

# Chapter 7

## Electroanalysis and Chemical Speciation

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### 7.1 Basic Definitions and Terms

The greatest concern for speciation of the elements relates to their impact on biological systems depending on their physical and chemical form,<sup>1,2</sup> occurrence, behaviour, and actual circulation in the environment (see scheme in Fig. 7.1; and reference (3)), toxicological profile,<sup>4-7</sup> and bioactivity and bioavailability.<sup>5-7</sup>

In terms of the official terminology and IUPAC recommendation,<sup>8</sup> speciation analysis can be defined as a tool to find and identify the individual forms for a given element and to determine their concentration level in the sample, both with a goal to define the actual distribution of the respective species.

For instance, in the case of metal ions, speciation analysis classifies *three basic forms*:

1. Single/free ions of various valence, e.g.  $\text{Me}^{n+}$  and  $\text{Me}^{(n+1)}$
2. Hydrated/labile forms  $[\text{Me}^{\text{N}}(\text{H}_2\text{O})_m]^{n+}$ ,  $[\text{Me}^{\text{N}}(\text{OH})_2(\text{H}_2\text{O})_{m-2}]^{n+}$
3. Complex stable structures of either inorganic or organic origin, such as the anionic species  $[\text{Me}^{\text{N}}\text{L}_m]^{(m-n)-}$

The total content of the metal to be analysed is then given as a sum of the concentrations of all its forms found out in the sample.

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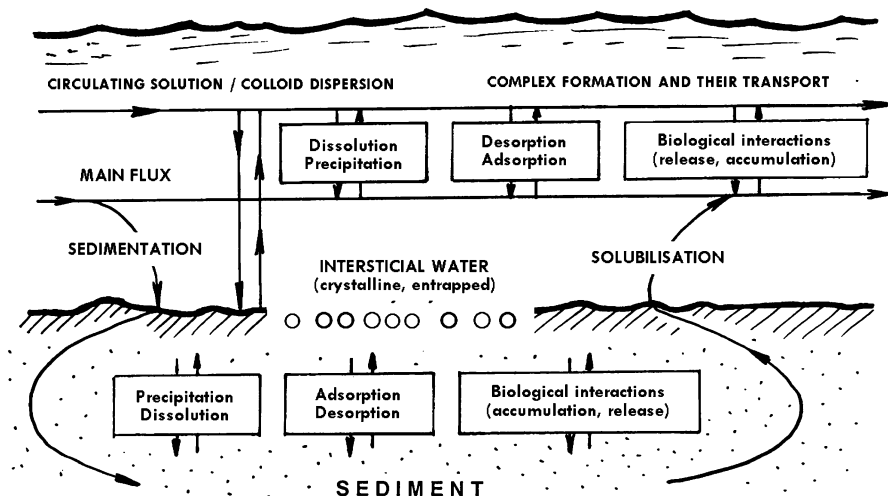


Fig. 7.1 Physicochemical processes of inorganic species in the environmental cycle of life. A scheme (adapted and rearranged from reference (3))

## 7.2 Electrochemical Measurements

In combination with electrochemical principles, speciation has a long tradition and at least since the last third of the twentieth century<sup>9–15</sup> this special area skilfully utilises the ability of electroanalysis to indicate the changes in chemical equilibrium and redox state of various substances, which allows—together with determinations of their total content—the identification and quantification of the individual forms and their actual distribution—a problematic deal for many other instrumental techniques. In this respect, specialised teams have elaborated to a remarkable extent mainly the electrochemistry of natural aquatic systems, covering for two decades the dominant part of chemical speciation in environmental electroanalysis (see, e.g., references (15, 16)).

Concerning the most convenient electrochemical techniques for speciation analysis, there is (equilibrium) potentiometry and, mainly, stripping techniques with the effective pre-concentration step for accumulating many species at a high concentration level.

### 7.2.1 Potentiometry with Ion-Selective Electrodes (ISEs)<sup>17</sup>

This is the traditional technique for indication of the changes in chemical equilibrium and requires zero-current conditions. This may be advantageous with respect to the high selectivity achieved; however, common potentiometric measurements are not sufficiently sensitive to be used for monitoring at the trace concentration

level typical for environmental samples, except for special types of ISEs with non-Nernstian responses, reportedly able of operating even at the nanomolar level or even below (see, e.g., reference (18) and references therein).

### **7.2.2 *Anodic and Cathodic Stripping Voltammetry (ASV and CSV<sup>19, 20</sup>)***

This technique coupled with differential-pulse or square-wave potential ramp (DPASV and SWASV) is able to detect extremely low concentration levels (down to  $1 \times 10^{-11}$  mol/L<sup>-1</sup>), when still distinguishing the labile and non-labile fractions of the corresponding metal(s). Electrochemical deposition within the stripping procedure enables to accumulate onto the electrode the labile forms of metal(s) under controlled—usually, constant—potential, when the effectiveness of such depositions is strongly dependent upon the type of electrode and the composition of supporting/background electrolytes (type of major components, pH, ionic strength, the presence of complex-forming anions or other ligands).

### **7.2.3 *Stripping (Chrono)potentiometry***

Stripping (chrono)potentiometry in its two common variants, potentiometric stripping analysis (with chemical oxidation, PSA<sup>21,23</sup>) and constant current stripping analysis (CCSA<sup>21,22</sup>) closely related to both ASV and CSV, is also convenient for studying metal complexation because it offers comparable sensitivity to stripping voltammetry; moreover, it is less vulnerable to the undesirable phenomena as adsorption of metal species or insufficient availability of a ligand during the measurement.<sup>24,25</sup> Furthermore, PSA has been shown to be a useful tool for studying the stability and kinetics of metal ions bound by heterogeneous ligands (e.g. fulvic acid), especially thanks to the operability at a wide range of the ligand-to-metal ratio.<sup>24</sup> Yet another advantage of (chrono)potentiometry is its capability to eliminate the induced adsorption of metal ions and to minimise a ligand concentration excess.<sup>25</sup>

### **7.2.4 *Working Electrodes for Electroanalytical Speciation***

Similarly like in other areas of applied electrochemistry, the leading scientists and teams<sup>9,10,12–15</sup> were usually preferring the reliable constructions of commercially available mercury-drop-based electrodes, i.e. Kemula's HMDE and occasionally also Heyrovský's DME (see Chap. 1), or their mercury-film alternative, MFE.<sup>21,23</sup>

In a lesser scope, the applicability of some carbonaceous and metallic materials as the electrodes of choice was also reported; for instance, the bare glassy carbon<sup>26</sup> or easily renewable (unmodified) carbon pastes.<sup>27,28</sup> For special determinations, (solid) gold-disc,<sup>29</sup> gold-film,<sup>27</sup> screen-printed gold,<sup>30</sup> or lithographically sputtered bismuth<sup>31</sup> electrodes were successfully used, too.

The second large group of frequently used working electrodes is represented by chemically modified electrodes (CMEs) expanding substantially the possibilities in chemical speciation thanks to selectively acting modifiers entrapped at the electrode surface or in the electrode bulk as a suitable ligand,<sup>32</sup> ion exchanger,<sup>33</sup> or even enzyme.<sup>34</sup>

Ligands immobilized in these ways form complexes with metals in solution; the electrochemical response of a given metal can then be directly related to the stability constant of a given complex. Such modified electrodes have been applied to investigate the complex-forming properties of humic substances,<sup>33,35,36</sup> for example, by using them in solid form for direct modification of a CPE and, in this way, proving the formation of Cu<sup>II</sup> complex structures with solid humic acids/salts.<sup>36</sup> In this study, Cu<sup>II</sup>-humate complexes exhibited labile or slow dissociation character in dependence of pH. Similarly, a formation of Cu<sup>II</sup> complexes with humic acid and humates at the surface layer of CPE(s) containing these substances also in the bulk could be used to quantify the respective metal ions.<sup>37</sup> These complexes were proved by IR spectra indicating the existence of COOH groups. Finally, the heterogeneous stability constant of the Cu<sup>II</sup>-humic acid complex could also be determined with the aid of such modified CPE.<sup>38</sup>

### 7.3 Basic Strategies in Electroanalytical Speciation

In environmental analysis, representing the prevailing but not exclusive applications, several fundamental approaches can be noticed as documented in the following sections.

#### 7.3.1 *Speciation of Metal Forms and Their Overall Distribution in Aquatic Systems*<sup>9-16,39-41</sup>

In brief, there are four fundamental forms of metal species: (1) free metal ions, (2) hydrated metal ions, (3) metal complexes with inorganic and/or organic ligands, and finally (4) metal species adsorbed/entrapped onto solids or colloidal particles.

The early methods for assessment of such metal fractions had employed mainly voltammetric techniques,<sup>9,10,12-15,39</sup> later supplemented or also altered by stripping (chrono)potentiometry.<sup>24,25,42</sup> The corresponding procedures were designed as more or less uniform schemes combining the identification and determination of

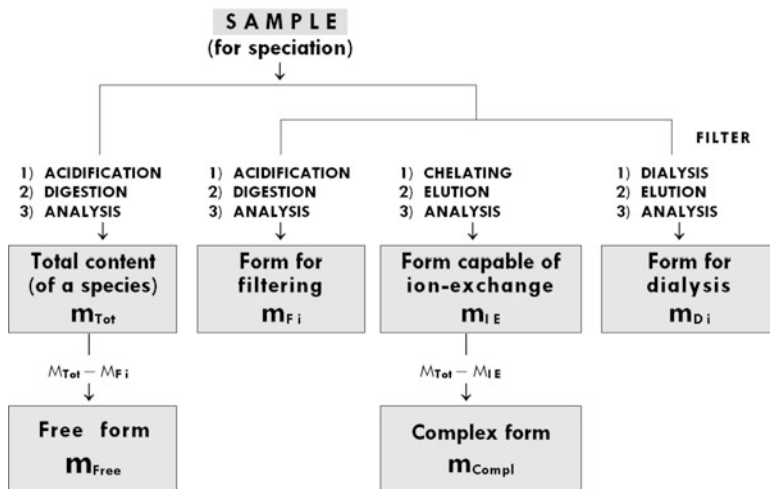


Fig. 7.2 Algorithm for chemical speciation of water samples in electroanalysis (drawn and rearranged from reference (44))

the individual metal species in untreated natural water, in acidified sample, and after the UV irradiation of the sample. In detail, a typical speciation procedure for the metal classification in natural waters was proposed by Nürnberg,<sup>14</sup> one of the true legends of environmental analysis and co-founder of the “Environmental Specimen Banking” programme (see Chap. 1). During such speciation, the natural water is being subjected to the following steps and operations:

- Filtration to remove and analyse solid matter (with filter porosity: 0.45  $\mu\text{m}$ ) → filtrate is subjected to analyses described in the subsequent steps (b), (c), and (d).
- Voltammetric determination of heavy metals in filtrate at natural pH → information on the dissolved metal species (free ions, hydrated cations, labile complexes with inorganic ligands).
- Voltammetric determination of heavy metals in filtrate after acidifying to pH 2 → amount of heavy metals related to their complexes (with dissolved organic matter or metals in colloids).
- Voltammetric determination of heavy metals after UV irradiation of the acidified filtrate → amount of heavy metals relating to their stable and non-labile complexes with organic ligands.

Eventually, the above-described procedure was further adapted for the use of chelating resins,<sup>41</sup> or amended with the use of (transfer) stripping voltammetry with medium exchange,<sup>43</sup> when one might, e.g., suppress the undesirable interferences from some matrix constituents. Subsequently, as depicted by the scheme in Fig. 7.2 (sketched after Hart et al.; see reference (44)), the procedures had become yet more sophisticated after incorporation of additional separations in an ion-exchange column or by membrane dialysis, nevertheless, having still pursued the basic idea

of separation and differentiation of two ultimate forms with free and complexed/bound species.

In aquatic systems chemical equilibrium processes and their qualitative and quantitative characterisation by means of dissociation constants ( $pK_A$ ), stability and conditional stability constants ( $K_{ML}$  and  $K'_{ML}$ , respectively), solubility products ( $pK_S$ ), distribution pH diagrams, or reaction rate data have been studied into detail and well defined (see, e.g., reference (45)), which had inspired some scientists to combine these databases with modern computation modelling and chemometric methods.

One of the results of such efforts is shown in Tables 7.1 and 7.2, presenting a model composition of natural river water (Table 7.1) and of seawater (Table 7.2) with respect to all the chemical species that could be identified and determined by suitable instrumental techniques. In contrast to the original way of presentation,<sup>46</sup> the values listed in both parts have been rearranged in a reader-friendly form illustrating explicitly the abundance of the individual ions and complexes together with their corresponding contents in relation to the distribution for each chemical element and, at the same, with respect to the grand total of all the species in the water model given.

All the methods and procedures dealing with the metal speciation and distribution were mostly used for speciation of Cu, Cd, Pb, and Zn in natural waters—in these cases, predominantly with mercury electrodes (see, e.g., references (9–15) and references therein)—and speciation of Hg and As at gold electrodes,<sup>27,47,48</sup> as well as various types of CMEs<sup>32,35,36,41</sup> and biosensors.<sup>34</sup>

Concerning the former group of heavy metals, it is worth of to mention, e.g., a systematic study on the complexing capacity of Cu(II), Cd(II), and Pb(II) towards various complexing agents (fulvic acid, alginic acid, tannic acid, surfactant Triton X<sup>®</sup>) while incorporating the double-acidification procedure of polluted natural waters and synthetic wastes.<sup>16</sup> Also, electroanalytical speciations focused on organometallic and organosemimetallic species are always attractive, especially those like  $(CH_3)_2Hg$  and  $CH_3Hg^{+34,49}$ ;  $(CH_3)_4Pb$ ,  $(CH_3)_3Pb^+$ ,  $(CH_3)_2Pb^{2+}$ ,  $(C_2H_5)_4Pb$ , etc.<sup>50</sup>; nearly twenty organostannic compounds, including  $(C_6H_5)_4Sn$ ,  $(C_6H_5)_3Sn^+$ , and  $(C_4H_9)_4Sn^{51}$ ; and some organoarsenic derivatives.<sup>52</sup>

### 7.3.2 Differentiation of the Valence/Oxidation State

Certain elements and their single ions or complex forms are of interest with respect to this specific feature,<sup>1</sup> potentially playing a principal role in the final toxicity and bioactivity<sup>4–7</sup> with the subsequent impact on environmental and biological systems.

In electroanalysis, differentiation between two or even more oxidation states has been in focus mainly in the case of (1) arsenic ( $As^{III}$  and  $As^V$ ,<sup>48</sup> occasionally also  $As^{-III}$  (53)), (2) chromium ( $Cr^{III}$  and  $Cr^{VI}$  in chromates),<sup>54</sup> and in lesser extend also (3) mercury ( $Hg_2^{2+}$  and  $Hg^{II}$  (55)) and some other metallic elements like

**Table 7.1** Chemical species in river water and their overall distribution<sup>a-c</sup>

Major constituents				Minor/trace constituents			
Element	Form (species)	Content		Element	Form (species)	Content	
		(mg kg <sup>-1</sup> )	%			(µg kg <sup>-1</sup> )	%
<i>Metals</i>				<i>Metals</i>			
Na	Na <sup>+</sup>	12,065	99.6	Fe	Fe <sup>2+</sup>	8,880	88.3
	NaHCO <sub>3</sub> <sup>0</sup>	0.025	0.2		FeOH <sup>+</sup>	1,165	11.6
	NaSO <sub>4</sub> <sup>-</sup>	0.025	0.2		Fe(OH) <sub>4</sub> <sup>-</sup>	0.006	0.1
Ca	Ca <sup>2+</sup>	11,825	92.1		Fe <sup>3+</sup>	5 × 10 <sup>-12</sup>	–
	CaHCO <sub>3</sub> <sup>+</sup>	0.505	4.0	Mn	Mn <sup>2+</sup>	3,460	96.5
	CaSO <sub>4</sub> <sup>0</sup>	0.385	3.0		MnSO <sub>4</sub> <sup>0</sup>	0.090	2.5
	CaCO <sub>3</sub> <sup>0</sup>	0.125	0.9		MnOH <sup>+</sup>	0.035	1.0
Mg	Mg <sup>2+</sup>	7,340	91.2	Ni	Ni <sup>2+</sup>	1,175	38.2
	MgSO <sub>4</sub> <sup>0</sup>	0.425	5.3		NiCO <sub>3</sub> <sup>0</sup>	1,900	61.8
	MgHCO <sub>3</sub> <sup>+</sup>	0.270	3.4	Zn	Zn <sup>2+</sup>	0.410	44.8
	MgCO <sub>3</sub> <sup>0</sup>	0.010	0.1		ZnCO <sub>3</sub> <sup>0</sup>	0.375	41.0
K	K <sup>+</sup>	1,450	99.8		Zn(HS) <sub>2</sub> <sup>0</sup>	0.130	14.2
	KSO <sub>4</sub> <sup>-</sup>	0.003	0.2	Al	Al(OH) <sub>4</sub> <sup>-</sup>	0.380	100
Bi	BiO <sup>+</sup>	0.015	–		Al <sup>3+</sup>	3 × 10 <sup>-7</sup>	–
	<i>Non-metals</i>				Cu	Cu <sup>2+</sup>	0.060
C	HCO <sub>3</sub> <sup>-</sup>	72,135	99.6	Cd		Cd <sup>2+</sup>	0.055
	CO <sub>3</sub> <sup>2-</sup>	0.300	0.4	Pb	CdOH <sup>+</sup>	0.001	1.8
Si	H <sub>4</sub> SiO <sub>4</sub> <sup>0</sup>	28,360	–		PbCO <sub>3</sub> <sup>0</sup>	0.035	93.8
Cl	Cl <sup>-</sup>	10,005	–		PbOH <sup>+</sup>	0.002	5.4
S	SO <sub>4</sub> <sup>2-</sup>	7,115	–	Pb <sup>2+</sup>	0.001	0.8	
B	H <sub>3</sub> BO <sub>3</sub> <sup>0</sup>	0.270	91.5	Ag	AgHS <sup>0</sup>	0.055	100
	B(OH) <sub>4</sub> <sup>-</sup>	0.025	8.5		Ag <sup>+</sup>	2 × 10 <sup>-8</sup>	–
F	F <sup>-</sup>	0.095	–	Cr	Cr <sup>3+</sup>	5 × 10 <sup>-11</sup>	–
O	OH <sup>-</sup>	0.005	–	Hg	Hg <sup>2+</sup>	2 × 10 <sup>-12</sup>	–
H	H <sup>+</sup>	1 × 10 <sup>-5</sup>	–	<i>Non-metals and semimetals</i>			
				N	NO <sub>3</sub> <sup>-</sup>	895	86.9
					NH <sub>4</sub> <sup>+</sup>	135	13.1
				P	HPO <sub>4</sub> <sup>2-</sup>	150	85.7
					H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	25	14.3
				As	HAsO <sub>4</sub> <sup>2-</sup>	3.5	–
				I	I <sup>-</sup>	2.0	–
					S	HS <sup>-</sup>	1.5
				H <sub>2</sub> S <sup>0</sup>		0.2	11.8
				Se <sup>d</sup>	HSeO <sub>4</sub> <sup>-</sup>	1 × 10 <sup>-10</sup>	–

<sup>a</sup>Prepared from the results published in Batley GE (ed) (1989) *Trace Element Speciation*, CRC Press. For full citation, see the reference list and item<sup>46</sup>

<sup>b</sup>All data given for t = 25 °C. Further, the individual values are recalculated to the content in mg L<sup>-1</sup> or µg L<sup>-1</sup>, resp., when considering the density of seawater of ρ<sub>w</sub> = 1.0 kg L<sup>-1</sup>

<sup>c</sup>Percentage, when all the species listed give the grand total of 100 %

<sup>d</sup>Data from another source (see reference (3))

**Table 7.2** Chemical species in seawater and their overall distribution<sup>a-c</sup>

Major constituents				Minor/trace constituents			
Element	Form (species)	Content		Element	Form (species)	Content	
		(mg kg <sup>-1</sup> )	%			(μg kg <sup>-1</sup> )	%
<i>Metals</i>				<i>Metals</i>			
Na	Na <sup>+</sup>	10,900	93.5	Li	Li <sup>+</sup>	170	–
	NaSO <sub>4</sub> <sup>-</sup>	750	6.4	Rb	Rb <sup>+</sup>	120	–
	NaHCO <sub>3</sub> <sup>0</sup>	15	0.1	Ba	Ba <sup>2+</sup>	20	–
Mg	Mg <sup>2+</sup>	1,090	61.3	Al	Al(OH) <sub>4</sub> <sup>-</sup>	3.90	74.3
	MgSO <sub>4</sub> <sup>+</sup>	660	37.5		Al(OH) <sub>3</sub> <sup>0</sup>	1.35	25.7
	MgHCO <sub>3</sub> <sup>+</sup>	15	0.9		Al <sup>3+</sup>	3 × 10 <sup>-9</sup>	–
	MgCO <sub>3</sub> <sup>0</sup>	5	0.2	Zn	Zn <sup>2+</sup>	2.05	56.2
	MgF <sup>+</sup>	3	0.1		ZnCO <sub>3</sub> <sup>0</sup>	1.60	43.8
K	K <sup>+</sup>	410	95.3	Ni	NiCl <sub>2</sub> <sup>0</sup>	1.05	38.2
	KSO <sub>4</sub> <sup>-</sup>	20	4.7		NiCO <sub>3</sub> <sup>0</sup>	0.95	34.6
Ca	Ca <sup>2+</sup>	380	48.0		Ni <sup>2+</sup>	0.75	27.2
	CaCl <sup>+</sup>	270	34.1	Mn	MnCl <sup>+</sup>	0.15	71.4
	CaSO <sub>4</sub> <sup>0</sup>	135	17.1		Mn <sup>2+</sup>	0.06	28.6
	CaHCO <sub>3</sub> <sup>+</sup>	4	0.5	Cd	CdHS <sup>+</sup>	0.115	45.5
	CaCO <sub>3</sub> <sup>0</sup>	2	0.3		CdCl <sub>2</sub> <sup>0</sup>	0.075	29.6
Sr	Sr <sup>2+</sup>	7	–		CdCl <sup>+</sup>	0.060	23.7
					Cd <sup>2+</sup>	0.003	1.2
<i>Non-metals</i>				Pb	PbCO <sub>3</sub> <sup>0</sup>	0.045	67.2
Cl	Cl <sup>-</sup>	19,900	–		PbI <sub>2</sub> <sup>0</sup>	0.015	22.4
S	SO <sub>4</sub> <sup>2-</sup>	1,350	–		Pb <sup>2+</sup>	0.007	10.4
C	HCO <sub>3</sub> <sup>-</sup>	75	97.4	Hg	HgCl <sub>3</sub> <sup>-</sup>	0.040	100
	CO <sub>3</sub> <sup>2-</sup>	2	2.6		Hg <sup>2+</sup>	2 × 10 <sup>-15</sup>	–
Br	Br <sup>-</sup>	70	–	Cu	Cu(OH) <sub>2</sub> <sup>0</sup>	0.031	96.9
B	H <sub>3</sub> BO <sub>3</sub> <sup>0</sup>	20	80.0		Cu <sup>2+</sup>	0.001	3.1
	B(OH) <sub>4</sub> <sup>-</sup>	5	20.0	Ag	AgCl <sub>4</sub> <sup>3-</sup>	0.003	100
Si	H <sub>4</sub> SiO <sub>4</sub> <sup>0</sup>	7	–		Ag <sup>+</sup>	1 × 10 <sup>-7</sup>	–
F	F <sup>-</sup>	0.80	–	Cr	Cr <sup>3+</sup>	5 × 10 <sup>-18</sup>	–
O	OH <sup>-</sup>	0.04	–		<i>Non-metals and semimetals</i>		
H	H <sup>+</sup>	8 × 10 <sup>-6</sup>	–	N	NO <sub>3</sub> <sup>-</sup>	297	99.7
					NH <sub>4</sub> <sup>+e</sup>	3.0	0.3
					NO <sub>2</sub> <sup>-e</sup>	1 × 10 <sup>-5</sup>	–
				I	I <sup>-</sup>	65	–
					P	HPO <sub>4</sub> <sup>2-</sup>	10
				H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>		0.40	3.9
				PO <sub>4</sub> <sup>3-</sup>		0.01	0.1
				As	HAsO <sub>4</sub> <sup>2-</sup>	2.05	–

<sup>a-c</sup>See footnote in Table 7.1, except for the seawater density, which is ρ = 1.3 kg L<sup>-1</sup>



(4) antimony ( $\text{Sb}^{\text{III}}$  and  $\text{Sb}^{\text{V}}$  <sup>(56)</sup>), (5) iron ( $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$ , <sup>(57)</sup> or (6) vanadium ( $\text{V}^{\text{III}}$ ,  $\text{V}^{\text{IV}}$ , and  $\text{V}^{\text{V}}$  <sup>(58)</sup>).

After basic studies on the speciation of arsenic by polarography with the DME (see, e.g., references (52, 59)), recent methods are based on more efficient electrochemical stripping analysis with gold electrodes, <sup>42,48</sup> either in the disc configuration <sup>29</sup> or as the gold-film-plated carbon electrode support. <sup>27</sup> However, differentiation between  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  in freshwater can also be performed on the HMDE <sup>60</sup> in combination with CSV via varying the supporting electrolyte composition and using mannitol (polyalcohol) as the activator for the electroreduction of  $\text{As}^{\text{V}} \rightarrow \text{As}^{\text{III}}$  with the consecutive determination of the latter after medium exchange.

Similarly, an electrolyte with varied pH enabled to determine first  $\text{As}^{\text{III}}$  (with an LOD of 0.2 nM, pH 8) and afterwards the total content of arsenic, i.e.  $\text{As}^{\text{III}} + \text{As}^{\text{V}}$  (LOD: 0.3 nM, pH 1), both when employing ASV and a gold microwire electrode. <sup>61</sup> An analogous approach to determine total arsenic as  $\text{As}^{\text{III}}$  after chemical reduction of  $\text{As}^{\text{V}}$  (in this case, using  $\alpha$ -cysteine) and, in the second step,  $\text{As}^{\text{III}}$  alone utilised the above-mentioned AuF-CPE in combination with CCSA. <sup>27</sup> The respective method was particular in a simple regeneration of the gold electrode used, as well as by finding that the CCSA signals for  $\text{As}^{\text{III}}$  differed notably in shape and overall appearance from those obtained for chemically pre-reduced  $\text{As}^{\text{V}}$ , apparently caused by the effect of residual reductant.

Finally, again by employing CCSA, one can determine pentavalent arsenic directly <sup>62</sup> by imposition of extremely negative deposition potential (close to  $-2$  V vs. SCE) where the otherwise almost impossible electrode reduction of  $\text{As}^{\text{V}} \rightarrow \text{As}^0$  is initiated, assisted, and propelled—in the right sense of this word—by the hydrogen bubbles formed during the pre-concentration process.

Concerning the speciation of chromium, one can choose from two fundamental approaches: (1) definition of the actual valence/redox state with the aid of direct electrochemical measurement of one of the two oxidation states (either  $\text{Cr}^{\text{VI}}$  in chromates <sup>54</sup> or  $\text{Cr}^{\text{III}}/\text{Cr}^{3+}$  <sup>(63)</sup>) with previous pre-concentration of the respective form and (2) redox-state specification by separation (via ion exchange, chromatography, or micro-extraction), enabling the selective isolation of one particular chromium species and the subsequent (unspecific) electrochemical determination. <sup>64</sup> From the individual methods, one can quote catalytically assisted adsorptive stripping voltammetric determination combined with tangential flow filtration <sup>65</sup> enabling the speciation of  $\text{Cr}^{\text{III}}$  and  $\text{Cr}^{\text{VI}}$  as well as the partitioning of chromium ions between the dissolved and colloidal forms in river water. Two other examples manifest the portability of electrochemical instrumentation for the field monitoring enabling the analysis immediately after sampling, minimising possible contamination during transport and storage of the samples. Such remote and fully automated electrochemical analysers were described in the reports of van-den-Berg's <sup>66</sup> and "Joe" Wang's <sup>67</sup> teams. The former had been employed at a shipboard laboratory, where the vertical depth profile was analysed with respect to the content of  $\text{Cr}^{\text{III}}$ ,  $\text{Cr}^{\text{VI}}$ , and total Cr in a locality in the Mediterranean Sea.

Last but not least, speciation of mercury represents a global and, for lengthy decades, challenging problem of environmental analysis. Particular interest attracts methylmercury species,  $\text{CH}_3\text{Hg}^+$ , representing the ultimate product in metabolism of marine fauna<sup>4,6</sup> and also the main reason for a mass poisoning in Japan in the mid-1950s (the so-called Minamata disease<sup>68</sup> having left almost 2,500 victims). As already mentioned, the typical mercury species are  $\text{Hg}^{2+}$ ,  $\text{Hg}^{\text{II}}$  (i.e. non-dissociated  $\text{HgCl}_2$  and related  $\text{HgCl}_3^-$ ) and  $\text{CH}_3\text{Hg}^+$ .<sup>6,34,47,49,55</sup> Further details on inorganic, organic, and organometallic forms of mercury are beyond the scope of this text, but some examples on the determination of Hg were quoted in the previous chapter (see Tables 6.3 and 7.1, and references (69–71)).

In many cases, speciation of mercury is made with CMEs, e.g. those based on modification with silicates that, in general, exhibit strong adsorption capacity towards inorganic forms of mercury—namely  $\text{HgCl}_3^-$ ,  $\text{HgCl}_4^{2-}$ , and  $\text{Hg}(\text{OH})_3^-$ —often occurring in aquatic systems.<sup>72</sup> Similarly, clay-modified CPEs could be also used to study the cationic forms of  $\text{Cu}^{\text{II}}$  ( $\text{Cu}^{2+}$ ,  $\text{CuAc}^+$ ) and the anionic forms of  $\text{Hg}^{\text{II}}$  ( $\text{HgAc}_4^{2-}$ ,  $\text{HgCl}_4^{2-}$ ,  $\text{HgCl}_3^-$ ) and  $\text{Au}^{\text{III}}$  ( $\text{AuCl}_4^-$ ), where “Ac” means acetate.<sup>73</sup>

### 7.3.3 Chemical Speciation with the Aid of the DGT

This special approach concerns a relatively new method for metal speciation in the presence of natural organic ligands and is named *diffusive gradients in thin films (DGT)*.<sup>74–76</sup> Largely based on the transport of substances through a gel, the individual forms of metals and their complexes are distributed via their sizes on the gels with specific porosity, when inorganic species can pass through whereas larger complexes with organic ligands cannot. After such elimination, an ASV method or a similar procedure is then applied to determine the corresponding metal forms. Here, it can be quoted yet that although the DGT method is being co-named “in situ” because of a direct speciation of metals in natural waters, the real outdoor operation is sampling only, while the proper electrochemical analysis usually takes place in laboratories.

## 7.4 Concluding Remarks

As can be seen in a collection of reviews published since the beginning of the new millennium,<sup>77–82</sup> speciation analysis by means of electrochemical measurements is now a firmly established area of special environmental analysis capable of pursuing the newest trends and absorbing almost all progressive achievements.

At present, many methods for electroanalytical speciation involve miniaturised and portable instrumentation,<sup>77,81</sup> electrodes and sensors made by modern printing and sputtering technologies<sup>77,81</sup> in configurations with various nanoparticles,<sup>81</sup> or

utilising in more extent environmentally friendly materials<sup>79</sup> when satisfactory ecological profile can be attributed to the respective procedures themselves.<sup>78,80</sup>

Thus, it can be concluded that electrochemical measurements employing various types of traditional as well as new electrodes are fully compatible with the latest trends and may compete with highly sophisticated instrumental techniques like ET-AAS, CV-AAS, ICP-MS, CE, or HPLC-NAA. This statement applies pretty well to chemical speciation, where electrochemical principles belong for lengthy decades among the most flexible and powerful tool in inorganic environmental analysis.

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