Fresenius J Anal Chem (2000) 367 : 635–640

ORIGINAL PAPER

V. R. Bellotto · N. Miekeley

Improvements in calibration procedures for the quantitative determination of trace elements in carbonate material (mussel shells) by laser ablation ICP-MS

Received: 10 January 2000 / Revised: 16 March 2000 / Accepted: 26 March 2000

Abstract A better repeatability and accuracy in the quantitative determination of trace elements in mussel shells or carbonate-based materials by LA-ICP-MS was achieved by using a series of multielement calibration standards prepared by co-precipitation of twelve elements into a $CaCO_3$ matrix in order to improve the homogeneity of the resulting powder samples. Pressed powder discs of good mechanical stability could be obtained at a pressure of 50 MPa, without the addition of a binder. An UV laser (modified Nd:YAG, 266 nm) was used in the Q-switched mode at a repetition rate of 10 Hz and an energy level of 3.5 mJ. Correlation coefficients (R) for the linear calibration graphs (concentration range: 1.5–400 μg/g) for Cr, Mn, Co, Cu, Zn, As, Cd, Sn, Ba, and Pb are generally better than 0.997. The detection limits for all elements investigated are in the sub-μg/g range. Incorporation of elements into the matrix by co-precipitation has shown as a superior method for producing calibration standards than the simple mixture of the analytes (in carbonate or oxide form) with the matrix ($CaCO_3$) or addition of standard solutions to a carbonate powder base. Two examples of the quantitative determination of toxic elements in mussel shells will be presented.

Introduction

Concentrations of toxic metals in soft tissue of marine shellfish are commonly used as an indicator of marine pollution [1–3]. However, major and trace element compositions of hard biological structures, such as teeth [4], coral skeleton [5], fish otholit [6] and shells [7], have long been recognized as a potential source of environmental information. Wilburg and Saleuddin [8], describing shell formation of mollusks, pointed out that trace metals incorporated into the shell matrix must have been assimilated by organism as an active process. Additionally, unlike soft tissue, there is no significant process of metal mobilization from the shell, once the metals are deposited [9]. Another advantage is that shells are composed of sequentially deposited layers of mineralized material, which are laid down according to the growth rate of the shellfish. For this reason, chemical analysis of discrete bands of growth can reveal historical records of environmental changes.

In most previous investigations, conventional solution techniques were applied in which the shells were digested prior to analysis [10, 11]. In this destructive way, information about temporal concentration changes was lost. Microbeam techniques have already been used to analyze shells as a solid; however, resolution and detection limits were modest [12]. Recent applications of laser ablation (LA) ICP-MS to the analysis of major and trace elements in hard biological structures, such as teeth [4], coral [13] and shells [14, 15, 16] have shown the potential of this technique for environmental applications. Furthermore, unknown samples can be characterized much faster by LA-ICP-MS than by some other current solid sampling techniques (SSMS, GDMS and LIMS) with respect to their major, minor and trace element compositions [17, 18].

Another advantage of LA-ICP-MS over conventional solution nebulization (SN)-ICP-MS is the reduction of polyatomic interference due to the “dry plasma” in which the formation of $^{40}Ar^{16}O^+$, $^{15}N^{16}O^+$, $^{16}O_2\,H^+$ and other species, produced mainly by the interaction of water and acid (HNO_3) with the argon plasma, is much less probable [19].

However, quantification of the analytical results proves still to be difficult in LA-ICP-MS due to a combination of various problems, including: uneven ablation of the mate-

V. R. Bellotto (✉)
CTTMar – Center for Technology, Earth and Ocean Sciences,
Vale do Itajaí University (UNIVALI), PO Box 360, 88302–202,
Itajaí, Santa Catarina, Brazil
e-mail: bellotto@cttmar.univali.rct-sc.br

N. Miekeley
Department of Chemistry,
Pontifical Catholic University (PUC-Rio),
Rua Marquês de São Vicente 225, 22453–900,
Rio de Janeiro, Brazil

rial, non-representative sub-sampling, differences in the transport efficiencies of components to the plasma and, last not least, the lack of suitable matrix-matched standards for calibration purposes. Some of these aspects have been reviewed recently by Durrant [19].

Concerning the problem of calibration, Perkins and coworkers [14] described the quantitative analysis of carbonate materials using a series of standards based on a solid $CaCO_3$ matrix spiked with oxides of the desired elements, mixed with a binder and then pressed into 30 mm diameter pellets. While this method gives calibration graphs with reasonable correlation coefficients and produces acceptable results for major and minor elements in geological materials, there are no data reported for trace elements. Additionally, the procedure described above presents two major problems, pointed out by Pearce and co-workers [20]: (1) mechanical mixtures of powder addition to a powder matrix appear to be relatively inhomogeneous and (2) elemental oxides are generally more refracting than carbonates of the same element. In order to overcome these problems, the authors cited above have produced standards of some elements by the addition of 1000 µg/mL single-element standard solutions into a defined mass of the $CaCO_3$ matrix, mixed then with a binder and pressed into discs. This procedure resulted in better homogeneity of the standards and improved correlation coefficients. However, none of these studies achieved sufficient accurate results required for the quantitative analysis of trace elements in biological materials and for environmental studies. There are also few records on the detection limits obtained.

The present study reports results on the quantitative determination of trace elements in carbonate materials (mussel shells and a limestone reference material) by LA-ICP-MS using matrix-matched standards, prepared by co-precipitation of 12 elements (Cr, Mn, Co, Cu, Zn, As, Cd, Sn, Hg and Pb) at minor and trace levels into a $CaCO_3$ matrix, aiming at the improvement of the calibration procedure. These elements were selected because of their recognized bioaccumulation in and toxicity for marine organisms [1–3], while Sr and Ba were chosen because of their potential use as indicator of environmental temperature and productivity, respectively [7].

Experimental

Instrumentation. The measurements were carried out using an Elan 5000A (Perkin Elmer- SCIEX) ICP-MS in combination with the laser sampler LSX-100 (CETAC Technologies Inc.). A software program controls the sampler. The ablation target can be viewed through a color CCD camera for precise location of the analysis spot. An argon stream (0.85 dm^3/min) carries the ablated material from sample/standard through a Teflon coated tube into the plasma, for ionization and subsequent analysis in the mass spectrometer. The laser used was a modified Nd:YAG type operated at 266 nm. Experimental conditions for the ICP mass spectrometer and the laser system are given in Table 1. The repetition rate, laser beam energy and focusing depth were optimized for best efficiency and stability of the system in accordance to the $CaCO_3$ matrix used. Many theoretical and technical aspects of the laser ablation processes and systems were recently reviewed by Durrant [19]. Optimum sensitivity and repeatability of the analytical signals are often obtained with laser beam focusing displaced from the sample surface, but the effectiveness of this procedure is material dependent [19]. For the $CaCO_3$ matrix used in this study, optimum conditions were obtained when focusing was about 1.5 mm below the sample surface. Laser energies higher than the selected one (3.5 mJ) resulted in more unstable signals, higher memory effects due to the increased ablated mass and a consequent more rapid clogging of the sampler/skimmer cones. Increase of the repetition rate above 10 Hz had a similar negative effect. The isotopes used for quantification were: ^{43}Ca, ^{53}Cr, ^{55}Mn, ^{59}Co, ^{63}Cu, ^{66}Zn, ^{75}As, ^{86}Sr, ^{114}Cd, ^{118}Sn, ^{138}Ba, ^{202}Hg and $^{206,\ 207,\ 208}$Pb.

Table 1 Operating conditions for the ICP-MS and the modified Nd:YAG laser (266 nm) used

ICP MASS SPECTROMETER:	Elan 5000 (PE-Sciex)
Sweeps/reading	2
Replicates	3
Scanning mode	“Peak hop”
Dwell time	100 ms
Forward power	1200 W
Carrier gas flow	0.85 dm^3/min
Outer gas flow	15 dm^3/min
Intermediate gas flow	1 dm^3/min
LASER	LSX-100 (CETAC)
Mode	Q- switched
Laser beam energy	3.5 mJ
Beam divergence	0.8 mRad
Beam diameter	1.0 mm
Pulse width	< 8–12 ns
Repetition rate	10 Hz
Rastering rate	100 µm/s
Distance between lines	80 µm
Pre-ablation time	25 s
Measuring time	34 s

Solution nebulization ICP-MS was performed with the same instrument (Elan 5000) using a cyclonic spray chamber and concentric Meinhard nebulizer. Standard operational conditions were applied in all measurements (power: 1050 W; argon in dm^3/min: nebulizer –0.950, plasma –15.00, auxiliary –1.00; sample aspiration rate: 1.00 mL/min). The sensitivity obtained for Rh using Pt sampler and skimmer cones was > 7 M cps mg^{-1} L^{-1}, typically. The measured isotopes were the same as shown above. Calibration and quantification was performed in the standard addition and/or external calibration mode.

Solid standard preparation. In order to improve repeatability and accuracy of the measurements and to determine detection limits for the quantitative analyses of trace elements in shells or similar materials, low concentration standards of some elements (1.5–100 µg/g of Cr, Co, Cu, Zn, As, Cd, Sn, Ba, Hg and Pb) and moderate concentration ones of others (6.3–400 µg/g of Mg and Mn) were produced by co-precipitation of the elements into a $CaCO_3$ matrix. 1000 µg/mL single-element solutions (Merck-Titrisol$^{®}$) were spiked into a Ca^{++} solution obtained by acid dissolution (HNO_3 p.a., twofold subboiled) of $CaCO_3$ (Merck, suprapur). Reprecipitation of the matrix was then performed at room temperature by addition of Na_2CO_3 (Merck, suprapur) dissolved in high purity water (> 16 MΩ). The precipitate was then filtered, washed thoroughly with high purity water until the absence of Na^+, dried, homogenized and pressed into discs of 30 mm diameter at 50 MPa, for approximately 5 min, without addition of a binder, resulting in solid pellets of good mechanical stability. For each pressed pellet, a mass of about 2 g of the powder standard was used. Blank sam-

Table 2 Effective concentrations and relative standard deviations (RSD, %) for three measurements of each pressed powder standard by SN-ICP-MS. Comparison of nominal and effective concentrations shows that co-precipitation was nearly quantitative for most elements; exceptions are As and Hg

Low concentration standards [µg/g]							
Nominal concentrations	1.5	3.0	6.3	12.5	25.0	50.0	100.0
Element	Effective concentrations and RSD (%)						
Cr	1.3 (7.4)	2.1 (5.2)	4.9 (1.7)	9.2 (1.3)	19.0 (2.1)	35.5 (3.6)	73.0 (1.7)
Co	2.1 (2.2)	2.9 (0.7)	5.1 (1.0)	9.6 (0.6)	21.7 (3.5)	41.2 (1.6)	83.3 (2.6)
Cu	1.0 (7.0)	2.1 (8.1)	4.6 (4.5)	9.4 (3.0)	21.1 (1.9)	41.1 (3.2)	84.5 (3.3)
Zn	3.3 (2.9)	2.5 (5.5)	6.5 (7.3)	16.0 (9.1)	26.3 (0.4)	50.6 (3.3)	103.5 (3.)
As	1.3 (5.5)	2.1 (4.5)	3.1 (2.4)	4.4 (0.8)	9.5 (1.7)	11.7 (2.9)	22.8 (3.6)
Cd	2.1 (2.1)	2.9 (1.4)	6.9 (1.9)	13.7 (1.1)	31.1 (2.1)	57.1 (1.6)	115.0 (1.2)
Sn	1.5 (1.9)	2.7 (1.4)	5.5 (0.8)	11.0 (1.4)	22.1 (3.5)	41.8 (2.4)	87.8 (1.0)
Ba	2.3 (3.2)	4.0 (3.7)	7.4 (2.2)	14.0 (1.6)	28.9 (2.0)	51.5 (2.4)	104.8 (3.2)
Hg	0.7 (3.2)	1.4 (4.3)	3.2 (5.0)	3.7 (9.8)	21.0 (2.0)	26.4 (7.1)	54.1 (10.4)
Pb	1.5 (4.8)	2.9 (4.3)	5.8 (3.8)	11.2 (1.2)	23.2 (5.2)	44.5 (5.7)	91.5 (0.8)
Moderate concentration standards [µg/g]							
Nominal concentrations	6.3	12.5	25	50	100	200	400
Element	Effective concentrations and RSD (%)						
Mg	7.4 (7.9)	12.5 (4.6)	25.2 (3.9)	48.0 (1.2)	92.8 (2.4)	181.2 (2.2)	354.2 (2.7)
Mn	6.7 (1.6)	13.2 (1.3)	26.7 (1.5)	53.5 (2.6)	103.8 (1.0)	201.9 (1.6)	401.6 (3.0)

ples were prepared in a similar way by direct pressing of $CaCO_3$ (Merck, suprapur) into pellets.

Results and discussions

Assessment of the final elemental concentrations

Concentration of the elements recovered in the $CaCO_3$-matrix and therefore the efficiencies of co-precipitation were determined by conventional solution nebulization (SN)-ICP-MS analysis of 3 dissolved sample aliquots of each standard produced. The samples were analyzed in the fully quantitative mode (external calibration) using ^{115}In and ^{203}Tl as internal standards and calibration curves, which were matrix-matched in Ca concentration.

The mean recovery was about 92% for the elements studied, with the exception of As and Hg (20–50%). This low recovery of As and Hg is probably a consequence of their different chemical characteristics when compared to the others, causing a poorer affinity to the carbonate matrix. The co-precipitation process resulted in more homogeneous standards as shown by the generally smaller RSDs (Table 2), even for the very low concentration standards, when compared with previous work (e.g.: Pearce and co-workers [20], Mean RSD = 3% for a concentration range of 10 to 30 µg/g).

Validation for calibration purposes

The pressed powder $CaCO_3$ standards were analyzed by LA-ICP-MS to produce calibration graphs as exemplified in Fig. 1. The experimental conditions were those from Table 1. Signal data were collected under steady state conditions and normalized with reference to ^{43}Ca (a = 0.145%) as a true internal standard. A known concentration of strontium was also incorporated into the $CaCO_3$ matrix and tested as an internal standard, however, better results were achieved with ^{43}Ca. For many elements, the correlation coefficient is better than 0.998 (see Table 3). Comparing with the previous work [20], it becomes once more evident that incorporation of trace elements into the carbonate matrix by co-precipitation produces more homogeneous samples and consequently better correlation coefficients.

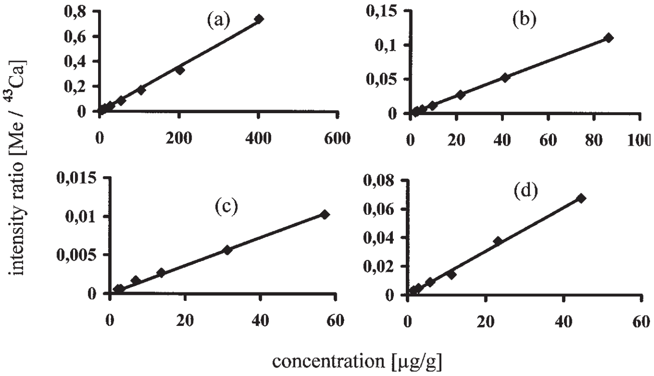

Fig. 1 a–d Examples of calibration graphs for pressed powder standards produced by co-precipitation: (**a**) Mn; (**b**) Cr; (**c**) Cd and (**d**) As. (^{43}Ca was used as an internal standard; ablation and ICP-MS experimental conditions as in Table 1)

The blank counts are derived from the pressed powder discs of suprapur grade $CaCO_3$ (Merck), instead of the generally used Ar-gas blank (i.e. no sample introduction [16]). This procedure has the advantage that the background counts are produced under nearly identical laser

Table 3 3σ-Detection limits, background equivalent concentrations (BEC) and correlation coefficients of calibration curves for co-precipitated elements in a $CaCO_3$ matrix, obtained by LA-ICP-MS

Element	Concentration range [μg/g]	3σ-DL [μg/g]	BEC [μg/g]	R
Cr	1.3– 73	0.72	0.91	0.9933
Mn	6.7–402	0.06	0.10	0.9977
Co	2.0– 83	0.03	0.11	0.9998
Cu	1.0– 85	0.07	0.07	0.9969
Zn	3.3–104	0.12	0.17	0.9975
As	1.3– 23	0.03	0.11	0.9980
Cd	2.0–115	0.07	0.06	0.9978
Sn	1.7– 88	0.78	5.52	0.9946
Ba	2.3–105	0.70	0.71	0.9991
Hg	0.7– 54	0.21	1.35	0.9901
Pb	1.5– 92	0.02	0.02	0.9978

Table 4 Results from the quantitative analysis of the reference material Limestone JLs-1 (Japan), obtained by LA-ICP-MS and SN-ICP-MS. All concentrations expressed in μg/g

Element	LA-ICP-MS (*n* = 6)	SN-ICP-MS (*n* = 6)	Literature [citation]	Reference values
Cr	3.9 ± 0.5	1.7 ± 0.1		3.37
Mn	15.7 ± 0.7	17.0 ± 0.9	24.5[20]–11[14]	15
Co	0.098 ± 0.004	0.058 ± 0.007		0.083
Cu	0.32 ± 0.02	0.37 ± 0.03	0.27[20]	0.36
Zn	3.1 ± 0.1	3.3 ± 0.1	2.87[20]	3.19
As	0.17 ± 0.03	0.27 ± 0.03		0.15
Sr	224 ± 6	262 ± 5	331[20]–261[14]	295
Cd	0.23 ± 0.01	0.18 ± 0.02		0.16
Ba	610 ± 45	504 ± 34	528[20]	476
Pb	0.12 ± 0.01	0.08 ± 0.01		0.7

and plasma conditions as the sample counts and those polyatomic interferences caused by the $CaCO_3$ matrix (p.ex. $^{43}Ca^{16}O^+$ interfering on $^{59}Co^+$) are subtracted in this way. The detection limits (3σ-DL) and background equivalent concentrations (BEC) are shown in Table 3. BEC is by definition the analyte concentration producing a net signal equal to the background intensity at the line, and the estimate is equal to $\overline{x}_b / S$, where $\overline{x}_b$ is the mean background intensity and S is the sensitivity (given by the slope of the calibration curve). Comparing these data with the results of Price and Pearce [16] (DL of 1.3, 1.0, 1.2 and 0.2 for Cu, Zn, As and Pb, respectively), a good improvement in the detection limits was obtained. For some elements, however, quantification levels are more modest due to contamination of the $CaCO_3$ blank and (or) polyatomic interferences caused by the matrix (e.g. $^{43}Ca^{16}O^+ \rightarrow {}^{59}Co$; $^{43}Ca^{16}O\ {}^{16}O^+ \rightarrow {}^{75}As$).

Accuracy of the method was evaluated by analyzing one of the few available substances with similar matrix, the reference material JLs-1 (Limestone, Geological Survey of Japan), as pressed powder against the calibration graphs produced from the $CaCO_3$ standards. Table 4 shows mean concentrations and standard deviations obtained by quantitative analyses using LA-ICP-MS and SN-ICP-MS, literature reported data and the proposed values for this RM. Hg was not considered for quantitative analysis because its recommended value (0.056 μg/g) in the reference material is lower than the DL obtained in this study (see Table 3). For SN-ICP-MS analysis of this material, the more accurate standard addition calibration was used instead of the external calibration method. With the exception of Cr, Co and Pb, there is a good agreement between the values obtained in this study, for both techniques, and the recommended ones, taking into account the not reported uncertainties of the reference material. For these three elements, however, considerably lower concentrations than those proposed were obtained by SN-ICP-MS. In the case of Pb, the low concentration was also confirmed by the laser technique, indicating that the proposed value for this reference material may not be correct. For Cr and Co, there is a reasonable agreement of the laser results with the proposed values, however, the lower concentrations obtained by SN-ICP-MS could indicate that this is only an apparent agreement caused by not properly corrected polyatomic interferences from the solid $CaCO_3$ matrix : $^{40}Ar^{13}C$ on the ^{53}Cr- signal and $^{43}Ca^{16}O^+$ on $^{59}Co^+$. In SN-ICP-MS, due to the acid dissolution of the sample (in the case of Cr) and the calibration procedure (standard addition), both interferences would be of minor influence. In any case, due to the not known uncertainties of the proposed reference values, the observed differences should not be taken so seriously at this moment. Nevertheless, comparing the results obtained with those reported in the literature [14, 20], this study presents a general improvement in the accuracy of the quantitative analysis of carbonates by LA-ICP-MS (see Table 4).

Comparison with NIST glass standards.

Calibration with CRM glass standards (NIST 614, 612, 610) has been the most frequently employed procedure for the quantitative and semi-quantitative analysis of carbonates [7, 16] and similar matrices. However, as emphasized in previous work and reviewed by Durrant [19], the efficiency of the ablation process is much poorer in glass than in pressed powder carbonate materials and this figure arises mainly from the nature and hardness differences between them. Figure 2 shows images produced by scanning electron microscopy (SEM) of typical ablation craters produced by ablation of a fused glass disc (NIST 612), a pressed powder carbonate standard and a mussel shell *(Perna perna)*. For the same laser conditions, the shape, depth and morphology of the craters and, consequently, the ablated masses are very different for glass and carbonates. This results in a poorer sensitivity for glass standard calibration curves (see Fig. 3) and therefore in an overestimation of trace element concentrations in samples with carbonate matrix.

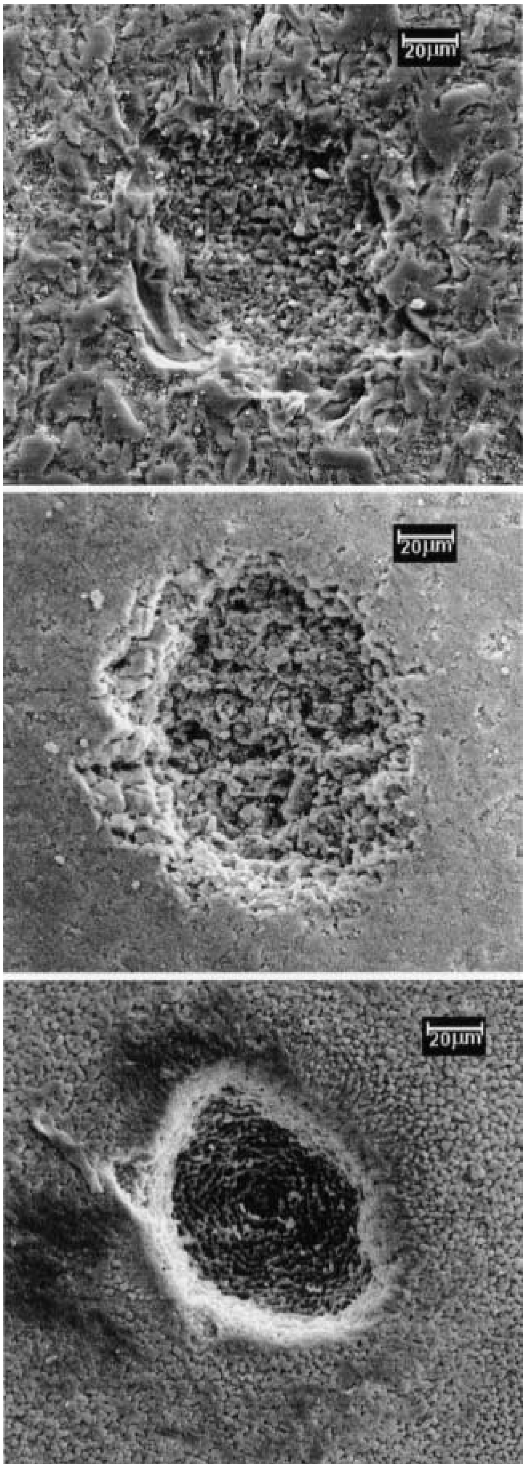

Fig. 2 Scanning electron microscope photographs of ablation pitches produced in: fused glass disc, pressed powder $CaCO_3$ standard and mussel shell (from the top to the bottom; magnification 500×; pitches produced by 10 shots, repetition rate 10 Hz, energy 4.5 mJ and defocus of 10 µm)

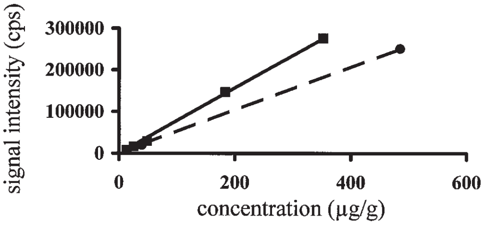

Fig. 3 Calibration graphs, exemplified by Mn, produced with $CaCO_3$ standard pellets and fused glass discs (NIST 614, 612, 610) showing the different sensitivities (S in cps/µg.g^{-1}) obtained in both matrices (S_{glass}: 519.3; $S_{calcite}$: 783.7); dashed line: NIST standards, solid line: $CaCO_3$ pellets

Examples of LA-ICP-MS applications in environmental monitoring using mussel shells.

Although it is not the primary purpose of this work to discuss trace metal accumulation in hard biological structures, at least two examples will be given to illustrate the application of the here introduced calibration procedure for the quantitative determination of elements in mussel shells. These discussions with biological and environmental focus will be presented elsewhere . Results of concentration profiles in shells of two specimens of *Perna perna* are presented in Fig. 4. In both cases, specimens collected from less polluted waters were introduced into a heavily polluted environment and maintained there until sufficient development of newly formed growth bands for analysis by LA-ICP-MS.

One example (Fig. 4a) is from an aquarium experiment in which implanted specimens of *Perna perna* were grown up, under controlled conditions, in seawater, which was changed daily and spiked at a concentration of 0.5 mg/L with the elements of interest (Cu, Cd, Pb, Zn and others). During a time period of 60 days, in which the animals were fed with phytoplancton, a mean growth band of about 3 mm was formed. Implantation of the specimens into the spiked seawater resulted in an sharp concentration increase of toxic elements, as exemplified by Cu, Cd and Pb, within the newly formed shell structure (Fig. 4a: > 25 mm), which follows the order: Pb > Cu > Cd. Preliminary results show, in general, preferential enrichment of these elements in soft tissue samples, however, for Pb enrichment is less pronounced than for Cd (e.g. $[Pb]_{tissue}$: $[Pb]_{shell} \approx 2.5$; $[Cd]_{tissue}$: $[Cd]_{shell} \approx 200$). Better knowledge about the distribution ratios of elements between both compartments, obtained under controlled conditions, will help to understand detoxification mechanisms for metals and to validate the use of shells as biological monitor.

The second example (Fig. 4b), obtained from a natural environment, confirms once more the ability of shells to register changes in metal water concentrations. In this case, specimens of *P. perna* were sampled from a moderately polluted oceanic beach (Itaipu, State of Rio de Janeiro), transplanted into a heavily polluted site within the Guanabara Bay (same state) and collected one month after exposure. During this time, a new growth band of

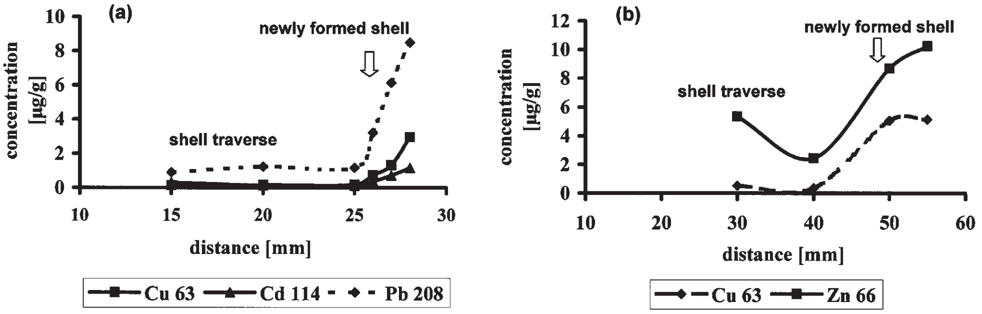

Fig. 4 a, b Examples of quantitative concentration profiles (from the inner to the outer shell) across the growth bands of two specimens of *Perna perna* showing the accumulation of some trace metals in the newly formed shell after different exposure conditions: (**a**) laboratory experiment; (**b**) environmental experiment (see text for further explanations)

about 15 mm had formed (Fig. 4 b: > 40 mm) in which the concentrations of Cu and Zn are significantly increased when compared to the levels before transplantation (< 40 mm). In terms of concentration, both elements are the most serious metal contaminants in this environment [21].

Conclusion

Incorporation of trace elements into the $CaCO_3$ matrix by co-precipitation is a better method for producing homogeneous standards than simple mixture of analytes, in solid or solution form, with the solid $CaCO_3$ matrix. The availability of these standards permitted quantitative analysis of carbonate materials, such as limestone and mussel shells, by LA-ICP-MS, avoiding systematic errors caused by calibration with materials of different ablation characteristics (e.g. glass standards). The ease and rapidity of analysis, without necessity of laborious sample preparation, and the space resolution are the main advantages for environmental studies as demonstrated in this study on mussel shells. The preliminary data shown here on the significant increase of toxic metals in the newly formed growth bands of shells from *P. perna*, after transplantation of specimens from less polluted into heavily polluted water, is a strong argument for the validation of shell material in biological monitoring.

Acknowledgments We acknowledge gratefully the dedication and skill of our laboratory technician A. J. Pereira in ICP-MS measurements. SEM pictures were made by M.F. da Silva Lopes from the DMCM of PUC. Shells from the Guanabara Bay were kindly provided by E.F. de A. Lima. This work was financially supported by FINEP/PADCT, Brazil (research contract NR. 65.92. 0012). One of the authors (V.B.) thanks for a research grant received from CAPES, Brazil.

References

1. Goldberg ED (1975) Mar Pollut Bull 6: 111
2. Cossa D (1989) Oceanol Acta 12: 417–432
3. Daskalakis KD (1996) Mar Pollut Bull 32: 794–801
4. Outridge PM, Evans RD (1995) J Anal At Spectrom 10: 595–600
5. Allison N (1996) Geochim Cosmochim Acta 60: 3457–3470
6. Thresher R E (1999) Fisher Res 43: 165–204
7. Stecher III HA, Krantz DE, Lord III CJ, Luther GW, Bock KW (1996) Geochim Cosmochim Acta 60: 3445–3456
8. Wilbur KM, Saleuddin ASM (1983) In: Saleuddin ASM, Wilbur KM (eds) The Mollusca Physiology, Vol. 4, Academic Press, New York, pp 238–235, 249–257
9. Lingard SM, Evans RD, Bourgoin BP (1992) Bull Environ Contam Toxicol 48: 179–184
10. Sturesson U (1978) Ambio 7: 122–125
11. Bourgoin BP (1990) Mar Ecol Prog Ser 61: 253–262
12. Carricker MR, Swann CP, Prezant RS, Counts CL III (1991) Mar Biol 109: 287–297
13. Sinclair DJ, Kinsley LPJ, McCulloch MT (1998) Geochim Cosmochim Acta 62: 1889–1901
14. Perkins WT, Fuge R, Pearce JG (1991) J Anal at Spectrom 6: 445–449
15. Raith A, Perkins WT, Pearce NJG, Jeffries TE (1996) Fresenius J Anal Chem 355: 789–792
16. Price GD, Pearce N J G (1997) Mar Pollut Bull 34: 1025–1031
17. Becker JS, Dietze H-J (1999) Fresenius J Anal Chem 365: 429–434
18. Denoyer ER, Kenneth JF, Hager JW (1991) Anal Chem 63: 445A–457A
19. Durrant SF (1999) J Anal At Spectrom 14: 1385–1403
20. Pearce NJG, Perkins WT, Fuge R (1992) J Anal At Spectrom 7: 595–603
21. Rebello AL, Haeckel W, Moreira I, Santelli R, Schroeder F (1986) Mar Chem 18: 215–225