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Introductory Chapter: An Introduction to Trace Elements

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1. Introduction

"Trace elements" are such building blocks of our planet and all living organisms, which, although occurring in rather modest concentration levels, are indispensable for a plethora of metabolic processes. Especially since the last decades, we observe enormously increasing efforts devoted by the scientific community to investigate, characterize and quantify trace elements. So-called "essential trace elements" are important constituents of human food, animal fodder, plant fertilizers, or cultivation media to form biotechnologically relevant microbes. Trace elements travel from the soil through the food chain, starting from phytoplankton until reaching our dinner tables; apart from food, drinking water is another important source for trace element uptake by all organisms. This makes trace elements interesting for diverse scientists such as analytical chemists, biochemists, geologists, physiologists, zoologists, and botanists [1].

In dependence on the scientific realm, different definitions for the terminus "trace elements" are found. An analytical chemist considers an element in a given sample with an average concentration of less than 100 ppm on an atomic counting basis or less than 100 µg/g on a mass basis, a "trace element". In contrast, biochemists define "trace elements" as those elements, which, although present only in tiny amounts, are needed to maintain the physiological balance of an organism, often acting as cofactors in enzymatic reactions; this biochemical definition encompasses various heavy metals (iron, copper, nickel, vanadium, cobalt, manganese, molybdenum, chromium, and zinc), some nonmetals (boron and iodine), and certain metalloids (selenium, silicon, and arsenic). This definition implies a daily requirement for "essential trace elements" by humans in amounts between 50 µg and 18 mg/day [2]. To become susceptible toward metabolizing by animals and humans, some trace elements need to undergo transformation by microbes into complex bioavailable forms, as observed in the case of cobalt, which is utilized mainly as cyanocobalamin (vitamin B_{12}) [3, 4]. Moreover,

geologists define trace elements by concentrations not surmounting 1 pro mille of a rock or mineral. In addition, the term "trace element" is frequently used when analyzing the elemental composition of igneous rocks, hence those rocks formed by magma. In mineralogy, trace elements can substitute network-forming ions in mineral crystal structures; here, trace elements are not vital to a mineral's defined composition and do not appear in the mineral's chemical formula. However, as well known in the case of quartz, those metals occurring in trace quantities result in characteristic coloration of the minerals; for example, the substitution of silicon by iron in traces gives the quartz amethysts its famous purple coloration [5].

Keeping with trace elements playing a role in human metabolism, we find at least two of them as so-called "vital poisons" in the periodic system of elements, namely chromium and arsenic, well-known toxins, which, nevertheless, are essential for the functioning of our metabolism. Apart from the 14 undisputed essential trace elements mentioned in the above paragraphs, others, such as fluorine, strontium, or lithium, are suggested to also display biological functions in humans, which, although not clearly elucidated yet mechanistically, are evidenced by element deprivation effects in diverse metabolic studies [1, 6]. In addition, limited circumstantial evidence for certain benefits or biological function in mammals is reported in the case of the metals aluminum, rubidium, cadmium, germanium, tin, and lead, the so-called "ultra-trace elements" [7]. Only for prokaryotes, a physiological role of tungsten [8] and lanthanum [9] is generally accepted. What is not included in this list are all those elements which are present in significant amounts in our body, such as the four biological basic elements hydrogen, oxygen, carbon, and nitrogen and the macroelements sulfur, chlorine, phosphorus, magnesium, sodium, potassium, and calcium.

2. Determination of trace elements

However, trace elements are not only blessing but also curse by generating environmental and health-related concerns when exceeding certain concentration levels. In the context of environmentally sensitive trace elements, it is often not easy to draw a clear line between the desired concentration range of a trace element and the range in which it already exerts toxicity [10]. Aquatic environments, soil, organisms, food, fodder, energy carriers like coal, and airborne particles are targets, which are potentially contaminated with trace elements; this, in turn, provokes the need for modern, reliable, and fast tools for determination of trace element in diverse matrices. Although many problems caused by trace elements are already well managed in the meanwhile, constant vigilance in environmental exposure, application, and nutritional supply of trace elements still displays the *conditio sine qua non*, and calls for intensified research in trace element determination. For example, during mining, beneficiation, and combustion of coal as well as during metal mining and follow-up treatments, a total of about 26 trace elements, among them toxic heavy metals like mercury, need to be considered and quantified [6]. In the biological field, many plants are described to heavily accumulate trace elements from soil (metal "hyperaccumulator"

plants); to understand these uptake mechanism and how the plants develop the required resistance factors needed to withstand the high concentration of trace elements, which often are highly toxic heavy metals, needs highly precise detection devices [11, 12]. The determination of type and concentration of trace elements in nutrition, body tissue and liquids, coal, water, soil, and so on is regarded as the first and most important step to follow the mechanisms controlling the dispersal and accumulation of trace elements. Element speciation in different media (water, soil, food, plants tissue, coal, biological matter, food and fodder, minerals, etc.) is pivotal to assess an element's toxicity, bioavailability, environmental mobility, and biogeochemical performance. Classical methods for elemental analysis, such as gravimetric, titrimetric, calorimetric, and so on, do not sufficiently address the precision requirements when analyzing elements in trace concentrations. Therefore, new analytical techniques have been developed, which greatly simplified the quantitation of many trace elements and considerably extended their detection range. In this context, the development of reproducible and accurate techniques for trace element analysis in different media using spectroscopic instrumentation is continuously advanced. Here, inductively coupled plasma mass spectroscopy (ICP-MS) analysis of trace elements is of increasing importance; among the different ICP-MS techniques, modern developments like dynamic reaction cell inductively coupled plasma mass spectrometry (DRC-ICP-MS) was successfully used to simultaneously determine 17 trace elements in blood samples [13]. Similar techniques encompass sector field inductively coupled plasma mass spectrometry (SF-ICP-MS), which was successfully used for determination of aluminum, beryllium, cadmium, cobalt, chromium, mercury, manganese, nickel, lead, and vanadium in urine, serum, blood, and cerebrospinal fluid [14]. Moreover, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) constitutes a quantitative microbeam technique for rapid and accurate determinations of trace element concentrations in the sub-ppm range in various target materials [15]. A classical method, atom absorption spectroscopy (AAS), is still widely used to quantify various trace elements [16, 17], for example, the well-known graphite furnace atomic absorption spectrometry, which was, *inter alia*, successfully used for trace element determination in fish samples [18]. Prior to AAS measurement, biological samples to be investigated for trace elements need to be solubilized by different ashing techniques; here, a multitude of methods exists, with the use of nitric acid for "wet ashing" often being the method of choice [19]. Decades ago, X-ray fluorescence analysis was recognized as a viable tool to determine trace elements in geological samples [20–22]; in this context, a study reported by Leoni and Saitta in 1976 illustrated the viability of this technique to determine a total of 29 metals in rock and mineral samples in an astonishingly broad concentration range between 1 and 5000 ppm [20]. This AAS technique was later advanced to make it more custom-oriented and better applicable to different types of samples. Moreover, radiochemical trace element analysis is also widely used, mainly using radiochemical neutron activation analysis [23, 24]. By resorting to this method, trace elements were accurately determined in various samples, which are as diverse as human tissue [23], food products [16], and also in terrestrial, lunar, and meteoritic rock samples [24].

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