element is entirely dependent on our ability to measure its concentration in different matrices. In this context, tantalum and niobium qualify as a particularly difficult cases. Tantalum (Ta) and niobium (Nb) are two strategic metals essential to several key sectors, like the aerospace, gas and oil, nuclear and electronic industries, but their separation is really difficult due to their almost identical chemical properties.

Tantalum analysis is a serious bottleneck in tantalum environmental research. The main problems are the mineralization of solid samples (e.g., water suspended sediments, soils, aerosols, etc.) and the measurement of 'dissolved' concentrations in natural water. There is a lack of CRMs (certified reference material) for aerosols and water matrices. Existing data suggest that 'dissolved' tantalum concentrations in natural water are not limited by the solubility of Ta_2O_5. There are no sorption studies on tantalum binding to natural organic matter or inorganic particles [36, 37].

An important characteristic of tantalum chemistry is the insolubility of its compounds, with alkali metal tantalates being more soluble than alkaline-earth ones. Some tantalate compounds are being extensively investigated for new applications, such as catalysts for water electrolysis and hydrogen production [38].

Group speciation is difficult due to the similar chemical properties of these two elements and methods are currently being developed to separate Nb and Ta, including a capillary zone electrophoresis (CE), a method which is able to separate and quantify Nb and Ta directly in alkaline media [39].

Indium Speciation

Only In(III) compounds are stable in aqueous systems. Indium compounds of toxicological interest include indium trichloride, indium oxide, indium sulfate, indium sesquioxide, and colloidal indium hydroxide. Indium also forms organometallic compounds, such as trimethylindium which is a polymeric solid. Indium phosphide and indium arsenide are used in the manufacture of semiconductors, and indium phosphide is used in the production of nanoparticles, nanowires, and nanodots [40-43].

Metallic indium and its oxides are useful in electronic applications, in transparent conducting electrodes, as well as in electrocatalytic applications. The active environment should be considered in indium catalysis and the synthesis of indium materials, since the surface speciation is a sensitive to the composition of the oxidizing atmosphere. A speciation method was developed for the determination of inorganic indium compounds in emissions of particulate matter and in the workplace, based on selective sequential extractions. To determine the role of the indium oxidation state in aqueous electrochemical CO_2 reduction to formate, a deeper understanding of the interfacial speciation at the electrode surface was necessary [44].

The main inorganic indium compounds that are expected to be present in the atmospheric particulate matter from the industrial production of indium and the manufacture of indium compounds were separated and determined. The procedure has been tested on standard reference materials. The indium recovery was in the range 93-105% [45]. The pH dependent separation of indium and germanium was investigated by the means of nanofiltration. In a binary salt mixture of $In_2(SO_4)_3$ and GeO_2, indium and germanium can be separated from one another by varying the pH value. This is related to a change of speciation and a change of membrane charge due to a variation in the pH value in the range of pH 2-12 [46]. The geochemical fate of indium in natural water is still poorly understood. The total and free indium concentrations in solution were studied using two complementary electroanalytical techniques, SCP (Stripping chronopotentiometry) and AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) implemented with the TMF/RDE (Thin Mercury Film/ Rotating Disk Electrode) [47].

Recently, In_2O_3 was discovered as a highly selective and stable catalyst for the production of green methanol from CO_2. Activity boosting by promotion with palladium, an efficient H2-splitter, was partially successful since palladium nanoparticles mediate the parasitic reverse water–gas shift reaction, reducing selectivity, and producing sinter or an alloy with indium, limiting the use and robustness of the metal. Palladium atoms that replace indium atoms in the active In_3O_5 ensemble attract additional palladium atoms that are deposited onto the surface, thus forming low-nuclearity clusters, which foster H2 activation and remain unaltered, enabling record productivities for 500 h [48].

Ion forms of indium are used for *in vivo* biotransformations and could be used in strategies to drive the design of future applied materials for nanotechnology-based diagnosis and therapeutics. In(III) was used in the study of a simple model organism (*Hydra vulgaris*) that presented a tissue grade of organization, to determine the biodistribution of indium phosphide quantum dots revealed by x-ray microspectroscopy. The results are parallel with those achieved by treating animals with an equivalent dose of indium salts, confirming the preferred bonding type of In^{3+} ions in Hydra tissues [49].

Even at a moderately acidic pH, indium solution chemistry is often dominated by its strong hydrolysis.

When the alkalinity of the system increases, indium hydroxide precipitates due to its extremely low solubility. This explains the low concentrations of free indium in the environment. Given the relevant role of speciation in the ecotoxicological effects of a certain total amount of indium, it is crucial to develop proper techniques to determine free concentrations of indium. The electroanalytical technique AGNES has already proved useful for such a goal. A new strategy has been developed, based on the technique of ADLC (Accumulation under Diffusion Limited Conditions), to determine lability degrees, which apart from their intrinsic physicochemical interest, by comparing reaction kinetics with diffusion rates it provides useful guidelines for AGNES deposition times [50, 51].

In the study on the short-term biouptake of indium (In), a trivalent metal that is a byproduct of zinc extraction and is used in numerous applications, including the semiconductor industry, was evaluated under controlled conditions. The short-term (i.e., 60 min) biouptake of indium by *Chlamydomonas reinhardtii* was measured as a function of pH in order to verify the validity of the BLM (biotic ligand model). It has been shown that pH will play a critical role in the bioavailability measurements of the trivalent cations in natural water [52].

The nature of the indium(III) chloride complexes present in the organic and aqueous phase during the solvent extraction of indium(III) are described in the work of Deferm et al. [53]. It turns out that indium(III) is present in the ionic liquid phase as the tetrahedral $[InCl_4]^-$ complex. The rising demand for III/V-based products is leading to the increasing generation of effluents containing ionic species of gallium, indium, and arsenic. The research was conducted on gallium arsenide (GaAs), indium gallium arsenide (InGaAs), and other III/V materials which are used in microelectronic components. It has been shown that As(III), As(V), and In(III) caused PMR (photomotor response) hypoactivity (49-69% of control PMR) at 900-1000 μM, and As(V) exposure was associated with significant mortality at 63 μM [54].

Speciation of Tellurium

In the tellurium speciation, as in the case of other ultra-trace elements, combined techniques are dominant. One such technique is headspace single-drop microextraction combined with graphite furnace atomic absorption spectrometry, based on combining headspace single-drop microextraction for Te(IV) and total Te, i.e., Te(IV) + CdTe QDs determination [55] $NaBH_4$ is not able to generate H_2Te from CdTe QDs, so the hydride generation technique can be efficiently applied when combined with single-drop microextraction (HS-SDME) and graphite furnace atomic absorption spectrometry (GFAAS) for Te speciation. The oxidative degradation of CdTe QDs, presumably caused by the triiodide ion, opens the door to hydridation of samples containing both Te species.

Another technique used in tellurium speciation is dispersive liquid-liquid microextraction combined with electrothermal atomic absorption spectrometry (DLLME) [56]. This speciation is based on the selective complex formation of APDC (ammonium pyrrolidine dithiocarbamate) as a chelating agent with Te(VI). After the complexation of Te(VI) with ADPC, it is extracted using the DLLME technique and measured using palladium-modified graphite tube atomizer atomic absorption spectroscopy. The concentration of Te(IV) is calculated as the difference between the total tellurium and Te(VI) concentrations.

Other authors also used APDC as a complexing agent in tellurium speciation by solid-phase extraction and the inductively coupled plasma mass spectrometry technique. A method was developed on the basis of the selective retention of the Te(IV)-APDC complex on the C18 SPE cartridge for the determination of the total inorganic and Te(VI) in the aqueous phase of the sample by ICP-MS [57]. Tellurium is considered toxic and teratogenic and there are indications that tellurite, Te(IV), would be more toxic than tellurate [58]. For this reason, techniques for the direct determination of both tellurium forms are used. One such technique is ion chromatography-hydride generation-atomic fluorescence spectrometry speciation (LC-HG-AFS) [59]. Anion-exchange chromatography with complexing agents in the mobile phase, ethylenediaminetetraacetic acid (EDTA) and potassium hydrogen phthalate (KHP), were used for the separation of Te(VI) and Te(IV). Using this method, the content of both the forms of tellurium was determined simultaneously in drinking water and sewage samples, with a low detection limit (LOD of Te(VI) = 0.69 μg/L, LOD of Te(IV) = 0.76 μg/L). In the literature we can find many examples of tellurium speciation where atomic absorption spectrometry (AAS) or atomic fluorescence spectroscopy (AFS) are most often used to detect one form of tellurium and the total content of this element [60-64].

It is difficult to detect tellurium with ICP-MS because of the poor sensitivity of tellerium due to the high ionization energy and the fact that it has many isotopes, nearly all interfered by isobaric Xe. Fortunately, accurate results can be obtained in the majority of matrices using both the ^{125}Te and ^{126}Te isotopes. Thanks to this, it is possible to combine analytical techniques in tellurium speciation studies using ICP-MS, so as to use the excellent sensitivity of this technique to detect multi-trace amounts of tellurium [65-69]. Sophisticated, hyphenated analytical techniques enable the determination of extremely small amounts of tellurium species. In seawater Te(VI) prevails quantitatively, and the concentration of Te(VI) and Te(IV) in drinking water is almost at the limit of detection, 3 ng/L [70]. There are very few publications on the speciation of tellurium in soils, and in the available literature on the tellurium speciation in soils many authors have only

studied the total content of tellurium in soils, or one of the ionic forms. Te in the soil-water system was mainly found in the IV and 0 oxidation states [70]. Tellurium was found in strong association with Fe(III) hydroxide particles, with the Te(IV) and Te(VI) species forming inner-sphere complexes [71].

Like other members of group 16 of the periodic table, tellurium can form organic compounds, which could exhibit post-accident dispersion that is different to that for inorganic tellurium species. In the Fokushima Dai-ichi nuclear power plant, the main volatile tellurium species were organic tellurides (e.g., dimethyl telluride, diethyl telluride), which could be produced by radiolytic or biochemical routes and have reasonable stability under environmental conditions. Organic tellurides have been observed in nature, particularly in anaerobic environments, but their formation is not favored in aerobic environments such as a reactor containment or the atmospheric environment.

Germanium Speciation

The most important germanium forms in aqueous solutions are germanic acid (H_4GeO_4) and its dissociation products $GeO(OH)_3$ and $GeO_2(OH)_2$, and Ge-fluoride complexes at high fluoride concentrations. In addition to its elemental form, Ge occurs in the oxidation states +II and +IV. Monomethylgermanium (MMGe) and dimethylgermanium (DMGe) have been found in natural water [72]. Trimethylgermanium (TMGe) has been shown to be stable for about 6 months when stored at 4^0C, but it was not found in natural water [73].

Ge species may be separated by liquid chromatography, often with the addition of chelating agents for complexation. Inorganic Ge forms stable chelate complexes with aliphatic alcohols, acids, phenolic moieties, and carboxylates [74]. These properties were used in the work on germanium speciation using liquid chromatography inductively coupled plasma triple quadrupole mass spectrometry (HPLC-ICP-QqQ-MS) [75]. The authors optimized the method for the chromatographic separation and determination of $Ge(OH)_4$, MMGe, and DMGe from leaches. The addition of 80 mM tartarate resulted in a baseline separation of DMGe, MMGe, and $Ge(OH)_4$ using an anion exchange column. In the determination of germanium and its species, special attention should be paid to any interference occurring during its determination. In ICP-MS techniques the application of a dynamic reaction cell (DRC) allows for the elimination of mass spectral interference [76].

The redox potential of natural environments is too high, so divalent species rarely occur [72]. Ge(IV) is very stable and therefore it typically occurs in the environment. Divalent compounds of germanium are mainly produced synthetically and are only important in the chemical industries. Inorganic compounds and complexes of germanium and organometallic compounds are of biogeochemical and environmental relevance, which in fact are almost exclusively the methylated germanium species. It was found that Ge(IV) displays a nutrient-like behavior in estuaries and surface waters, similar to silicon [73]. The total Ge content is a primary measurement index for evaluating the hydrochemical behavior and environmental hazard of germanium. However, along with the development of chemical analytics and the possibility of detecting elements at very low levels, the purpose of many scientific studies is to determine not only the content of elements, but elements in different states of oxidation (species).

For several years organogermanium-containing medicine has been used in special treatments for cancer and AIDS. The active substances contain germanium as beta-carboxyethylgermanium sesquioxide ($(GeCH_2CH_2COOH)_2$/"Ge-132"), spirogermanium, germanium-lactate-citrate, or an unspecified form. Hyphenated techniques are useful for analyzing different germanium forms [74-76]. Presently, little is known about the geochemical behavior and speciation of Ge in soils [77]. The speciation of Ge in soil solution and therefore its mobility in soils may strongly depend on the pH.

Conclusions

The one certainty about TCEs is that their release will increase; the global demand for REE, for example, is expected to grow by hundreds of percent in the next 20 years. It is also clear that these elements will be released to the environment not as pure materials but rather as a mixture with many other substances [78]. Therefore, it is necessary to fully characterize the source of this emission, i.e, e-waste plants, especially the WEEE (Waste of Electrical and Electronic Equipment) and the dust that arise during its recycling. This type of information on the pollution emitted to the environment by e-waste plants is still not well recognized.

The environmental implications and adverse effects on living organisms due to contamination by elements in the LSTCE group are still not well documented, and there are still a gaps in our knowledge and understanding of their cycles, environmental levels, and (eco)toxicological effects.

This is due to the ultra-trace concentrations of LSTCEs, making it extremely difficult and time-consuming to determine them analytically, especially in the analysis of element species. This situation is changing since most of these trace elements are now key components in the development of new technology. In addition, the development of analytical techniques significantly increases the interest of researchers in these elements and species. In particular, there is still little information in the literature on the speciation of niobium and tantalum.

Wastes containing technology-critical elements (germanium, niobium, tantalum, indium, gallium, thallium, and tellurium) can cause serious environmental problems if they are not treated properly. LSTCEs are scarce in nature but solid wastes contain considerable quantities of these elements. Therefore, investigating the LSTCEs distribution, material flow, supply situation and recycling technologies of scattered metals is of great significance from both economical and environmental perspectives [79].

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Conflict of Interest

The authors declare no conflict of interest.

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