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Sample Pretreatment for Trace Speciation Analysis

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1 Introduction

Speciation analysis is already a challenge, and speciation analysis at trace levels is even more difficult [1]. The analytes might be of anthropogenic origin [2] (usually the concentrations are slightly increased) or naturally occurring (geochemical background) [3]. Procedures applied for speciation analysis must ensure low limits of detection as well as high selectivity, especially when the concentration of other sample compounds, potentially interfering, is much higher than the concentration of the analyte. Very often, there is no other choice but to use separation and/or preconcentration techniques. Methods applied for speciation studies should ensure isolation of the analyte from sample matrix without any changes of the original speciation and with highest possible efficiency [4–8]. The lower is the concentration of the analyte, the higher is the uncertainty of the results, because some additional steps have to be included in the analytical procedure. Deep interference in sample composition results in changes of the oxidation states and chemical compounds formed by the element of interest [9]. In case of water, soil or tissues the risk of changes in chemical speciation is created even by the sampling, not to mention chemical modifications or sample storage. Most published studies regarding speciation analysis were focused mainly on methods of separation and detection of the analytes. Determination is usually done using elemental detectors (inductively coupled plasma mass spectrometry [ICP-MS], ICP optical emission spectrometry [OES], graphite furnace atomic absorption spectroscopy [GF-AAS]) or molecular detectors (electrospray ionization [ESI] or time of flight [TOF] coupled with mass spectrometry [MS]) directly after separation on chromatographic column, or indirectly after separation using, for example, solid phase extraction (SPE).

Considering how fragile are the equilibria between speciation forms, the best solution would be to determine speciation directly in the analyzed object, using techniques that can differentiate between oxidation states. In general, only a few techniques allow performing nondestructive speciation analysis of solids or water samples. For water samples, the direct voltammetry technique could be applied [10] but the limit of quantification (LOQ) is too high for trace element speciation. Voltammetric methods can be proposed for (indirect) speciation analysis of As, Tl, and Se. In water samples containing As(III) and As(V) it is possible to perform speciation analysis based on cathodic stripping voltammetry (CSV) measurements. By varying the composition of the supporting electrolyte it is possible to differentiate between As(III) and As(V). Addition of mannitol into the supporting electrolyte leads to detection of only trivalent arsenic, and then As(III) is transferred to As(V) during ultraviolet (UV) oxidation of organic matter and the total As is determined [11]. Thallium speciation can be studied when glassy carbon working electrode is modified with an ion exchange resin, which allows to selectively accumulate trivalent thallium as a chloride complex. This method was applied to determine Tl speciation in water samples modified by an addition of large amounts of chlorides [12]. Another possibility is modification of the supporting electrolyte: addition of diethylenetriaminepentaacetic acid (DTPA) to inactivate Tl(III) (electrochemically) and addition (directly to the voltammetric cell) of anion exchange resin to adsorb the organic matter. In this case, only monovalent thallium is accumulated [13, 14]. Determination of Se(IV) and selenocysteine was done simultaneously in the aqueous phase using HCl as an electrolyte, while determination of dimethyldiselenide was performed in the organic phase after extraction with CH_2Cl_2. Detection was done with differential pulse CSV at a hanging mercury drop electrode [15]. Also chromium speciation in water can be determined indirectly after the addition of an anion exchange resin and a chelating agent to the cell. Then, only Cr(VI) is electroactive in the supporting electrolyte [16, 17].

For solid samples, all methods of speciation analysis, which do not require sample pretreatment, are based on the use of X-rays: Mössbauer spectroscopy, X-ray photoelectron spectroscopy, and X-ray absorption near-edge structure (XANES) spectroscopy [18–21]. Unfortunately, all of them have LOQ too high for the analysis of biotic environmental samples, especially on trace levels. However, XANES was successfully applied for speciation analysis of thallium in polluted soil, and allowed to determine the kind of minerals binding Tl(I) and Tl(III)

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on different soil layers [20]. In case of plant material, it was found that the dominant form of thallium in leaves of hyperaccumulating *Iberis intermedia* was Tl(I) [19]. An interesting overview on the use of X-ray absorption spectroscopy (XAS) for biological, agricultural, and environmental investigations was published [22]. XAS has been employed for studying of the phytoremediation of heavy metals from polluted soils [23]. The microscopic XANES (μ-XANES) spectroscopy and confocal microscopic X-ray fluorescence analysis were used for the in vivo determination of the distribution of total selenium and for the local speciation of selenium in roots and leaves of onion [24]. The spectroscopic methods, which are nondestructive and offer minor-level sensitivity as well as microscopic lateral resolution [23, 25, 26], can be used in speciation analysis as supporting methods. The results are often an indirect evidence in discussion about speciation of trace elements.

However, even the results obtained with the most reliable methods and procedures mean nothing if the sample does not represent the investigated object or the speciation has changed during the sampling step. Any chemical (pH, oxygenation, UV exposition) or physical changes (drying, fragmentation) has an influence on the speciation. For this reason all steps of analytical procedures (sampling, transport, storage, conservation), especially in case of procedures meant for trace speciation analysis, have to be very carefully studied for potential changes they may cause in sample's properties (Figure Figure 1).

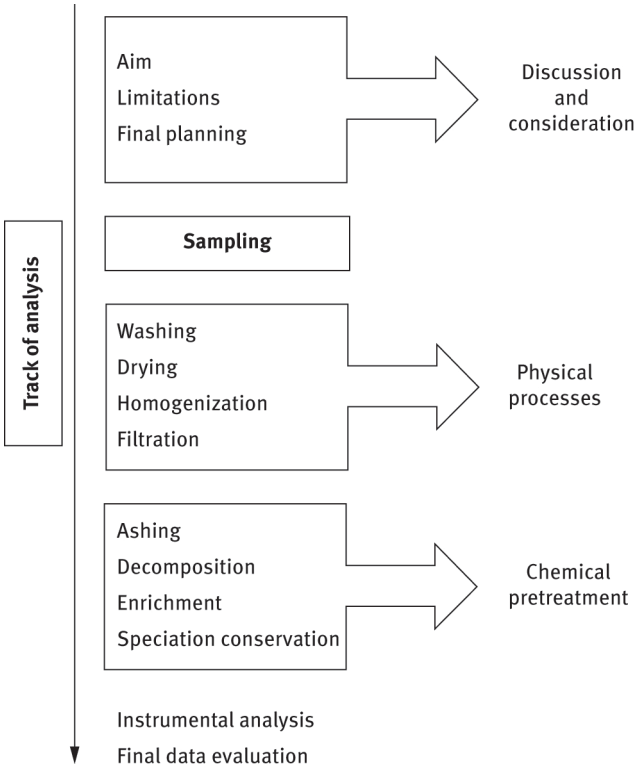

Figure 1 Simplified flowchart of environmental sample analysis.

The importance of sample pretreatment can be illustrated on the example of arsenic and its derivatives, where over 50 were identified in biological samples. In regions where significant amounts of organic compounds of As can be expected, groundwater (a deep intake) [2, 27–29] greatly differs in composition from groundwater sampled from soil level [30]. Arsenic comes in a variety of oxidation states and chemical compounds, and the content of organic compounds also differs [2, 3, 31, 32]. It is hard to imagine that there could be one method of sampling and sample conservation that meets all the needs of such challenging analysis.

It seems impossible that the speciation does not change during these critical stages of every trace analysis, but we have to strive for perfection and create procedures that would prevent the changes as much as possible.

2 Sampling and sample transport

Sampling of biotic or abiotic elements of the ecosystem is similar for both speciation analysis and the analysis of total content. Standard procedures of sampling are usually appropriate; however, in case of speciation analysis the conservation of the sample should be omitted and the time of transportation limited to a minimum. The unquestionable necessity of the sample to be representative is underlined by all scientists dealing with speciation analysis of traces. For the analysis of chemical speciation, physical speciation, or fractionation studies, it is

important to clearly define the aim of the analysis, that is, fraction/phase (e.g, suspension or dissolved fraction in water analysis) and the analyte of interest (e.g., organic or inorganic Hg compounds). This would enable to choose appropriate techniques and methods of sampling and transport, which would guarantee that the physical and chemical properties of the sample are representative for the whole studied object. It is important that there is no contamination or any losses of the analyte and that the fragile equilibrium between various species of the analyte stays intact.

In comparison to the total content analysis, in case of speciation analysis it is even more difficult to assure the immutability of the sample during sampling (e.g., exposition to sunlight of groundwater samples – limitation of photocatalyzed reactions) and transport (e.g., self-reduction of Tl(III) or self-oxidation of Cr(III) – high kinetic effects).

2.1 Selection of vessels

All vessels and tools should be made of materials that do not adsorb the studied species. For the speciation analysis of metals recommended are vessels made of polyethylene (PE) or polypropylene (PP). Glass should be avoided because of the risk of adsorption [33, 34]. The United States Environmental Protection Agency (US EPA) allows the use of plastic or glass bottles but plastic is preferred for drinking water sampling (US EPA). In the case of total mercury content or methylmercury compounds (MeHg) determination the collected water samples should be stored in glass bottles [36] or in fluorocarbon polymers and fluoropolymers such as Teflon®, Kynar®, and Tefzel® [37]. In general, mercury is widely considered to be a difficult element to determine, mainly because of its volatility, memory effects, and extraction problems [38, 39]. Also the stainless steel components in the liquid chromatograph system led to adsorption of the mercury compounds, which was more pronounced with $HgCl_2$ than methylmercury [40]. Mercury (II) is quickly lost from all containers except those made of aluminum, which rapidly convert mercury (II) to metallic mercury, which is stable [41]. Similarly to Hg compounds, organic compounds should not be collected nor stored in plastic containers [42], but glass bottles are required (US EPA). In case of both total and speciation analysis, stainless steel devices can cause contamination of the sample with traces of Fe, Ni, Cr, and Mn. Introduction of these elements, when none of them is the analyte, may cause species transformation of other analytes (indirect influence on equilibrium between species of the studied element) [44, 45].

2.2 Contamination of the sample with various substances

Uncontrolled introduction of inorganic ions or organic compounds may change not only the total content of the analyte but it can also affect the speciation. Contamination with the analyte can be easily revealed by the analysis of blank samples. However, when the sample gets contaminated with an unexpected substance like weak reducing (e.g., ascorbic acid) or oxidizing agent (e.g., H_2O_2), the oxidation state of many compounds will change (disturbance of the redox equilibria between Fe(III)/Fe(II), Mn(IV)/Mn(II), Tl(III)/Tl(I)) [46]. Not only the changes of the oxidation state of the studied species are problematic but also the increased solubility of compounds binding the analyte, such as MnO_2 and $Fe(OH)_3$ [47, 48], or decrease of Cr solubility [49]. Also the addition of one of the species perturbs the initial speciation. Even trace amounts of reducing agents will completely reduce the trivalent thallium species [13], and the addition of oxidizing agents will change the speciation of Cr and As. Even small amounts of oxidizing agents at pH 6 shift the equilibrium in favor of arsenate (V) [49]. The presence of sulfur compounds (both elemental S and sulfides) at temperature above 22°C promotes the reduction of Cr(VI) to Cr(III) [50]. Usually, the laboratory vessels are conditioned by washing in acidic solution (pH 1). If the acid is not properly washed out, the sample will be unintentionally acidified, and the pH changes influence directly or indirectly the equilibria between all speciation forms [32, 51]. Sometimes the influence of contaminants is unpredictable. For example, methylation of mercury (II) occurs in the presence of trimethyl lead but the process is inhibited by humic substances [52]. The presence of Fe(III) ions affects thallium speciation – oxidation of Tl(I)(aq) took place when natural water samples were exposed to either sunlight or UV light, notably at low pH [53]. Therefore, any uncontrolled substance introduction or loss should be avoided.

2.3 Elimination of UV-Vis irradiation

In practice, limited exposure to sunlight (UV-Vis radiation) is preferred for each environmental sample. UV light (wavelength 100–400 nm) is involved in the degradation of chemical bonds in large organic compounds, and it may cause reduction or oxidation of the analyte [54]. The United States Geological Survey (USGS) suggests

in most of the water sampling procedures to keep the sample in dark [37]. Thallium speciation study is a good example of how UV-Vis light affects the speciation. For thallium it was showed that oxidation of Tl(I) in an aqueous solution can take place when the sample is exposed to sunlight irradiation [55]. Ultraviolet irradiation of aqueous solutions containing Tl(III) and being in equilibrium with the atmosphere increases the reduction rate of Tl(III). In systems where photoreduction of Fe(III)(aq) takes place, a quantitative oxidation of Tl(I)(aq) was observed, notably at low pH. The process is reversible, as indicated by the formation of Tl(I) when the irradiated systems were kept in the dark [53]. Also high instability of Tl(III) in the presence of plant matrix is observed under UV exposition. For example, plant extract with an addition of Tl(III)DTPA standard was exposed to UV for 1 h. It was observed that 95% of Tl(III) added as Tl(III)DTPA was reduced to Tl(I) [14]. The data indicated that Tl(III) extracted as Tl(III)DTPA from plant tissue is not stable under UV irradiation. Therefore, plant extracts should be stored in dark till analysis. Similar study about the stability of Se(IV) extracted from plant tissue showed that it is most likely that Se(IV) is reduced to Se(0) or that an insoluble complex is formed [5]. Most data seem to indicate that darkness is necessary for preservation of mercury species during storage in biological matrices. Methylmercury and inorganic mercury in fish extract solutions were stable for 5 months at 4°C when stored in the dark [56]. The stability of butyltin species in lyophilized mussel samples was also affected by the light. Significant variations were found in the butyltin content after 3 and 6 months of storage at room temperature in daylight and in the dark, respectively [1].

2.4 Oxidation and desorption of carbon dioxide

Deep-sea water samples naturally contain small quantities of oxygen. Contact with air results in rapid dissolution of oxygen in the sample, and the effect is especially intense when the sample is shaken (during transport). The USGS suggests in most of the water sampling procedures to keep the sample without any contact with oxygen, to prevent metal-oxide precipitation [37]. In general, the zone of interest must be isolated, the sample pumped slowly to minimize turbidity, and collected in such conditions that eliminate O_2 and CO_2 exchange with the atmosphere [35, 37]. The redox equilibria are then shifted to oxidizing range, which affects the speciation of free ions within a matrix of a water sample, which is a noticeable effect in samples from reservoirs with low oxygenation of water. Consequently, oxidization of sulfides to sulfates and Fe(II) to Fe(III) will occur, and then precipitation of iron hydroxide with traces of Co, Ni, As, and Pb. Changing of pH and hardness (temporary hardness) of the water sample due to absorption of CO_2 from the air accelerates and increases the precipitation of calcium carbonate minerals [57, 58]. Also the oxidation of Mn(II) by oxygen dissolved in water brings some consequences for chromium speciation. MnO_2 particles, formed as a result of the process of oxidation of Mn(II) to Mn(IV) in dissolved fraction, accelerate the oxidation of Cr(III) to Cr(VI). The product of this reaction – Cr(VI) – is adsorbed on suspended particle matter (SPM) and therefore both physical and chemical speciation is changed in the water sample [59]. But unlike Cr, As speciation was not changed by oxygenating of the sample. After air exposure of wine and beer samples, arsenite, arsenate, monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA) were stable at 4°C for months, probably due to the acidic pH of the samples [60]. In contrast, storage of the samples for antimony determinations is very difficult, because Sb(III) easily transforms into Sb(V) in the oxidizing environment [61].

2.5 Solid sample for fractionation study

A special case of speciation analysis is fractionation, where the fractions are defined according to the physical properties of the solid samples such as soils [62, 63], sediments [64, 65], or solid wastes [66, 67]. Methods of sampling are the same as those used in the analysis of the total content [37, 68–70]. In the case of soil, the top layer (rhizosphere) is discarded, together with large objects such as stones, roots, or zoological specimens. Then, the top layer (0–10 cm) [71–74] or the bottom layer (10–30 cm) [71–73] is taken for the analysis. The samples are transported with natural water content in a cardboard box granting access to the air. The alluvial deposits depending on the size of river's backwaters are collected from various depths, usually 15–20 cm. The oxygenated layer is analyzed separately and it is taken from 1 to 3 cm depth [75]. The samples are then dried in the laboratory. Despite the fact that the process of drying affects the mobility of various metals [76, 77], fractionation studies (distribution evaluation) are rarely carried out on wet samples.

2.6 Temperature lowering just after sampling

The lowering of samples' temperature just after sampling and during transport is one of the most widely and longest used methods. The literature data about sample pretreatment indicate that freezing could decrease the

efficiency of extraction of the analytes from plant tissues [4, 78–80]. In the case of Tl speciation study in leaves of hyperaccumulating plant, the storage at −18°C for over one month lead to total reduction of Tl(III) [81]. The content of arsenobetaine in blue mussels was significantly reduced during storage of frozen material. The content of tetramethylarsonium in fishes as well as in seafood was generally lower after deep freezing and some days of storage [82]. Groundwater, which has naturally low temperature, after collection requires transport in cold state, especially if it was not possible to filtrate the samples and separate the SPM from the dissolved fraction. It is not recommended to freeze the water prior to analysis [35]. The increase of sample temperature causes absorption of carbon dioxide, which affects the pH. Also for biological samples lowering of the temperature (4°C), usually in combination with storage in complete darkness, may well reduce the activity of microorganisms and enzymes. Cooling limits the speed of these processes, but it does not eliminate them completely [83]. Samples of seafood were stored up to 9 months till analysis, and the arsenic organocompounds were not degraded [84]. Sometimes freezing (−17°C or −20°C) is recommended, or even rapid cooling in liquid nitrogen followed by lyophilization. However, this procedure is not suggested if the purpose of the analysis is determination of phytochelatins (PCs) in plant tissues, because these compounds are then degraded to peptides [1]. The analysis of PCs or their complexes is carried out using fresh material, as PCs are known to be unstable during sample preparation [85]. If the analysis cannot be done immediately after the extraction of PCs, derivatization has to be done (precolumn derivatization with monobromobimane), which prevents the process of PC degradation [86]. Only samples containing derivatized PCs can be kept refrigerated for a long time [85]. This limits the amount of information obtained, but the procedure is very useful as there is not always a possibility of carrying direct analysis using MS methods [87–91]. Lowering of the temperature is also suggested for physical fractionation of soil, within the SPM and the solid phase of water, but only when the separation of SPM or the specific soil pretreatment (to reduce putrefaction) cannot be performed on the sampling site. In the case of wastewater containing large amount of S(II) compounds, Cr(VI) was reduced to Cr(III) if the sample was not cooled down to 20°C [50].

A very particular case is transport of the samples at the boiling point of liquid nitrogen (−150°C). After sampling the sample is inserted into a labeled container and into thermos with liquid nitrogen. Most of the steps of sample preparation should also be carried out at this temperature, for example, cryomilling, lyophilization, and long-term storage. In such conditions, the samples collected by German Environmental Bank (UPB – Umwelt Proben Bank des Bundes) for long-term storage (over 50 years) are transported to laboratories [71, 72, 92–97].

3 Sampling with some pretreatment on sampling site

Both solid and liquid samples should be prepared directly after sampling, and this is often done immediately on the sampling site. However, keep in mind that both chemical and physical interventions in a sample have a smaller or greater impact on the equilibrium that we want to study.

The reaction of the analyte with stabilizing agents should be quick [98–100]. Currently, there are proposed some interesting solutions for sample modification (an addition of specific sorbent) which enables indirect speciation study. It can be achieved by an addition of the substance which is permanently binding one form of the analyte. In the case of chromium, the addition of multiwalled carbon nanotubes with coprecipitated MnO_2 selectively removed the trivalent Cr ions from water sample at pH 5 [44]. The addition of chitosan grafted with 2-hydroxyethyltrimethyl ammonium chloride stabilized the speciation, and the adsorption of Cr(VI) is favorable; therefore, only Cr(III) can be detected [101]. To preserve the samples, the researchers often use chelating reagents, such as ethylenediaminetetraacetic acid (EDTA) or DTPA. The authors do not agree on the stability and permanence of arsenic forms in water, especially at different pH and in the presence of other substances [102]. Generally, in river water As(V) is partially converted to As(III), but after 2 days this is followed by gradual oxidation of As(III) into As(V) to reach an equilibrium. Storage at 5°C delays this oxidation by about 6 days [103]. In the case of thallium, DTPA was used for stabilization of Tl(III). To prevent self-reduction of trivalent forms of thallium in water samples and in plant extracts the addition of DTPA was used [13, 104, 105]. Stabilization with DTPA was also applied in antimony speciation analysis [61]. If the object of study is arsenic speciation, the addition of EDTA must be done immediately after sample filtration on the sampling site [37].

3.1 Suspended matter separation – fractionation in water

SPM is an integral part of the hydrosphere. SPM is an important component of the water, and it is responsible for the transport of elements and substances in water currents [106]. SPM is composed of mainly inorganic colloidal particles in the form of oxides, hydroxides, metal carbonates, and organic components. Therefore, a significant effect on the physicochemical properties of SPM has its origin as well as the shape and size of the

suspended particles [107]. Due to the fact that processes of coprecipitation, adsorption, and desorption, as well as ion exchange take place between the dissolved fraction (solution) and SPM fraction (suspended solid phase), it is impossible to store water samples even for a short time without changes in the speciation. The border between SPM and the solution phase is conventional, and it is widely accepted that SPM phase is defined as a fraction bigger than 0.45 μ m. This idea came to Nürberg et al. in 1988 [108]. In case of physical fractionation of water samples, that is, to determine the content of SPM, the sampling of the water sample does not differ from the sample for other purposes. Usually, a few hundred milliliters is taken but in exceptional cases even some liters (nano-level or radiation study) but no pretreatment is performed. It is forbidden to add commonly used nitric acid, as such addition will disturb the equilibrium between the two phases of water – suspended and dissolved phases. Such analysis requires filtration just after sampling, on the sampling site, before the sample is oxygenated, warmed up, and/or exposed to UV-Vis radiation. The filtration through a filter with a pore size of 0.45 μ m is performed [35, 109–114]. The filter retains the suspended phase (SPM).

Often the mass of SPM is quantified as a gram per milliliter of the water, and then the SPM is decomposed in order to determine the total content of the elements. Usually a large volume of the sample is filtered (100–300 mL), and clogging of the pores could be observed during the filtration [35], which is a phenomenon that affects the quality of the obtained results. While the sampling is done in regions with considerable dustiness, the initial separation of "dust fraction" is suggested. The "dust fraction" is defined physically as a fraction of particles bigger than 100–125 μ m. Next, the appropriate fraction bigger than 0.45 μm is separated in sequence. The "dust fraction" plays an important role in the distribution of the contaminants during the dry seasons, but not during the rainy seasons [115, 116]. This part, which is associated with large particles, will quickly sediment and thus it is not responsible for the transport of the pollutants. The SPM fraction can be transported and it spreads the pollutants in the environment. Study of the distribution of As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Tl, and Zn indicated that the dissolved fraction contains the highest amount of trace elements [115]. Trivalent chromium in water remains bound to organic matter (SPM component), which decreases its mobility, but the toxic Cr(VI) is highly soluble [117, 118]. In the case of mercury speciation analysis on low level, filtration directly on the sampling field is required to separate SPM, and it is strongly recommended by the USGS [37]. Often, the removal of SPM is a step of preparation of a water sample for the analysis of total content of the elements (it is assumed that the share of SPM in the total content is negligible) [110] or it is the first step of speciation analysis (e.g., determination of chemical speciation of Tl within the dissolved phase [105] – SPM was not analyzed). However, leaving SPM in a nonacidified water sample even for a short time results in binding of the free ions of Cr, Mn, and Cu with the organic compounds suspended in solution, followed by their fast precipitation [119] or to adsorption of the free ions of Pb, As, Ni, and Co on the sediment containing Mn and Fe oxides (coprecipitation), which is formed during storage [94].

3.2 Chemical modification of the sample

Acidification with nitric acid is commonly applied in the analysis of trace metals, but in the case of speciation analysis it is not advisable to lower the pH [51]. Sometimes, however, in specific cases such as determination of As(III), acidification is not only permitted, but even required [120, 121].

Storage of water (chemical speciation) and soil extracts (fractionation) without any pretreatment results in coprecipitating of ions of As, Ni, Co, Pb, and Tl with Mn(II) and Fe(III) oxides [47, 72]. Limitation of this phenomenon can be achieved only through a significant acidification of the solution (pH < 2) or the addition of complexing ions (e.g., EDTA), but after such a modification, the sample is not suited for broadly defined speciation analysis. Hydrochloric acid (non-oxidizing acid) is sometimes used because of complexing properties of chlorides. Complexation of free ions (+2 and +3) influences the chemical equilibrium, but such modification (addition of complexing ions) is recommended when Mn(II) and Fe(III) are regarded as interferents [45]. The addition of another complexing agent, DTPA, is indispensable to perform speciation analysis of Cr and Tl. The compounds of Tl(III) are unstable and without DTPA they are slowly reduced [13, 122]. For arsenic speciation study the addition of ascorbic acid is recommended [121]. However, it is inadmissible in the case of trace speciation analysis of Cr and Tl [13, 16], because the ions with the highest oxidation state would be totally reduced. Also, the addition of phenol, previously used to prevent microorganisms' activity, leads to slight changes in the selenium speciation [5]. Therefore, the most suitable preservation scheme for determination of As(III), As(V), Cr(III), Cr(VI), Se(IV), and Se(VI) in water samples was found to be refrigeration at 10°C with no preservative, followed by the analysis as soon as possible (preferably within 24 h) [123]. Also mercury speciation is highly dependent on the presence of ions, such as chlorides, high content of SPM and pH of the solution. Therefore, any modification of water samples leads to a change in chemical equilibrium [124, 125].

To avoid changes of the analyte species it is important to analyze the samples as soon as possible after their collection.

4 Short- and long-term storage

The analysis of samples immediately after their collection and transport to the laboratory is not always possible. Usually speciation analysis requires sophisticated methods of separation and detection. A possibility to prolong the time between sampling and chemical analysis would be an important advantage of any analytical procedure. For this reason the methodology of material storage was studied by many authors. Storage of biological samples is not recommended even for such short period as 2 weeks [126]. But in some cases, various species of arsenic in algae were stable up to 12 months in dried material [127]. In the case of Tl the instability of Tl(III) was found, both freezing and drying caused significant changes in thallium speciation [81]. Recent studies of As speciation indicated that plant material containing As species should be kept at a low temperature, while others claim that the freezing/defrosting processes lead to species conversion, and therefore the samples must be kept at room temperature [128, 129].

For long-term storage deep freezing is recommended. Plant samples were stored at −80°C and the concentration of arsenic-PC complexes remained relatively constant during 21 days [88]. Samples may also be stored at the boiling point of nitrogen (−150°C). In such conditions soil and sediment samples are stored, as well as other materials collected by German Environmental Bank (UPB) [71, 72, 75, 94]. Long-term storage without any pretreatment exposes the samples to microorganisms' activity. It is important to avoid bacterial growth in the sample as this may cause changes in the speciation. In the case of Hg, for example, some species of mercury (II) may be reduced to volatile elemental mercury [1].

Samples for speciation analysis should not be stored for a long period, independently on the concentration of the analyte. For example, trivalent arsenic compounds should not be stored for longer than 24 h if the sample is stored without modification [130]. For thallium speciation, both freezing and drying cause significant changes in the speciation, so plant samples should not be stored. The quantitative analysis can be performed only on fresh tissues [81].

The time of storage can be slightly extended if the analyte is separated from the sample matrix.

4.1 Dehydration of samples

Dehydration is sometimes necessary for solid samples. The so-called drying is intended to remove the solvent from environmental samples. The main aims of this operation are limitation of the microbial activity and achieving a constant mass, which is taken for the analysis (results are usually given as the content in dry mass). The soil should be either stored deep frozen or after dehydration. Losses of the analyte and its mobility are much lower when the soil is kept dry (air dry) [75]. The procedure is well known and accepted, and routinely used in the analysis of soil for total content and speciation [131–135]. Usually, the samples of soil, sediment, or solid waste are brought to the laboratory with natural water content, and then slowly dried at room temperature in open-air conditions for 24 h. If necessary, the samples are oven dried at 40–50°C or 105°C for 5–10 h [67, 112, 126, 134–140]. However, in fractionation study the extractability from such prepared samples is different from the original: lower for K, Cr, Mn, and Fe [77], and higher for Pb, Cu, Cd, Zn, and Ni [76]. Soil and sediment samples, according to the BCR-SMT (Bureau of Reference – now the Standards, Measurements and Testing Programme – SMT) scheme (the standard procedure called BCR procedure), are dried at room temperature or in the oven at 30–80°C. If higher temperature is required for drying, it should be performed in an inert gas atmosphere to limit the oxidation processes [141]. Many authors claim that low-temperature drying in ambient air and freeze-drying are the most "neutral" methods for samples of soil and sediments and that these methods do not considerably influence the distribution (mobility) of metals in soil phases [142].

Storage of animal and plant tissues with natural moisture content does not limit the microbial activity, and the microorganisms are actively involved in changing the speciation. In the case of arsenic, the intrinsic microbial population causes demethylation of organoarsenic compounds [143]. Therefore, drying is considered also in case of biological samples, but usually the temperature does not exceed 95–98°C and not longer than 16 h after sampling [122, 144, 145]. Delicate plants are dried at a temperature not higher than 35°C [146, 147]. Also some analytes require lowering of the temperature of the drying process. For the analysis of Se, drying should be slow (over 48 h) and run at no more than 45°C [146]. Drying and storage of plants even at room temperature cause significant changes in the speciation of thallium. In contrast to the extract of fresh material, there was no measurable amount of Tl(III) in any of the stored samples [81]. The situation is opposite in the case of As speciation analysis, where drying of the plants is recommended because plant moisture can cause species conversion [148]. Many authors claim that biological samples should be dehydrated using freeze-drying systems (lyophilization – sublimation of frozen water under conditions of low pressure and temperature). The process consists of freezing of the sample, usually in liquid nitrogen or dry ice in ethanol, and drying at a very low pressure (10 Pa) in a round-bottom flask made of borosilicate glass [126, 149]. Certainly, the material that was

frozen after sampling should be dried by lyophilization [42, 75]. The method of sample preparation has an influence on the extraction process. Lyophilization can decrease the extraction efficiency even by 20% [79, 80]. But in some cases (e.g., As speciation study in *Brachiaria brizantha*), the extraction was more efficient from sample aliquots that were lyophilized and ground (extractability: 87–90%) than from those only stored under different temperatures (extractability: 53–66%) [4]. Usually, after drying the environmental samples are stored at room temperature in closed containers made of PE or PP [140, 150, 151] or cooled down to 4°C [152, 153].

5 Extraction as a method of sample pretreatment for speciation analysis

Extraction techniques are commonly used and widely accepted methods for trace analysis. The phenomena occurring during the extraction process in liquid–liquid and solid–liquid systems are well known. This simple technique can be the basis for procedures of selective isolation of a specific chemical form of the analyte. Theoretically, separated species of the analyte can be stored without any pretreatment for a long time. An example of such methodology is leaching of some selenium compounds from soil during solid (sample)–liquid (extractant) extraction. Selective separation of Se(IV) and Se-Cys from $(CH_2)_2Se_2$ was achieved by leaching of selenium species with 0.5 mol/L HCl. Then, the solution was extracted with CH_2Cl_2. In the aqueous phase Se(IV) and Se-Cys were found, while dimethyldiselenide was present in the organic phase [15]. Extraction from plant tissues using water–methanol mixture is proposed for arsenic species (MMA, DMA, As(III), As(V) and arsenosugars) separation from sample matrix [74]. For metal-PC complexes (Me-PCs) determination of a "soft" extraction procedure is required. For example 1% formic acid is applied for As-PCs [85, 154], 3 mL cold (4°C) aqueous dithiothreitol for Pb-PCs [155] and 0.5% $NaBH_4$ in NaOH solution for Hg-PCs [156]. In the case of Tl speciation in plant tissues the extraction using DTPA in acetic buffer (pH 6.2) is the only way to prevent self-reduction of Tl(III). The chromatograms (liquid chromatography [LC]-ICP-MS) of extracts were recorded just after extraction, and after 4 months of storage (−18°C). In most cases, the results were consistent (revealed the presence of both Tl forms). In some cases, however, there occurred a significant decrease or increase in the content of Tl(III). Therefore, freezing of the extracts is an option only for semiquantitative analysis [81]. Additionally, high efficiency of the extraction is essential for trace analysis. This parameter can be accelerated using an extraction assisted with microwaves or ultrasounds, especially in the case of soil and sediment samples [157–159]. Acceleration of the extraction is also applied in leaching of xenobiotics from plant tissues [160]. Cell wall is a barrier for the extractant, and grinding of the plant tissues in the presence of liquid nitrogen noticeably increases the extraction efficiency [122]. It is very difficult to reach 100% recovery of the analyte from extractant. A small addition of surfactant such as sodium dodecyl sulfate (SDS) made to the extractant led to leaching of fractions containing not only water-soluble but also water-insoluble protein complexes [104, 161]. The comparison of data obtained for extraction with and without the addition of SDS reveals the fraction of the analyte (e.g., Pt, Tl) bound to insoluble protein complexes. The efficiency of thallium extraction from the above-ground plant organs using SDS was on the same level as in the case of water extracts (50%), which shows that thallium is not bound to hydrophobic proteins [104]. In the case of platinum, there were significant differences between fractions of Pt extracted from plant material with and without SDS. The efficiency of leaching with water was about 55% of total Pt but the leaching with SDS increased it up to 70% [162]. If it is important to distinguish between inorganic and organic arsenic species, the extraction should be done using an organic solvent, for example, methanol [163]. An extraction with hot water was used to leach Se from onion [164], but similar extraction of methyl arsenic acid (III) from tissues of marine animals is not recommended because this compound is not stable at high temperature [165]. In the case of marine organisms (algae and seafood), separation of arsenolipids was achieved by extraction with nonpolar solvents, and the extraction efficiency was about 50% [166]. Preceding of the proper extraction with degreasing using acetone effects in lowering of the extraction efficiency to 30% of the total content of arsenic [167].

An interesting example of simultaneous separation and conservation of the analyte (prevention against the self-reduction) is thallium speciation analysis in SPM separated from wastewater. Trivalent thallium was transferred from its original compounds into Tl(III)DTPA [116]. This complex is very stable, and its stability is practically independent of pH and the presence of other ions. Thus, leaching based on formation of Tl(III)DTPA complex was applied. But even in that case the self-reduction took place, and after 1 week of storage its rate reached 25% [116], while without storage it is usually not higher than 3% [13, 168]. Extraction with DTPA solution is a widely accepted method of isolation of Tl(III) from plant tissues. Usually the material is ground to a fine powder using a mortar and pestle in a liquid nitrogen bath, and extracted using DTPA solution in acetic buffer (pH 6.2) (plant material is shaken with the extractant for 1 h at 37°C). After leaching the suspensions are filtered through a 0.45 μm filter to separate solid particles [122, 168, 169], and plant extracts are immedi-

ately analyzed by chromatographic methods coupled with elemental detectors [104, 122] or by electrochemical methods (after some "soft" modification).

Voltammetric methods are very sensitive and they are characterized by low limits of detection [170]. Stripping voltammetry enables determination of As, Cr, Tl, Se, Sn, Pt, Rh, Pd, and Pb at the level of ppb [13, 17, 171, 172] or even ppt [173]. However, they require special preparation of the extract or mineralization of organic compounds (significant interferent), which are present in significant quantities in water samples and extracts of plant products. Of course, mineralization of the sample is not acceptable in speciation analysis. Conservation of the plant extract or wastewater using DTPA, and an addition of resin (Amberlite XAD-7) just before the step of ion preconcentration on the working electrode allowed to indirectly define the speciation of Tl and Cr (only not complexed forms of the analyte are electroactive) [14, 17, 172, 174]. Such modification does not affect the speciation. The results obtained by voltammetry were confirmed by comparison with the results of LC-ICP-MS study [14].

Relatively new trend is application of extraction as a method of sample pretreatment, especially for the analysis of organic compounds, known as QuEChERS. This technique of separation of the analytes from complicated sample matrix was developed based on Anastassiades et al.'s work [175]. The acronym means **Qu**ick, **E**asy, **Ch**eap, **E**ffective, **R**ugged, and **S**afe. This extraction technique is a combination of extraction of organic compounds, mostly from food matrices, coupled with removing of another organic compounds (interfering substances) and the excess of _water. It is an alternative to traditional liquid–liquid extraction and SPE [176]. The methodology is suggested by AOAC International for the analysis of pesticides [177].

5.1 SPE – water analysis

In the analysis of water the major problem is low concentration of the analyte. SPE technique offers an interesting possibility of separation and considerable preconcentration of the analytes [178]. Combination of filtration through a 0.45 μm filter, and next preconcentration of pesticides on SPE column additionally allowed long-term storage of the samples [179, 180]. The sample of seawater collected for speciation analysis of Tl cannot be stored for a long time, as self-reduction of Tl(III) is observed even in the presence of DTPA. But after SPE separation, trivalent thallium as Tl(III)DDTC is selectively retained on the sorbent, and monovalent thallium is in the effluent. Such a way Tl species are collected separately and they can be stored without any problems till analysis [122]. Also Cr(III) was separated from Cr(VI) and preconcentrated using a column containing chelating resin. This method was successfully applied for speciation analysis of chromium in tap water, lake water, spring water, and wastewater samples [51]. Another SPE method was developed for on-site separation of inorganic arsenic from As-rich groundwater and applied for the study of arsenic removal from ferrihydrite in the absence of oxygen [181].

5.2 Extraction in fractionation study

A specific example of speciation analysis is fractionation, where the fraction is defined operationally by applying chemical and/or physical modifications to the sample. It is intended to indicate what fraction of the total content of the analyte is bound to particular phases of the soil (extraction under certain conditions). Fractionation is used as a source of information about xenobiotics' mobility and bioavailability, and for potential risk assessment. Several extraction procedures are used [182]. The most popular are the Tessier's procedure [183], and the BCR procedure [184] (Table Table 1). Nowadays, commonly used are single extractions with acetic acid or EDTA solutions, and three-step sequential extraction (in sequence: acetic acid, hydroxylamine hydrochloride, hydrogen peroxide solutions) developed by the former European Community Bureau of Reference (BCR), now going by the name of Standard Measurements and Testing Programme of the European Committee (SMT or BCR-SMT) [185, 186]. For fractionation study, dried materials are sieved through a 1 mm [67, 112] or 2 mm [135, 139] sieve or milled and sieved. Usually in sediment analysis the fraction smaller than 63 μm is taken [126, 134, 187] (after milling). Some solid samples as dust and flotation tailings are not ground, only the fraction smaller than 125 μm is used [188]. Dried material can be stored in darkness at ambient temperature until analysis for some months.

Table 1 Comparison of two sequential extractions applied for fractionation study in solid samples – BCR (BCR-SMT) and Tessier schemes.

	Tessier scheme **1 g of solid sample**

Ion exchange and carbonate fraction	Ion exchange fraction
	0.5 h at room temperature
	Continuous mixing
16 h at 22 ± 5°C	8 mL 0.1 M $MgCl_2$ pH 7(twice)
Continuous mixing	
40 mL 0.11 M CH_3COOH pH 4	
	Carbonate fraction
	5 h continuous mixing
	8 mL 1 M CH_3COONa pH 5
Oxide fraction	Iron and manganese oxide fraction
16 h at 22 ± 5°C	5 h at 96 ± 3°C
Continuous mixing	20 mL 0.04 M $NH_2OH\{\cdot\}HCl$ in 25% CH_3COOH pH 2
40 mL 0.1 M $NH_2OH{\cdot}HCl$ pH 2	
Organic fraction	Organic fraction
Substep (1) 2 h water bath 85 ± 2°C	Substep (1) 2 h water bath at 85 ± 2°C
10 mL 8.8 M H_2O_2 (twice)	3 mL 0.02 M HNO_3 + 5 mL 30% H_2O_2 pH 2
pH 2 or pH 3	
Substep (2) 16 h 22 ± 5°C	Substep (2) 3 h water bath at 85 ± 2°C
Continuous mixing	3 mL 30% H_2O_2
50 mL 1 M CH_3COONH_4 pH 2	
	Substep (3) after cooling 0.5 h
	Continuous mixing
	5 mL 3.2 M NH_4OAc in 20% HNO_3
Residual fraction	Residual fraction
Mineralization with mixtures of conc. acids (HF, HNO_3, $HClO_4$)	Mineralization with mixtures of conc. acids HCl + HNO_3 (1:3)

Note: M, mol/L.

German Environmental Bank (UPB) stores the samples of soil in liquid nitrogen and then the material is cryogenically ground, sieved, and dried using lyophilization. Only a portion of the material is analyzed for the purpose of long-term monitoring [71, 94].

6 Conclusion

There are not many reference materials available, for which sampling and pretreatment of samples for speciation analysis is proposed. Only Cr(III) and Cr(VI) in water and soil samples, as well as volatile Hg and MeHg in water, fish tissues, and soil were studied in the context of routine analysis. In case of other objects it is beneficial to become familiar with guidelines for the analysis of specific groups of analytes for their total content. Recommendations are published by institutions such as US EPA, Joint Research Centre Institute for Reference Materials and Measurements, and USGS[69, 189, 190], together with standard operating procedures for the collection of representative surface water samples from streams, rivers, lakes, ponds, lagoons, and surface impoundments [191]. There are no details regarding speciation analysis, because it is done in routine only for chromium and mercury. In case of other elements one has to choose the procedure of sample pretreatment according to their own best knowledge. Certified materials are not meant for validation of sampling and sample pretreatment before the analysis. Therefore, high experience of the analyst is of crucial importance, together with his awareness of possible mistakes. Adapting methods already published in the literature could prevent us from "reinventing the wheel." However, all of the procedures should be carefully checked, as sampling, sample transport, and conservation of the speciation are really difficult tasks.

Therefore, each sample and each analytic target are always a new challenge.

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