Talanta 115 (2013) 6–14

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Reproducibility of laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) measurements in mussel shells and comparison with micro-drill sampling and solution ICP–MS

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ARTICLE INFO

Article history:
Received 22 October 2012
Received in revised form
28 March 2013
Accepted 8 April 2013
Available online 17 April 2013

Keywords:
Trace elements
Shell
Laser ablation–ICP–MS
Micro-drill ICP–MS
Lake Balaton

ABSTRACT

The accumulation of trace elements (Mg, Mn, Sr, Ba) in *Unio pictorum L.* mussel shells from Lake Balaton has been assessed using a Laser Ablation (LA) system coupled to either a quadrupole-based or a sector-field inductively coupled plasma–mass spectrometer (ICP – MS), as well as by a combination of micro-drill sampling and solution ICP–MS. The LA–ICP–MS measurements were carried out in the holes made by the micro-drilling system. The longitudinal concentration profiles obtained with the different methods show similar patterns. However, the absolute concentrations determined at individual spots (holes) can be quite different. Especially Ba shows erratic peaks at a very small spatial scale. A paired, two-sample *t*-test between LA–ICP–MS longitudinal profiles and between LA–ICP–MS and micro-drill/solution ICP–MS profiles indicates that, in most cases, there is no significant difference between the concentration profiles of Ba, Mg, Mn and Sr.

Average shell concentrations of Mg, Mn, Sr and Ba, as obtained by LA–ICP–MS and micro-drill/solution ICP–MS, compare well with bulk shell concentrations as obtained by acid digestion/ICP–MS of larger shell pieces. Next to the four elements mentioned above, also the concentrations of Cd, Co, Cr, Cu, Ni, Pb and Zn could be determined by bulk shell analysis. The element concentrations in 11 shells, all sampled at the same site, show a relative standard deviation (RSD) between 2% (Ni) and 46% (Zn).

LA–ICP–MS and micro-drill solution ICP–MS are not sensitive enough for the determination of ultra-trace elements in Lake Balaton's mussel shells. We estimated the amount of shell material necessary to determine Ni, Pb, Cr and Cu by micro-drilling ICP–MS (for a concentration that equals 3 times their limit of detection) at, respectively, 0.04, 0.82, 2.7 and 0.4 mg, while the amount sampled by micro-drilling is about 0.06 mg.

1. Introduction

The accumulation of trace elements in mussel shell depends on several parameters, such as temperature, growth rate and the concentration at which the elements occur in their habitat. This in turn means that mussel shells can be used as a proxy for these and related parameters in the aquatic environment they lived in, in the context of, e.g., the determination of pollutant concentrations [1–3], and paleo-chemistry reconstruction [4,5]. During shell growth, the environmental conditions can change, resulting in fluctuating longitudinal concentrations along the shell's growth axis. To be able to detect these longitudinal concentration fluctuations, an analytical technique that is sufficiently sensitive and offers a high spatial resolution along the growth axis, is required. Laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) can respond to these requirements and has yet been widely used in studies of bivalve shells [1–3,5–12], but three limitations restrict its general application.

The first one is the lack of suited certified reference materials (CRMs) and calibration standards. Mussel shells are natural calcite/aragonite structures and this matrix cannot be synthesized artificially. Using natural shells is not a solution either, because the trace element concentrations in these shells can vary strongly. This calibration problem has been studied by various groups [13–16] and alternative calibration proxies have been proposed. The second limitation is the lack of sensitivity, which depends on numerous parameters such as the laser's wavelength (266, 213, 193 nm), flux and repetition frequency, the ablation cell geometry,

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http://dx.doi.org/10.1016/j.talanta.2013.04.019

the carrier gas flow, etc. while the type of ICP–MS instrument will determine the signal intensity for the same amount of material ablated [17]. Elements such as Ni, Cr, Cd, Cu, Pb, Zn etc. are generally not detectable with LA–ICP–MS in bivalve shells. Third, some trace elements are rather heterogeneously distributed in the shell structure. Therefore, it is important to clearly report the spatial distribution of the results in the shell (e.g., along the growth axis, perpendicular to this axis, randomly distributed).

The objectives of this paper are twofold: (1) the repeatability of longitudinal concentration profiles along the growth axis of mussel shells was assessed using LA–ICP–MS. Both a quadrupole-based and a double-focusing sector field ICP–MS instrument were used. The longitudinal element profiles obtained with LA–ICPMS were also compared to micro-drill sampling/solution ICP–MS results; (2) since the sensitivities of the new LA–ICP–MS set-ups at VUB and UGent were better than that of their predecessors, the determination of ultra-trace elements such as Cd, Co, Cr, Cu, Ni, Pb and Zn was examined.

2. Materials and methods

2.1. Sampling

Eleven mussels (*Unio pictorum L.*) with sizes ranging from 59 to 69 mm were collected in Lake Balaton, Hungary, at one of the sediment stations with high trace metal levels (station D3, see Fig. 1 [18]). The *Unio pictorum L.* species have an aragonite shell [19]. Samples were stored in polyethylene containers and then deep-frozen. Major and trace element concentrations in the water column, sediments and biota of Lake Balaton were reported in [18,20].

2.2. Preparation of the shells

After removal of the soft tissue, the shells were air-dried and the left and right valves were separated from one another. The left valves were kept for bulk analysis while the right valves were arranged for laser ablation analysis. For that purpose, they were cut with a diamond saw perpendicular to the growth line, from the umbo along the maximum height of the shell (Fig. 2) [21], rinsed with de-ionized water and air-dried.

2.3. Analysis

The right shell section was analyzed (1) using solution ICP–MS after acid digestion of shell powder obtained with a micro-drill (Merchantek Micromill Sampler) and (2) using LA–ICP–MS. Fig. 3 shows us where the micro-drill samplings and the laser shots were performed in the shell sections. In a first experiment, shell powder was sampled in shells 5 and 9 along the growth axis, by drilling holes of 300 μm in depth and 300 μm in diameter, using a Tungsten carbide micro-drill bit, similarly to Gillikin et al. [1]. The average distance between the holes was about 2 mm and these holes correspond to the upper series of craters shown in Fig. 3. All shell material obtained from this drilling experiment was mixed and used to obtain a rough estimate of trace element levels in the mussel shells of Lake Balaton.

In a second experiment, 12 elements (Ca, Mg, Mn, Sr, Ba, Cd, Co, Cr, Cu, Ni, Pb and Zn) were determined in the drill holes made in the first experiment. A UP193FX laser (New Wave Research) was coupled to a quadrupole-based ICP–MS instrument (ThermoFisher Scientific XSeries II), from the Laboratory of Analytical and Environmental Chemistry (ANCH), Vrije Universiteit Brussel, Brussels, Belgium. Helium was used as carrier gas and was mixed with argon before the plasma torch. Satisfactory sensitivity, and sufficiently low levels of oxide doubly charged ions were assured by daily optimization, consisting of adjusting the plasma power, gas flows, and lens settings during ablation of the NIST SRM-612 glass standard reference material. The laser was focused (~50 μm beam diameter) directly into the micro-drill holes of the mussel shells.

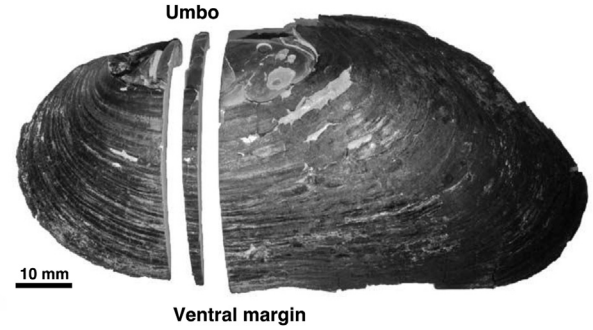

Fig. 2. *Unio pictorum L.* shells. White lines show where thin sections were cut from the umbo along the maximum height of the shell.

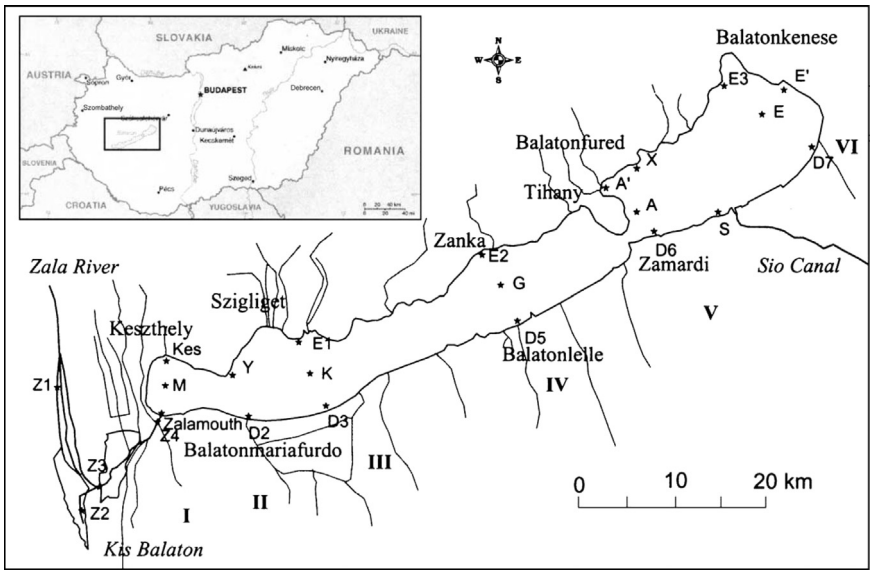

Fig. 1. Map of the study area and sampling station D3 (Balaton Lake, Hungary).