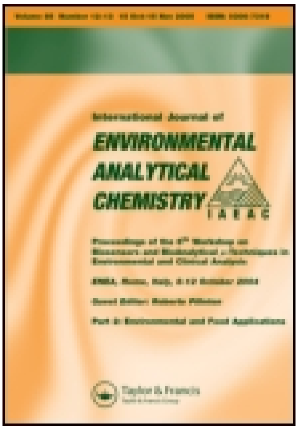

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

Determination of zinc in marine/lacustrine sediments by graphite furnace atomic absorption spectrometry using Pd/Mg chemical modifier and slurry sampling

Junling Bai [a] , Toshifumi Nakatani [a] , Yuuki Sasaki [a] , Hirotsugu Minami [a] , Sadanobu Inoue [a] & Nobuo Takahashi [a] [a]
[a] Department of Materials Science and Engineering, Kitami Institute of Technology, 165 Koen-cho, Kitami, Hokkaido 090-8507, Japan

To cite this article: Junling Bai, Toshifumi Nakatani, Yuuki Sasaki, Hirotsugu Minami, Sadanobu Inoue & Nobuo Takahashi (2011): Determination of zinc in marine/lacustrine sediments by graphite furnace atomic absorption spectrometry using Pd/Mg chemical modifier and slurry sampling, International Journal of Environmental Analytical Chemistry, 91:9, 856-865

To link to this article: http://dx.doi.org/10.1080/03067310903254610

Intern. J. Environ. Anal. Chem.
Vol. 91, No. 9, 10 August 2011, 856–865

Determination of zinc in marine/lacustrine sediments by graphite furnace atomic absorption spectrometry using Pd/Mg chemical modifier and slurry sampling

Junling Bai, Toshifumi Nakatani, Yuuki Sasaki, Hirotsugu Minami*,
Sadanobu Inoue and Nobuo Takahashi

Department of Materials Science and Engineering, Kitami Institute of Technology,
165 Koen-cho, Kitami, Hokkaido 090-8507, Japan

(*Received 9 March 2009; final version received 12 August 2009*)

Effectiveness of Pd/Mg chemical modifier for the accurate direct determination of zinc in marine/lacustrine sediments by graphite furnace atomic absorption spectrometry (GF-AAS) using slurry samples was evaluated. A calibration curve prepared by aqueous zinc standard solution with addition of Pd/Mg chemical modifier is used to determine the zinc concentration in the sediment. The accuracy of the proposed method was confirmed using Certified Reference Materials, NMIJ CRM 7303-a (lacustrine sediment) from National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, Japan, and MESS-3 (marine sediment) and PACS-2 (marine sediment) from National Research Council, Canada. The analytical results obtained by employing Pd/Mg modifier are in good agreement with the certified values of all the reference sediment materials. Although for NRC MESS-3 an accurate determination of zinc is achieved even without the chemical modifier, the use of Pd/Mg chemical modifier is recommended as it leads to establishment of a reliable and accurate direct analytical method. One quantitative analysis takes less than 15 minutes after we obtain dried sediment samples, which is several tens of times faster than conventional analytical methods using acid digested sample solutions. The detection limits are $0.13\,\mu g\,g^{-1}$ (213.9 nm) and $16\,\mu g\,g^{-1}$ (307.6 nm), respectively, in sediment samples, when 40 mg of dried powdered samples are suspended in 20 mL of $0.1\,mol\,L^{-1}$ nitric acid and a 10 µl portion of the slurry sample is measured. The precision of the proposed method is 8–15% (RSD).

Keywords: graphite furnace atomic absorption spectrometry (GF-AAS); slurry sampling; marine and lacustrine sediments; zinc; chemical modifier; palladium; magnesium

1. Introduction

Chemical processes occurring in subsurface marine and lacustrine sediments, such as reduction/oxidation, adsorption/desorption, and the like, have profound effects on the local and/or global cycling of elements. Determinations of trace elements such as (i) cadmium and lead and (ii) iron and manganese in sediments have received great interest due to their (a) hazardous effects on human beings and (b) important roles in the geochemical redox cycling [1], while zinc has been paid very little attention. In recent years,

---

*Corresponding author. Email: minamihr@mail.kitami-it.ac.jp

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310903254610
http://www.informaworld.com

however, determining the zinc distribution in sediments became important because (i) an anomalous depletion of zinc in marine sediments at a subsurface methane hydrate-bearing site was reported but the detailed information was not given [2], and (ii) zinc dissolution and reprecipitation in marine sediments could be associated with bacterial sulphate reduction [3]. Since methane hydrate in marine sediments of the continental-shelf floor of each country is one of the most important future energy resources in the world [4–6], the task to clarify the responsible correlations among the zinc variation, the chemical reactions and the methane hydrate occurrence became pressing. We must first determine the concentrations of zinc to prepare detailed zinc concentration-vertical/horizontal distribution profiles, especially around the depths where the bacterial sulphate reduction occurred in the hydrate-bearing sediments. Contrary to the sulphate reduction in common sediments, the concentration of sulphate decreased rapidly with depth and went down to the lowest values at approximately 0.4 m below the sea floor in methane hydrate-bearing sediments [7]. Additionally, as an international cooperative project, the methane hydrate-bearing core retrieved was used for different analysis by many researchers. Therefore, to prepare detailed zinc concentration-vertical/horizontal distribution profiles, we have to determine zinc in a large number of small amounts (less than 100 mg of a dried sample) of sediments.

Several studies determining the concentration of zinc in sediment samples have been reported; these have used sample solutions prepared mainly by acid digestion [8–10]. However, the preparation of sample solutions is time consuming and has a multistep procedure, which makes it difficult to analyse large numbers of sediment samples; e.g. more than several hundred samples per research voyage have to be analysed.

The direct determination of minor and trace metals by instrumental analysis such as GF-AAS, ICP-OES (inductively coupled plasma optical emission spectrometry) and ICP-MS (inductively coupled plasma mass spectrometry) using solid/slurry sampling techniques are very attractive because the analytical procedure has a number of advantages [11,12], which can be summarised as follows: (i) saving of the time required for sample dissolution; (ii) lower risk of contamination and analyte losses; and (iii) low detection limits based on the solids/slurries. However, when ICP-OES/ICP-MS were used, introduction of slurries by nebulisation into plasma requires extremely small particle sizes, typically <3 μm [13,14] (sediments from gas hydrate-bearing structures consist chiefly of particles larger than 2 μm [15,16]), or a vaporisation system, such as an electrothermal vaporisation device, is required [11,12]. On the other hand, the application of direct solid/slurry sampling in GF-AAS has attracted much attention [11,12,17–20], and a significant number of papers reported on this technique (nearly one order of magnitude larger than those reported on ICP-OES/ICP-MS) during the last two decades, a trend that continues up to the present [11]. GF-AAS holds advantage in terms of there being no strict size limitation of samples. It is reported that slurry samples with particle size of ca.50 μm were introduced into a graphite furnace quantitatively and analysed [17,18], while solid samples with a maximum of 10 mg were measured without special device/equipment [19,20]. Furthermore, from the perspective of the detection limit, GF-AAS is suitable for the determination of zinc in samples based on the previously reported detection limit values of commonly used instrumental analyses, as follows: (a) GF-AAS: $0.01\,\mu g\,L^{-1}$ [21], (b) ICP-MS: $0.15\,\mu g\,L^{-1}$ [21], (c) ICP-OES: $1\,\mu g\,L^{-1}$ [21].

Although Brady *et al.* attempted a direct determination of zinc in a coastal bay sediment sample by GF-AAS, a problem with the accuracy of their analytical value was found [22]. Nimmerfall and Schron reported the direct solid sample analysis of geological samples with GF-AAS using 3D calibration [23]. Their 3D calibration method, however, was complicated and time consuming since the 3D calibration is represented as a 3D calibration plane (analyte content (x-axis), sample weight (y-axis) and analyte absorbance (z-axis)) prepared by using 13 different certified reference materials with about 90 repetitive measurements. And a problem of the accuracy of their analysis of zinc was found in their report. That is to say, an accurate, rapid and direct determination of zinc in sediment samples by slurry/solid sampling using GF-AAS is yet to be reported.

The importance of chemical modifiers in GF-AAS has been reported [24], i.e. the use of a chemical modifier is required to increase the thermal stability of the analyte, to minimise the organic or inorganic matrix effects and background signals, and to allow their determinations in real samples [25]. Yang *et al.* reported the formation of a stable intermetallic solid solution of zinc and palladium in solutions based on the observation/analyses by scanning electron microscopy, X-ray diffraction and X-ray photoelectron spectrometry [26]. Cabon and Bihan reported that zinc in aqueous standard solution was stabilised by the adsorption of zinc on the magnesium nitrate salts [27]. However, there was no report on the use of chemical modifiers for the direct determination of zinc in sediment samples. Here we report on an accurate, rapid and direct determination of zinc in marine and lacustrine sediment samples by GF-AAS with a slurry sampling technique using palladium-magnesium nitrate as a chemical modifier, of which the effectiveness was evaluated.

2. Experimental

2.1 *Apparatus*

A Hitachi Model Z-2700 polarised Zeeman-effect background correction GF-AAS (Hitachi, Tokyo, Japan) and a model HR platform-type Cuvette (Hitachi Ltd., Tokyo, Japan) were used for the determination of zinc. A Mettler Toledo AG245 microbalance was used for weighing samples. An ultrasonic homogeniser VP-55 (Taitec, Japan) and a Model G-560 vortex mixer (Scientific Ind., USA) were used to mix the slurry samples. An Eppendorf Model 4700 micropipette (Eppendorf, Hamburg, Germany) was used for the injection of the zinc standard solution, slurry and a chemical modifier solution.

2.2 *Reagents and materials*

The zinc standard solution was prepared by diluting the zinc standard solution for AAS ($1000\,\mathrm{mg\,L^{-1}}$ solution; $Zn(NO_3)_2$ in $0.1\,\mathrm{mol\,L^{-1}}$ nitric acid, Wako Pure Chemical Industries, Japan). Certified reference materials of marine/lacustrine sediments (NRC MESS-3, NRC PACS-2, NMIJ CRM 7303-a) were obtained from the National Research Council (NRC; Ottawa, Canada) and National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology (NMIJ, AIST; Ibaraki, Japan). The Pd/Mg chemical modifier solution was prepared by diluting the palladium-magnesium nitrate chemical modifier solution (1% palladium, 1% magnesium, 15% nitric acid, Kanto Chemical Company, Japan). The other chemicals were of super special grade, and were used without further purification. Deionised water was purified by a Milli-Q water purification system (Elix UV5 and Milli-Q Gradient, Millipore, Japan). Argon was used as an internal gas and external gas for GF-AAS.

Table 1. Instrument setting and thermal program.

Instrument setting	
Wavelength	307.6 nm (working range: 0.6–40 ng)
Lamp current	5.0 mA
Slit width	1.3 nm

Thermal programme	Temperature (°C)	Ramp time(s)	Hold time(s)	Internal gas flow (mL min^{-1})
Drying	80–140	40	0	200
Pyrolysis	500	0	20	200
Atomisation	2000	0	5	30
Cleaning	2200	0	4	200

2.3 *Preparation of slurry samples and GF-AAS measurement with slurry samples*

Slurry samples were prepared as follows. A sample of 40 mg dried marine/lacustrine sediment was weighed and placed in a 30 mL polyethylene bottle, and a 20 mL portion of 0.1 mol L^{-1} nitric acid was added to the bottle. The slurry sample was then mixed for 10 min using an ultrasonic probe.

A 10 µL portion of the slurry sample without any dilution was injected into a graphite furnace using a micropipette. Prior to pipetting, the slurry sample in the bottle was mixed for a few seconds using either an ultrasonic probe or a vortex mixer. A 10 µL portion of Pd/Mg chemical modifier solution (Pd: 10 µg; Mg: 10 µg) was then injected into the graphite furnace. Premixing of the chemical modifier with sediment slurry in the 30 mL polyethylene bottle was also possible since there is no difference between zinc absorbance in sediment with premixing and without premixing (chemical modifier was added directly in the furnace) of Pd/Mg chemical modifier. The slurry sample was then dried, pyrolysed and atomised in the graphite furnace according to the results of the examination for the measurement of zinc given in Table 1. Wavelength 307.6 nm (working range: 0.6 ng–40 ng) was used to analyse zinc in marine/lacustrine sediment slurries. The detection limit of zinc using wavelength 213.9 nm was measured and given to show the possibility of a higher sensitive determination. Peak area absorbance was utilised. Zinc aqueous standard solution was used for the preparation of the calibration curve with addition of Pd/Mg chemical modifier.

3. Results and discussion

3.1 *Optimisation of heating conditions*

To obtain accurate and reproducible analytical results, it was necessary to optimise the conditions of both pyrolysis and atomisation as important factors for GF-AAS measurement with the slurry sampling technique. We investigated the relationship between the pyrolysis temperature and the zinc absorbance for sediment slurry (NRC MESS-3, NMIJ CRM 7303-a) and 1 mg L^{-1} zinc aqueous standard solution with addition of Pd/Mg modifier, and found that zinc absorbance was constant between 400°C and 600°C for all samples, as shown in Figure 1A. Accordingly, a pyrolysis temperature of

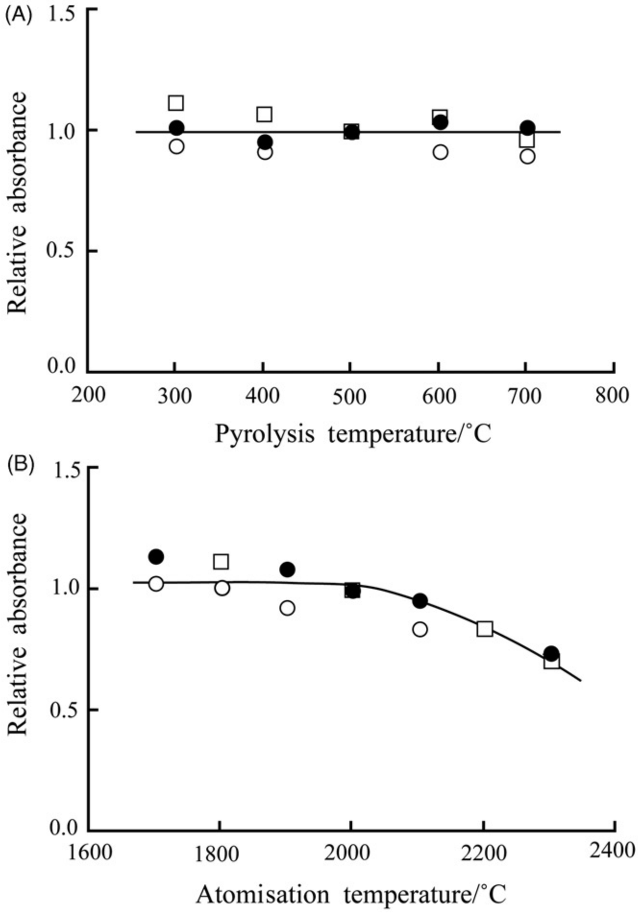

Figure 1. Relationship between zinc absorbance and pyrolysis temperature (A) and atomisation temperature (B). Sample: $1\,\mathrm{mg\,L^{-1}}$ zinc standard solution (closed circles); 40 mg NMIJ 7303-a in 20 mL of $0.1\,\mathrm{mol\,L^{-1}}$ nitric acid (open circles); 40 mg NRC MESS-3 in 20 mL of $0.1\,\mathrm{mol\,L^{-1}}$ nitric acid (open squares). Injection volume, 10 µL. Chemical modifier: 10 µg of palladium and 10 µg of magnesium.

500°C was selected. Similarly, the atomisation temperature was fixed at 2000°C (Figure 1B). In order to simultaneously and clearly show the variation trend of the absorbances of the three samples depended on the pyrolysis/atomisation temperature, the ratio of zinc absorbance obtained at each pyrolysis/atomisation temperature to that obtained under the thermal programme of 500°C (pyrolysis temperature) and 2000°C (atomisation temperature) is shown in Figure 1, and we call it relative absorbance.

3.2 *Analytical results obtained without a chemical modifier*

Although the standard addition method is considered to have an advantage over a calibration curve prepared by aqueous standard solution when the matrix of the sample influences the accuracy of the analyses, the standard addition method is a complicated and time-consuming procedure. To achieve a simplified and straightforward procedure by slurry sampling GF-AAS, the most important condition is to use the calibration curve prepared by zinc aqueous standard solution.

Zinc in marine/lacustrine sediments (NRC MESS-3, NMIJ CRM 7303-a, NRC PACS-2) was determined by GF-AAS with slurry sampling without any chemical modifier. Except for the NRC MESS-3, the analytical results obtained are found to disagree with certified values, mostly higher even when the standard addition method was used. It is therefore obvious that (i) zinc in sediment samples might be more thermally stable compared to that in aqueous standard solution, and/or (ii) the matrix effect of the samples could not be avoided even by using the standard addition method. To test this assumption, we investigated the absorption-time profiles for zinc without Pd/Mg chemical modifier (Figure 2A). The appearance times of the zinc absorption signals were quite similar for zinc aqueous standard solution and marine sediment (NRC MESS-3), while the absorbance peak obtained from lacustrine sediment (NMIJ CRM 7303-a) appeared later. We concluded that zinc in marine sediment (NRC MESS-3) and in aqueous standard solution had the same or similar chemical properties so that they are present in the same chemical form prior to the atomisation step. This may also explain why the analytical results for MESS-3 were in good agreement with the certified value without Pd/Mg chemical modifier. On the other hand, zinc in lacustrine sediment (NMIJ CRM 7303-a) seemed to appear in a different, more stable form. This is consistent with the higher

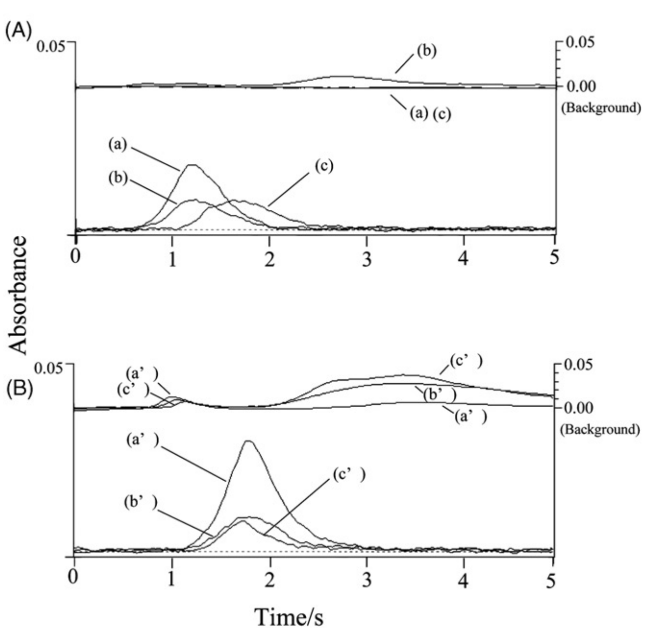

Figure 2. Absorption-time profiles of zinc without (A) and with (B) palladium-magnesium chemical modifier. (a) and (a′): 0.5 mg L^{-1} and 0.75 mg L^{-1} zinc standard solution (b) and (b′): 40 mg NRC MESS-3 in 20 mL of 0.1 mol L^{-1} nitric acid (c) and (c′): 40 mg NMIJ 7303-a in 20 mL of 0.1 mol L^{-1} nitric acid. Upper and lower profiles in both Figure 2A and Figure 2B are background absorbance and background corrected zinc absorbance, respectively. Injection volume, 10 µL. Chemical modifier: 10 µg of palladium and 10 µg of magnesium. The thermal programme used is shown in Table 1.

analytical results of the lacustrine sediment. Accordingly, accuracy problems may occur when zinc in sediment samples were determined without Pd/Mg chemical modifier.

3.3 *Effect of Pd/Mg chemical modifier on zinc absorbance*

The absorption-time profiles for zinc with the addition of palladium-magnesium nitrate as a chemical modifier are shown in Figure 2B. When a 20 µg Pd/Mg modifier as solution (Pd: 10 µg; Mg: 10 µg) was added, absorbance peaks obtained from all three samples (zinc aqueous solution and marine and lacustrine sediments) were delayed and appeared at almost the same time. Welz *et al.* reported that a later signal appearance time meant that the analyte atoms were in a hot gas environment that had already reached its final temperature, resulting in improved atomisation efficiency [28]. The chemical modifier added into the furnace presumably stabilised the zinc that presented in the same chemical form prior to the atomisation step for these three different samples.

In addition, a comparison between Figures 2A and 2B was made. The difference between the time of the zinc absorbance peak for the lacustrine sediment (NMIJ CRM 7303-a) with and without use of Pd/Mg chemical modifier was not observed. In other words, zinc in NMIJ CRM 7303-a was more stable than that of the other two samples, even without Pd/Mg chemical modifier. The reason why the lacustrine sediment slurry particles have an effect on the stabilisation of zinc is not clear yet, and further investigation is left to a future study.

On the other hand, MESS-3 shows identical absorbance-time profiles with those of zinc aqueous standard solution both with ((a′) and (b′) of Figure 2B) and without ((a) and (b) of Figure 2A) Pd/Mg chemical modifier. Accordingly, for some sediment, such as MESS-3, the determination of zinc without Pd/Mg chemical modifier, which leads to faster measurements and avoids using the valuable mineral palladium, is possible. However, the use of Pd/Mg chemical modifier is recommended as it leads to establishment of a reliable and accurate direct analytical method.

A series of measurements was carried out to determine the optimal mass of the Pd/Mg modifier to be used. Variations in the peak area absorbance for different mass (0–40 µg) of Pd/Mg modifier (Pd : Mg = 1 : 1, mass ratio) for sediment slurry (NMIJ CRM 7303-a and NRC MESS-3) and aqueous zinc standard solution were discussed. Zinc absorbances of all the samples increase with mass of Pd/Mg chemical modifier and reach the maximum and constant absorbance value more than 20 µg Pd/Mg (Pd: 10 µg, Mg: 10 µg); therefore, 20 µg Pd/Mg modifier (Pd: 10 µg; Mg: 10 µg) was used in this study.

In addition, the ratio of zinc absorbance without Pd/Mg chemical modifier to that with addition of 20 µg Pd/Mg chemical modifier is evaluated. The zinc absorbance ratio of NRC MESS-3 is almost the same as that of aqueous zinc standard solution, while NMIJ CRM 7303-a shows higher value than aqueous zinc standard solution, which is in good agreement with the fact that zinc in NRC MESS-3 is successfully determined without Pd/Mg modifier whereas the determination of zinc in NMIJ CRM 7303-a has an accuracy problem without Pd/Mg modifier, as described above.

3.4 *Relationship between concentrations of slurries and zinc absorbances*

To confirm quantitative sampling of the slurry into the furnace, we investigated the influence of the concentration of the sediment slurry on zinc absorbance. A calibration

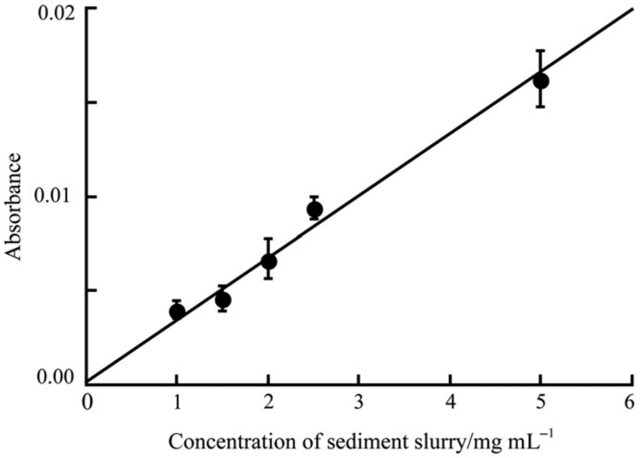

Figure 3. Relationship between concentration of sediment slurry and zinc absorbances. Sample: NRC MESS-3 in 20 mL of 0.1 mol L^{-1} nitric acid. Injection volume, 10 µL.

Table 2. Analytical results for zinc (µg g^{-1}) in certified reference materials of marine/lacustrine sediments by slurry sampling GF-AAS using calibration curve prepared by zinc standard solution.

NRC MESS-3 Marine sediment		NRC PACS-2 Marine sediment		NMIJ CRM 7303-a Lacustrine sediment	
Found value	Certified value	Found value	Certified value	Found value	Certified value
With Pd/Mg Modifier					
162 ± 23 ($n = 25$)	159 ± 8	364 ± 29 ($n = 20$)	364 ± 23	110 ± 17 ($n = 8$)	107 ± 5
Without Pd/Mg Modifier					
158 ± 15 ($n = 30$)	159 ± 8	489 ± 17 ($n = 10$)	364 ± 23	148 ± 14 ($n = 10$)	107 ± 5

curve was prepared by varying the concentration of marine sediment NRC MESS-3 in slurries, which were prepared by suspending different masses of sediment in 20 mL of 0.1 mol L^{-1} nitric acid. A linear relation between concentrations of slurries and zinc absorbances is shown in Figure 3. We confirmed that the quantitative sampling of the slurry was achieved within these slurry concentrations. Therefore, a slurry concentration of 2 mg mL^{-1} (40 mg of sediment in 20 mL of 0.1 mol L^{-1} nitric acid) was used in this study.

3.5 *Accurate direct determination of zinc by using calibration curve prepared by aqueous zinc standard solution with Pd/Mg chemical modifier*

Sediment reference materials were analysed by slurry sampling employing Pd/Mg modifier. The calibration was run against aqueous standard solutions with the chemical modifier. The analytical results are given in Table 2. The results of analyte found are in good agreement with the certified values. The accurate direct determination of zinc in various sediment samples is established by slurry sampling GF-AAS using calibration curves prepared by zinc aqueous standard solution with Pd/Mg chemical modifier.

For comparison purposes, analytical results of zinc in NRC MESS-3, NRC PACS-2 and NMIJ CRM 7303-a determined without Pd/Mg modifier are also shown in Table 2. An agreement between the found value of NRC MESS-3 and the certified value is obtained. However, the use of Pd/Mg chemical modifier is recommended as it leads to establishment of a reliable and accurate direct analytical method.

The detection limits for zinc are $16\,\mu g\,g^{-1}$ (wavelength: 307.6 nm) and $0.13\,\mu g\,g^{-1}$ (wavelength: 213.9 nm), respectively, in sediment samples, when 40 mg of powdered samples are suspended in 20 mL of $0.1\,mol\,L^{-1}$ nitric acid and a $10\,\mu L$ portion of the slurry sample is measured. The precision of the proposed method is 8–15% (relative standard deviation).

4. Conclusion

The use of slurry sampling GF-AAS using calibration curve prepared by aqueous zinc standard solution with Pd/Mg modifier provides an accurate and speedy analysis that can greatly enhance the technical ability to determine zinc in sediment samples.

Acknowledgement

This work was supported by the funding agency in Japan: The Japan Society for the Promotion of Science KAKENHI (No. 19550077).

References

[1] D.J. Burdige, *Geochemistry of Marine Sediments* (Princeton University Press, Princeton, 2006), p. 107.

[2] R.E. Cranston, G.D. Ginsburg, V.A. Soloviev, and T.D. Lorenson, Bull. Geol. Soc. Denm. **41**, 80 (1994).

[3] S. Severmann, R.A. Mills, M.R. Palmer, J.P. Telling, B. Cragg, and R.J. Parkes, Geochim. Cosmochim. Acta **70**, 1677 (2006).

[4] E.D. Sloan and C.A. Koh, *Clathrate Hydrates of Natural Gases* (CRC Press, Taylor & Francis Group, USA, 2007).

[5] C.K. Paull and W.P. Dillon, editors, *Natural Gas Hydrate: Occurrence, Distribution, and Detection, Geophysical Monograph 124* (American Geophysical Union, Washington, DC, 2001).

[6] M.D. Max, *Natural Gas Hydrate in Oceanic and Permafrost Environments* (Kluwer Academic Publishers, Dordrecht, 2003).

[7] H. Minami, A. Krylov, H. Sakagami, A. Hachikubo, K. Hyakutake, H. Tomaru, M. Kida, N. Takahashi, H. Shoji, T. Matveeva, Y.K. Jin, A. Obzhirov, and J. Poort, J. Geogr. **118**, 194 (2009).

[8] K. Inageki, A. Takatsu, T. Kuroiwa, A. Makama, S. Eyama, K. Chiba, and K. Okamoto, Anal. Bioanal. Chem. **378**, 1271 (2004).

[9] B. Schenetger, Fresenius' J. Anal. Chem. **359**, 468 (1997).

[10] G. Adami, I. Cabras, S. Predonzani, P. Barbieri, and E. Reisenhofer, Environ. Monit. Assess. **125**, 291 (2007).

[11] M. Resano, F. Vanhaecke, and M.T.C . de Loos-Vollebregt, J. Anal. At. Spectrom. **23**, 1450 (2008).
[12] U. Kurfürst, *Solid Sampling Analysis – Direct and Slurry Sampling using GF-AAS and ETV- ICP* (Springer-Verlag, Berlin, Heidelberg, 1998).
[13] F. Goodall, M.E. Foulkes, and L. Ebdon, Spectrochim. Acta, Part B **48**, 1563 (1993).
[14] L. Ebdon, M.E. Foulkes, and S. Hill, J. Anal. At. Spectrom. **5**, 67 (1990).
[15] D.J. Burdige, *Geochemistry of Marine Sediments* (Princeton University Press, Princeton, 2006), p. 46.
[16] T. Matveeva, V. Soloviev, H. Shoji, and A. Obzhirov, editors, *Hydro-Carbon Hydrate Accumulations in the Okhotsk Sea (CHAOS Project Leg I and Leg II). Report of R/V Akademik M.A.Lavrentyev Cruise 31 and 32* (VNIIOkeangeologia, St.Petersburg, 2005).
[17] H. Minami, T. Yoshida, K. Okutsu, Q. Zhang, S. Inoue, and I. Atsuya, Fresenius' J. Anal. Chem. **370**, 855 (2001).
[18] H. Minami, M. Yada, T. Yoshida, Q. Zhang, S. Inoue, and I. Atsuya, Anal. Sci. **20**, 455 (2004).
[19] H. Minami, Q. Zhang, H. Itoh, and I. Atsuya, Microchem. J. **49**, 126 (1994).
[20] H. Minami, Q. Zhang, S. Inoue, and I. Atsuya, Anal. Sci. **13**, 199 (1997).
[21] C. Vandecasteele and C.B. Block, *Modern Methods for Trace Element Determination* (Wiley, Chichester, 1993).
[22] D.V. Brady, J.G. Montalvo Jr, G. Glowacki, and A. Pisciotta, Anal. Chim. Acta **70**, 448 (1974).
[23] G. Nimmerfall and W. Schron, Fresenius J. Anal. Chem. **370**, 760 (2001).
[24] W. Salvon, D.C. Manning, and G.R. Carnrick, At. Spectrosc. **2**, 137 (1981).
[25] O. Acar, Anal. Chim. Acta **545**, 244 (2005).
[26] P. Yang, Z. Ni, Z. Zhuang, F. Xu, and A. Jiang, J. Anal. At. Spectrom. **7**, 515 (1992).
[27] J.Y. Cabon and A. Le Bihan, J. Anal. At. Spectrom. **9**, 477 (1994).
[28] B. Welz, G. Schlemmer, and J.R. Mudakavi, J. Anal. At. Spectrom. **7**, 1257 (1992).