



The Use of Complexing Agent 1-5Diphenylthiocarbazone in the Analysis of Heavy Metals Cu, Pb, Zn, Mn and Ni in Seawater Samples: Application of Solvent Extraction Learning in Analysis Separation Subject

Muti'ah^(✉), Jackson Siahaan, and I. Nyoman Loka

Chemistry Education Department, Faculty of Teacher Training and Education, University of
Mataram, Mataram, Indonesia
Mutiah_fkip@unram.ac.id

Abstract. This research investigates the use of 1-5diphenylthiocarbazone in the analysis of heavy metals Cu, Pb, Zn, Mn, and Ni in seawater samples collected from Alas Strait Waters. The aim of this research is to find out the optimum conditions in analyzing heavy metals, such as optimum pH, extraction time, recovery percentage, and detection limit in the analysis method analyzing those heavy metals. This research is conducted in two steps, firstly, solvent extraction by using complexing agent dithizone in chloroform and secondly, measurement of metals by using an Atomic Absorption Spectrophotometer (AAS). From the results of the method investigation, it is found that the optimum conditions are as follows: (a) pH 8 for Pb, Mn, Ni, and Zn, at the meanwhile pH 4 for Cu; (b) time for extraction 5 min, (c) percentage of recovery 101 for Cu, 105 for Mn, 111 for Ni, 91 for Pb and 104 for Zn and (d) detection limits 0.0027, 0.0023, 0.0030, 0.0070 and 0.0006 ppm for Cu, Mn, Ni, Pb, and Zn respectively. Results of six samples at the optimum conditions show that the concentration of Cu, Mn, Ni, Pb, and Zn are (0.0253 ± 0.0038) , (0.0018 ± 0.0002) , (0.0018 ± 0.0002) , (0.0283 ± 0.0160) and (0.0889 ± 0.0138) ppm respectively. Conclusions of this research are: (1) from the value of % recovery and detection limit, dithizone can be used properly as a complexation agent for heavy metals analysis in seawater samples, (2) results of those heavy metals analysis show that their concentrations are high enough although they are lower than allowed concentration.

Keywords: dithizone · heavy metals analysis · seawater

1 Introduction

Heavy metals in the seawater environment, such as water columns, sediments, or organisms, need great attention since the availability of those metals in excess amounts would cause water pollution problems [1, 2], although they contribute to seawater richness [3].

© The Author(s) 2023

S. Hadisaputra et al. (Eds.): NiTRIC 2022, AHCPs 4, pp. 51–59, 2023.

https://doi.org/10.2991/978-94-6463-130-2_7

Hence, it is important to conduct research on the availability of heavy metals in seawater regarding the increasing of industries. Some heavy metals such as Pb, Zn, Cr, Cu [4], and Ni are often principal parameters in doing seawater research [5–7], and reported that heavy metals Pb, Cr, Cu, Ni, Zn, Fe, Mn, and Co play a role in seawater organisms [8–10]. Increasing attention on marine research in Lombok-NTB Waters, especially for heavy metals such as Pb, Zn, Mn, Ni, and Cu, must be followed by ability and capability in chemical analysis. For instance, the issue of pollution of heavy metals by gold mining companies has been a big problem that has not been solved yet. This exists because there is no result of research that students or lecturers do because of unavailable a cheap, simple, fast, and convenient method.

The analysis method for seawater samples differs from that for freshwater because the chemical composition of seawater is more complex than that of freshwater itself [11]. As a consequence, we often experience mistakes in the analysis due to existing of an interference matrix, which gives an error. This is also because heavy metals' concentration in seawater is low as <0.01 ppm, so it needs a special analysis method. To solve this problem, we need a method that can eliminate matrixes and reduce the sample volume through a dense process, so the measured analysis would be higher than the existing analysis in the sample itself (before the dense process). The method is expected can overcome those two problems in the analysis method through the solvent extraction step [12].

Here are some researchers who conducted solvent extraction process as a step in seawater analysis, for examples, [13, 14]. They used complexing agent iminodiacetate at the meanwhile, [15] used ammonium pyrrolidine dithiocarbamate (APDC), [16] use hexamethylene-dithiocarbamate and organic solvent such as methyl isobutyl ketone (MIBK). Hutagalung also used MIBK solvent and complexing agent APDC [17]. Siahaan and Muti'ah investigated an analysis method for heavy metals in seawater by using the co-precipitation iron(III) hydroxide method, and this work gave a less satisfying result due to existing of sodium matrix that adsorbed by coagulant [18]. Siahaan and Sukib have completed that method by eliminating the sodium matrix by using the extractor APDC [19]. The constraint we faced was difficulty in having a complexing agent because it was not available in the laboratory and also because it was expensive. As a result, that method is not used yet by beginners, for instance, students who are taking the final project for their thesis. In order to solve the above problem, an effort is needed to use other complexing agents that are easy to be purchased and, of course, inexpensive. In this research, we investigated the effectiveness of the complexing agent dithizone or 1–5 diphenylthiocarbazone. Firstly, it is easy to use this chemical, and its price is relatively low compared with APDC. Secondly, dithizone has been proven to show high effectiveness and selectivity in the separation of heavy metals from a solution [20, 21]. Some other references also mentioned that by controlling of pH of a solution, dithizone gives high selectivity and percentage of extraction up to 100% for Pb, Cu, Zn, Cr, and Ni [22].

The aims of this research are: (1) to find the optimum conditions of pH and extraction time for Pb, Cu, Mn, Ni, and Zn, (2) to find the value of % recovery and detection limit, and (3) to apply the method in the analysis of heavy metals.

2 Methods

2.1 Samples

Artificial seawater with concentrations of 0.00, 0.01, 0.02, 0.04, 0.06, 0.08, and 0.10 ppm heavy metals was used in order to arrange a method according to procedure Noor et al. [23]. This work used high-purity chemicals (p.a) from Sigma. Sea water samples were collected from Alas Strait where close to the gold mining company and illegal mining by society.

2.2 Procedure

The procedure in this research follows Sembiring [20].

- 1) *Optimum pH in the extraction of heavy metals Pb, Cu, Mn, Ni, and Zn.*
100 mL of the sample, which contains trace element 0.02 ppm with pH 4, 6, 8, 10, and 12, and then add 10 mL dithizone reagent 2% in chloroform, pour into a separator funnel. Extraction is run for 5 min, and the organic phase is separated; then continue to do re-extraction with 10 mL HNO₃ 1 M. Water phase is measured with AAS.
- 2) *Optimum time for extraction Cu, Mn, Ni, Pb, and Zn*
Similar to procedure 2.2.1 above, which relates to optimum pH, this is conducted in a variety of extraction times: 1, 5, 10, and 15 min.
- 3) *Percentage of recovery*
Similar to procedure 2.2.1 above, which relates to optimum pH and extraction, this is conducted in a variety of heavy metals with concentrations of 0.00, 0.01, and 0.02 ppm.
- 4) *Detection limit*
Similar to procedure 4.2.3., but in this step, there is an extra treatment such as six times measurement for the blank solution and used heavy metals with concentration: 0.00, 0.01, 0.02, 0.02, 0.04, 0.06, 0.08, and 0.1 ppm.
- 5) *Application of method resulted from research on seawater samples*
This part is conducted to analyze seawater samples collected from Alas Strait and the surrounding by using the method that resulted from research.

2.3 Data Analysis

- 1) *Percentage of recovery is calculated by using the formula:*

$$\% \text{ recovery} = \text{gained concentration divided with given concentration} \times 100\% \quad (1)$$

- 2) *Detection limit is calculated by using the formula:*

$$\text{Detection limit} : C_L = k \cdot S_D/s \quad (2)$$

where C_L is the detection limit, k is 3, S_D is the standard deviation of the blank solution, and s is the curve slope of the regression curve.

3 Results and Discussion

3.1 The Effect of pH Extraction

In doing analysis of heavy metals with AAS through solvent extraction process by using dithizone, it extremely depends on optimum extraction conditions such as pH of heavy metals solution and on extraction time. Finding optimum pH aims to reach pH, which can give optimum % recovery of extraction of metals from the water phase to the organic phase. The extraction process may occur according to a reaction between heavy metal ions with dithizone molecules in the water phase regarding the formation of a neutral complex compound, so it is easily solved in the organic phase (chloroform). Because the structure of dithizone molecules (H_2Dz) is affected by pH, the formation reaction of complex compound metal – dithizone also affected by the pH of the solution. This is raised from the ionization of dithizone in water:



The first ionization takes place in acid condition, and on the contrary, the second ionization takes place in base condition. Metal ions in solution can form a complex compound with primary and secondary dithizone depending on the pH. Primary dithizone can be formed at low pH, while secondary dithizone at base pH. The result of this research shows that the formation of the complex compound takes place in secondary dithizone except for Cu. Hence, optimum pH usually is found at pH close to 8 for Mn, Ni, and Zn, except Cu at pH 4.

The meaning of this research is that in doing extraction of heavy metals by using the complexing agent dithizone, the optimum pH is 8–10 for Mn, Ni, Pb, and Zn. And the optimum pH for Cu is 4. The result of this research accords with to result reported by Sembiring [20].

3.2 The Effect of Time Extraction

A study about time extraction towards the number of metals extracted optimally relates to the kinetics of the reaction of metal and dithizone molecules to yield complex compounds. The result shows that the maximum number of metal extracted was found in the time of extraction, 5 min. It decreases at 10 min and then back to increasing after 15 min. This relates to the process involved in the extraction, that is chemical reaction and distribution process. The chemical reaction is involved in the formation of the complex compound in the water phase and distribution process, which is resulted from the movement of the complex compound from the water phase to the organic phase. Such a process is an equilibrium reaction, so in a certain condition, that reaction may reverse. This is, so the optimum reaction needs to be conducted empirically. The meaning of empirically from the result of this investigation is that for extraction of heavy metals by using complexion agent dithizone and organic phase chloroform is properly conducted in 5 min.

Table 1. Recovery of heavy metals

Conc. Ppm	Gain Conc. (ppm)	% Recovery
Cu 0.01	0.0107	107
Cu 0.02	0.0201	101
Mn 0.01	0.0091	91
Mn 0.02	0.0209	105
Ni 0.01	0.0089	86
Ni 0.02	0.0223	111
Pb 0.01	0.0159	159
Pb 0.02	0.0182	91
Zn 0.01	0.994	99
Zn 0.02	0.0209	104

3.3 Recovery

Finding the value of % recovery aims to define the level of validity of this method. A good analysis method is one that has a value of % recovery close to 100%. This means the method has high precision both in the analysis process and in measurement. The result of finding the value of % recovery for some heavy metals can be seen in Table 1. Table 1 shows that, in general, the deviation value of % recovery from 100% for concentration 0.02 ppm is lower than concentration 0.01 ppm. For example, in Cu analysis, the value of % recovery for concentration 0.01 ppm is 107%, while for concentration 0.02 ppm, it is gained 103%.

This can be explained by the fact that this method is proper for metals analysis in the samples with a concentration ≈ 0.02 ppm. On the contrary, for metals analysis with a concentration of 0.01 ppm, the error that can be faced in the extraction process will have a strong effect.

If we compare with the available literature, the value of % recovery in this method is good enough. For instance, the value of % recovery in an analysis of metals in seawater with a chelating method is gained 117% for Ni, 90% for Pb, 87% for Cu, and 93% for Cd [24]. Furthermore, Cuong *et al.* reported that the analysis method for heavy metals from seawater with solvent-ICP MS extraction way: Zn 110%, Pb 111%, Ni 109%, Cu 105%, Cr 136%, and As 91% [25].

3.4 Detection Limit

The detection limit in chemical analysis is a like an analyte concentration that gives a response or absorbance to tools as big as a response of blank solution added three times.

The standard deviation of blank response. The lower the detection limit, the more sensitive the method. In this research, the detection limit is defined as three times the value of the deviation standard of the blank solution divided by the value of the standard regression curve slope.

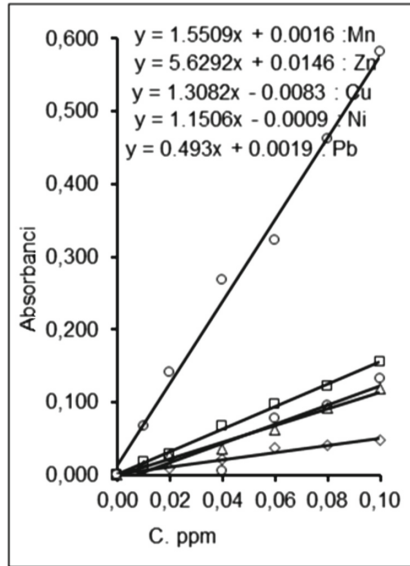


Fig. 1. The curve of Standard Regression for Extracted Metals

Table 2. Date of detection limit in heavy metals analysis

Heavy Metals	C _L (ppm)
Cu	0.0027
Mn	0.0023
Ni	0.0030
Pb	0.0070
Zn	0.0006

Figure 1 confirms that the response of tools resulted from heavy metals in some different concentrations. The higher the curve slope, the more sensitive the analysis method. Hence, based on the gain curve, the increasing sensitivity of metals are as follows: Pb < Ni < Cu < Mn < Zn. From the calculation result, the detection limit is given in Table 2.

Table 2 gives information that the lowest detection limit is found in Zn analysis as 0.0006 ppm, while the highest is found in Pb analysis as 0.007 ppm. This shows that this method can be used in the analysis of heavy metals Cu > 0.0027, Mn > 0.0023, Ni > 0.0030, Pb > 0.0070, and Zn > 0.0006 ppm, respectively.

If we compare it with other analysis methods for heavy metals, the detection limit gained from this method is relatively high. As an example, a method using the chelat-Graphite Furnace AAS system shows the detection limit for Pb is ≈ 0.28 ug/L and Cu 0.36 ug/L [24], and with analysis method via co-precipitation-extraction, the detection

Table 3. Heavy metals concentration in seawater sample collected from Alas Strait waters.

Heavy Metals	C (ppm)
Cu	(0.0253 ± 0.0038)
Mn	(0.0018 ± 0.0002)
Ni	(0.0032 ± 0.0005)
Pb	(0.0283 ± 0.0160)
Zn	(0.0889 ± 0.0138)

limit is not very different, such for Pb = 0.0024, Cu = 0.0029, Ni = 0.0012 and Zn = 0.0005 ppm respectively [19].

3.5 Analysis of Heavy Metals in Seawater Sample Collected from Alas Strait

The method for analysis of heavy metals in seawater samples through extraction by using dithizone in optimum conditions such as pH and extraction, the precise value of % recovery, and detection limit, then be applied to analyze heavy metals in seawater samples. Seawater samples were collected from Alas Strait Waters as an environment that activities of the gold mining company and society could impact. Samples collecting is carried out on six points sampling from the beach up to 10, 20, 30, 40, 50, and 60 m to the open seawater, respectively. Results analysis show that the heavy metals concentration for those six points varies, regarding the distance can be seen in Table 3.

Data in Table 3 shows that heavy metals concentration in Alas Strait Waters can be said to be high enough, although it is below the allowed values. The reason why the concentration of heavy metals is high enough is that their concentrations are higher than the concentration in seawater collected from open seawater such as Cu 0.0002 – 0.004, Mn 0.0007 – 0.0013, Ni 0.0008 – 0.0024, Pb 0.00002 – 0.0004 and Zn 0.001 – 0.008 ppm, respectively [5, 26] However, that concentration is still in under allowed upper limit as Cu 0.005, Ni 0.05, Pb 0.1 and Zn 0.1 ppm respectively.

4 Conclusions

The conclusions from this research are as follows:

1. The optimum condition for extraction in the analysis of heavy metals in seawater samples with chelating agent dithizone is at pH 8 for Mn, Ni, Pb, and Zn, while for Cu, the pH is 4, and the time for extraction is 5 min.
2. The value of % recovery, in general, is good enough, especially for a concentration of 0.02 ppm.
3. The value of the detection limit is very good, between 0.0006–0.007 ppm.
4. This analysis method can be used properly for the analysis of heavy metals in seawater samples. The result gained: Cu (0.0253 ± 0.0038), Mn (0.0018 ± 0.0002), Ni (0.0032 ± 0.0005), Pb (0.0283 ± 0.0160), and Zn (0.0889 ± 0.0138) ppm, respectively.

5. In general, the concentration of heavy metals in seawater collected from Alas Strait is higher than the concentration of those in open waters, although it is still below the allowed value.

References

1. A. N. Kamarudzaman, Y. S. Woo, and M. F. Ab Jalil, "Distribution and Analysis of Heavy Metals Contamination in Soil, Perlis, Malaysia," *E3S Web Conf.*, vol. 34, pp. 1–5, 2018, <https://doi.org/10.1051/e3sconf/20183402040>.
2. A. Gundogdu, S. T. Culha, F. Kocbas, and M. Culha, "Heavy Metal Accumulation in muscles and total bodies of mullus barbatus, trachurus trachurus and engraulis encrasicolus captured from the coast of sinop, black sea," *Pak. J. Zool.*, vol. 48, no. 1, pp. 25–34, 2016.
3. X. Sun, B. S. Li, X. L. Liu, and C. X. Li, "Spatial Variations and Potential Risks of Heavy Metals in Seawater, Sediments, and Living Organisms in Jiuzhen Bay, China," *J. Chem.*, vol. 2020, 2020, <https://doi.org/10.1155/2020/7971294>.
4. D. Kara and M. Alkan, "Preconcentration and separation of copper (II) with solvent extraction using N,N'-bis(2-hydroxy-5-bromo-benzyl)1,2 diaminopropane," *Microchem. J.*, vol. 71, no. 1, pp. 29–39, 2002, [https://doi.org/10.1016/S0026-265X\(01\)00115-1](https://doi.org/10.1016/S0026-265X(01)00115-1).
5. M. N. Quigley and F. Vernon, "Determination of Trace Metal Ion Concentrations in Seawater," *J. Chem. Educ.*, vol. 73, p. 671, Jul. 1996, <https://doi.org/10.1021/ed073p671>.
6. A. Muzuka, "Distribution of Heavy Metals in the Coastal Marine Surficial Sediments in the Msasani Bay-Dar es Salaam Harbour Area," *West. Indian Ocean J. Mar. Sci.*, vol. 6, no. 1, 2009, <https://doi.org/10.4314/wiojms.v6i1.48228>.
7. W. O. Rustiah, "Analisis Logam Berat CU dan CD Pada Sedimen di Sekitar Perairan Laut Dangkal Selat Buton Kab. Muna," *Teknosains*, vol. 9, pp. 253–264, 2015.
8. A. O. Bazzi, "Heavy metals in seawater, sediments and marine organisms in the Gulf of Chabahar, Oman Sea," *J. Oceanogr. Mar. Sci.*, vol. 5, no. 3, pp. 20–29, 2014, <https://doi.org/10.5897/joms2014.0110>.
9. A. Demirbas, A. M. Gozler, H. Baytasoglu, and C. Kaya, "Heavy metal concentration levels and biometric analysis of Liocarcinus depurator from different locations on the western Black Sea coast of Turkey," *Environ. Monit. Assess.*, vol. 193, no. 6, p. 346, 2021, <https://doi.org/10.1007/s10661-021-09113-y>.
10. A. El Gendy, S. Al Farraj, and M. El Hedeny, "Heavy metal concentrations in tissues of the shrimp Penaeus semisulcatus (De Haan, 1844) from Jazan, southern Red Sea coast of Saudi Arabia," *Pak. J. Zool.*, vol. 47, no. 3, pp. 671–677, 2015.
11. G. Du Laing, R. De Vos, B. Vandecasteele, E. Lesage, F. M. G. Tack, and M. G. Verloo, "Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary," *Estuar. Coast. Shelf Sci.*, vol. 77, no. 4, pp. 589–602, 2008, <https://doi.org/10.1016/j.ecss.2007.10.017>.
12. H. Irving, "Separation and preconcentration," *Fresenius' Zeitschrift für Anal. Chemie*, vol. 263, no. 4, pp. 264–271, 1973, <https://doi.org/10.1007/BF00426114>.
13. A. Siriraks, H. M. Kingston, and J. M. Riviello, "Chelation ion chromatography as a method for trace elemental analysis in complex environmental and biological samples.," *Anal. Chem.*, vol. 62, no. 11, pp. 1185–1193, Jun. 1990, <https://doi.org/10.1021/ac00210a018>.
14. K. W. Warnken, G. A. Gill, L.-S. Wen, L. L. Griffin, and P. H. Santschi, "Trace metal analysis of natural waters by ICP-MS with on-line preconcentration and ultrasonic nebulization," *J. Anal. At. Spectrom.*, vol. 14, no. 2, pp. 247–252, 1999, <https://doi.org/10.1039/A806822D>.

15. B. Magnusson and S. Westerlund, "Solvent extraction procedures combined with back-extraction for trace metal determinations by atomic absorption spectrometry," *Anal. Chim. Acta*, vol. 131, pp. 63–72, 1981, [https://doi.org/10.1016/S0003-2670\(01\)93534-2](https://doi.org/10.1016/S0003-2670(01)93534-2).
16. A. R. K. Dapaah, N. Takano, and A. Ayame, "Solvent extraction of Pb(II) from acid medium with zinc hexamethylenedithiocarbamate followed by back-extraction and subsequent determination by FAAS," *Anal. Chim. Acta*, vol. 386, no. 3, pp. 281–286, 1999, [https://doi.org/10.1016/S0003-2670\(99\)00075-6](https://doi.org/10.1016/S0003-2670(99)00075-6).
17. H. R. Hutagalung, H.P, Deddy Setiapermana, dan S, *Metode Analisis Air laut, Sedimen dan Biota. Buku 2. Puslibang. Oseanologi. LIPI.* 1997.
18. M. Siahaan, J., "Kopresipitasi Dengan Besi (III) Hidroksida Sebagai tahapan pada metode Analisis Logam berat Pb, Cu, Cr, Ni, Zn Dalam Air Laut. Laporan Penelitian Lemlit Unram," 2002.
19. S. Siahaan, J., "Metode Analisis Logam Berat Pb, Cu, Cr, Ni Zn Dalam Air laut Melalui Kopresipitasi Dengan Logam berat yang Dimodifikasi. Laporan Penelitian. Lemlit Unram," 2003.
20. Sembiring, "Penggunaan Ditizon Untuk Memantau Logam Reniko Title," 1992.
21. A. Kiwan, F. Hassan, W. Hamdan, A. Bahajaj, and M. Khaled, "Extraction Equilibria of Nickel(II) with 3Mercapto1,5-Diarylformazans in the Presence of 2,2'-Bipyridyl or 1,10-Phenanthroline," *J. Coord. Chem. - J COORD CHEM*, vol. 22, pp. 59–69, Oct. 1990, <https://doi.org/10.1080/00958979009408208>.
22. R. Minczewski, V. J., Chwastowska, J., & Dybczynski, "Spurenanalytik: Separation and Preconcentration Methods in Inorganic Trace Analysis.. John Wiley & Sons, New York – Chichester – Brisbane – Toronto 1982. XI, 543 S., \$90,-," *Nachrichten aus Chemie, Tech. und Lab.*, vol. 31, no. 1, pp. 25–26, Jan. 1983, <https://doi.org/10.1002/nadc.19830310117>.
23. M. Noor A., Liong S., "Metode analisa Kimia untuk Monitoring Lingkungan Laut. UNHAS".
24. T. D. Creed, J. T., & Martin, "Method 200.13 Determination of Trace Elements in Marine Waters by Off-Line ChelationPreconcentration with Graphite Furnace Atomic Absorption. U.S. Environmental Protection Agency," 1997. [Online]. Available: [https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NERL&dirEntryId=309395#:~:text=URLs/Downlo ads%3A-,Method 200.13,-\(PDF%2C NA pp.](https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NERL&dirEntryId=309395#:~:text=URLs/Downlo ads%3A-,Method 200.13,-(PDF%2C NA pp.)
25. D. T. Cuong *et al.*, "Heavy metal contamination in mangrove habitats of Singapore," *Mar. Pollut. Bull.*, vol. 50, no. 12, pp. 1732–1738, 2005, <https://doi.org/10.1016/j.marpolbul.2005.09.008>.
26. H. Hamesa, L. Lestari, and F. Budiyanto, "Distribusi Logam Berat Dalam Air Laut Dan Sedimen Di Perairan Cimanuk, Jawa Barat, Indonesia," *Oseanologi dan Limnol. di Indones.*, vol. 5, no. 1, p. 19, 2020, <https://doi.org/10.14203/oldi.2020.v5i1.310>.

Open Access This chapter is licensed under the terms of the Creative Commons Attribution-NonCommercial 4.0 International License (<http://creativecommons.org/licenses/by-nc/4.0/>), which permits any noncommercial use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license and indicate if changes were made.

The images or other third party material in this chapter are included in the chapter's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the chapter's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

