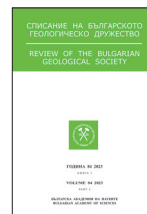




СПИСАНИЕ НА БЪЛГАРСКОТО ГЕОЛОГИЧЕСКО ДРУЖЕСТВО,
год. 84, кн. 3, 2023, с. 73–76

REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY,
vol. 84, part 3, 2023, p. 73–76



Национална конференция с международно участие „ГЕОНАУКИ 2023“
National Conference with International Participation “GEOSCIENCES 2023”

Efficient benchtop acid digestion of organic-rich sediments for ICP-MS analyses: testing analytical procedures on NIST 2702 standard reference material

Lora Bidzhova, Emiliya D. Raeva, Gatien L. F. Morin, Svetoslav V. Georgiev

Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; E-mail: lora.bidzhova@geology.bas.bg

Ефективно разтваряне на седименти, богати на органично вещество за ICP-MS анализ: тестване на аналитични процедури върху референтен материал NIST 2702

Лора Биджова, Емилия Д. Раева, Гатиен Л. Ф. Морин, Светослав В. Георгиев

Abstract. Trace element abundances in organic-rich sediments are widely used in various fields of the geosciences, yet few contributions discuss the effectiveness of low-cost benchtop acid digestion techniques for such samples. Here, we tested three different sample preparation methods (acid digestion in closed and open vessels, and fusion) on twelve powder aliquots of organic-rich sediment, standard reference material NIST 2702. Comparison of newly obtained ICP-MS and LA-ICP-MS results with their respective certificate values, facilitates the assessment of digestion efficiency and the effects of vessel size, acid mixture, and other parameters on the recoveries of 29 trace elements. Our results show that benchtop digestion of organic-rich sediment in closed 7 mL PFA vessels using HF+HNO₃+HClO₄ mixture is more efficient compared with open vessel digestion treated with the same acid mixture (± HCl), with closed or open vessel digestions without HClO₄, and with LA-ICP-MS measurements on fused glass discs.

Keywords: wet digestion, (LA) ICP-MS, digestion efficiency.

Introduction

The trace element content in organic-rich sediments is widely used for reconstructing the geologic history of rocks, regions, and our planet itself, particularly with regards to changes in climate, ocean redox state, water stratification, feeding provinces, continental runoff, surface water productivity, and for testing genetic links with hydrocarbons (e.g., Brumsack et al., 2006; Georgiev et al., 2019). Complete sample decomposition is needed for reliable trace element results measured by ICP-MS. Popular digestion methods include benchtop acid digestion in open and closed vessels, in sealed “bombs”, and

in specialized instruments (e.g., microwave, high-pressure asher), as well as alkali fusion (e.g., Cotta, Enzweiler, 2012; Hu, Qi, 2014). The advantages of benchtop digestion are ease of the setup (a fume hood, a hotplate and digestion vessels), low overall cost and large sample throughput. However, as with other decomposition techniques, care must be taken to ensure digestion of resistant minerals and to prevent newly formed precipitates. A number of studies compare the efficiency of benchtop acid digestion of mafic and felsic igneous rocks using different acids (HF, HNO₃, HClO₄, HCl; e.g., Balaram et al., 1995; Yokoyama et al., 1999; Cotta, Enzweiler, 2012), yet similar studies for organic-rich sediments

are relatively rare (e.g., Smirnova et al., 2002, Xu et al., 2012). To improve our understanding, we compared the efficiency of three sample preparation techniques by processing a standard reference material (SRM) and comparing our ICP-MS results with the known concentration of trace elements. The SRM included in this study was obtained from the National Institute of Standards and Technology (NIST).

Methodology

Ten aliquots of NIST 2702 (organic-rich marine sediment from Baltimore Harbor, USA) were acid-digested on a hotplate in closed and open vials with three different acid mixtures that are commonly used for silicate rock digestion: (i) $\text{HNO}_3 + \text{HF}$; (ii) $\text{HNO}_3 + \text{HF} + \text{HClO}_4$; and (iii) $\text{HNO}_3 + \text{HF} + \text{HClO}_4 + \text{HCl}$. These main variables (open versus closed vessel and type of acid mixture) account for five digestion series: closed vessel with HClO_4 ($n = 4$, n being the number of replicate digestions); closed vessel without HClO_4 ($n = 2$); open vessel with HClO_4 ($n = 1$); open vessel without HClO_4 ($n = 1$); and open vessel with both HClO_4 and HCl ($n = 2$). Approximately 100 mg of NIST 2702 powder aliquots were weighted out in three 15 mL and three 7 mL flat-bottom Savillex PFA screw-cap vials, and four 50 mL open PFA vials. Four total analytical blanks (TAB) in two 15 mL vials and two 7 mL vials followed the procedure for closed vessel acid digestion with HClO_4 . The reagent volumes and digestion parameters for the most efficient procedure (closed vessel acid digestion with HClO_4) are presented in Table 1 (all two- and

three-acid digestions follow similar procedures), which also shows details for the four-acid open digestion. For the quantification of 29 trace elements by ICP-MS at GI-BAS, a six-point calibration curve was constructed by ICP-MS analyses of freshly prepared multi-element calibration solutions (similar to analytical set up in Mihaylova et al., 2013).

In addition, two NIST 2702 aliquots were fused in a flux of lithium metaborate and lithium tetraborate, and fragments of the broken glass discs were mounted in epoxy resin and analyzed by LA-ICP-MS on the same ICP-MS instrument as acid-digested samples (for analytical details see Peytcheva et al., 2021).

Results and discussion

All four TAB samples have similar trace element patterns, with each element concentration roughly proportional to the volume of reagents used for digestion. In detail, TAB from 15 mL vials with $\sim 2\times$ more acid than 7 mL vials, have $\sim 2\times$ higher trace element contents, suggesting that measured TAB values are indeed representative for the acid contribution and indicating negligible random contamination during digestion.

The elements with highest overall recovery rates among the acid-digested series were Li, Be, V, Cr, Cu, Ga, Rb, Sr, Nb, Mo, Cd, Sn, Cs, Ba, Ce, Nd, Sm, W, Pb, Th, and U ($\pm 12\%$ of certificate values), followed by Sb, La and Tl ($\pm 15\%$ of certificate values). Somewhat lower recoveries for Sc, Co, Ni, Zn and As may reflect incomplete digestion but may also be related to technical issues during ICP-MS measurements that can be improved with in-house

Table 1. Details about acid digestion procedures in the closed vessel acid digestion group with HClO_4 and the open vessel acid digestion group with $\text{HClO}_4 + \text{HCl}$. All acids are concentrated; d H_2O = distilled water

	Acid	Vials mL	Stage	Reagents mL	Temperature/time $^{\circ}\text{C}/\text{h}$
Closed	3 acids + HClO_4	15 (7)	evaporate	0.5 (0.3) mL H_2O + 3 (1.5) mL HNO_3	25 $^{\circ}$ /15h \rightarrow 80 $^{\circ}$ /1h \rightarrow 150 $^{\circ}$ /1h
		15 (7)	digest/evaporate (2x)	3 (1) mL HNO_3 + 4 (2.5) mL HF + 1 (0.5) mL HClO_4	180 $^{\circ}$ /30h \rightarrow 80 $^{\circ}$ /20h 180 $^{\circ}$ /30h \rightarrow 180 $^{\circ}$ /4h
		15 (7)	evaporate (2x)	2 (1) mL HNO_3	150 $^{\circ}$ /1.5h
Open	4 acids + $\text{HClO}_4 + \text{HCl}$	50	evaporate	0.5 mL d H_2O + 2 mL HNO_3	180 $^{\circ}$ /1h
			digest/evaporate	1 mL HNO_3 + 5 mL HF	180 $^{\circ}$ /3h
			digest/evaporate	1 mL HClO_4	180 $^{\circ}$ /3h
			digest/evaporate	1 mL HNO_3 + 6 mL HF	180 $^{\circ}$ /3h
			digest/evaporate	2 mL HNO_3 + 1 mL HClO_4 + 5 mL HCl	180 $^{\circ}$ /3h
			evaporate (2x)	2 mL HNO_3	180 $^{\circ}$ /1h
All	–	–	final dilution	dilution to 50 mL with d H_2O	–

optimizations. Importantly, all results for the different sample preparation techniques were obtained on the same ICP-MS instrument and using similar procedures, suggesting differences between samples are likely related to the digestion procedures and not to ICP-MS measurements.

The digestion efficiency was estimated by comparing measured ICP-MS values relative to the SRM values (including certified, reference and information values). A statistical overview of all results shows the distribution of measurements from each digestion series that fall within a given accuracy range (Fig. 1). Open vessel acid digestion without HClO_4 is the least efficient, with recoveries lower than 65% of certificate values in 45% of all measurements and better than $\pm 20\%$ of certificate values in 35% of all measurements. In comparison, closed vessel digestion with HClO_4 yields the most satisfactory results with recoveries better than $\pm 20\%$ of certificate values in 80% of all measurements, and worse than $\pm 35\%$ for only 2% of all measurements. Open vessel digestion with HClO_4 , open vessel digestion with HClO_4 and HCl , as well as closed vessel digestion without HClO_4 , yield intermediate results (Fig. 1).

In addition, we note that closed 7 mL vials performed slightly better than closed 15 mL vials. The former have higher sample to reagent volume ratio (0.1:4) and less headspace (3 mL) compared

with larger vials (0.1:8 and 7 mL, respectively) (Table 1). Both factors might have contributed to relatively higher internal pressure, raising the boiling point during decomposition in the small vials and thus enhancing sample digestion. Based on the above considerations, we single out our most accurate results to closed vessel acid digestion with HClO_4 in small (7 mL) vials, raising recoveries to better than $\pm 20\%$ of NIST 2702 certificate values for most (85%) measurements, and better than $\pm 35\%$ of certificate values for virtually all (100%) measurements.

For comparison, 27 trace elements (Li and Be were not analyzed) determined by LA-ICP-MS show recoveries better than $\pm 20\%$ of certificate values in 67% of all measurements compared to 85% in the most accurate ICP-MS series; and recoveries worse than $\pm 35\%$ of certificate values for 14% of all measurements compared to none (0%) in the best ICP-MS series.

Conclusions and future directions

The efficiency of benchtop acid digestion of organic-rich samples was estimated based on comparison of ICP-MS measured trace element concentrations in NIST 2702 sediment with their referent values. Testing several variables including volume of the digestion vessel, type, and amount of acid, and

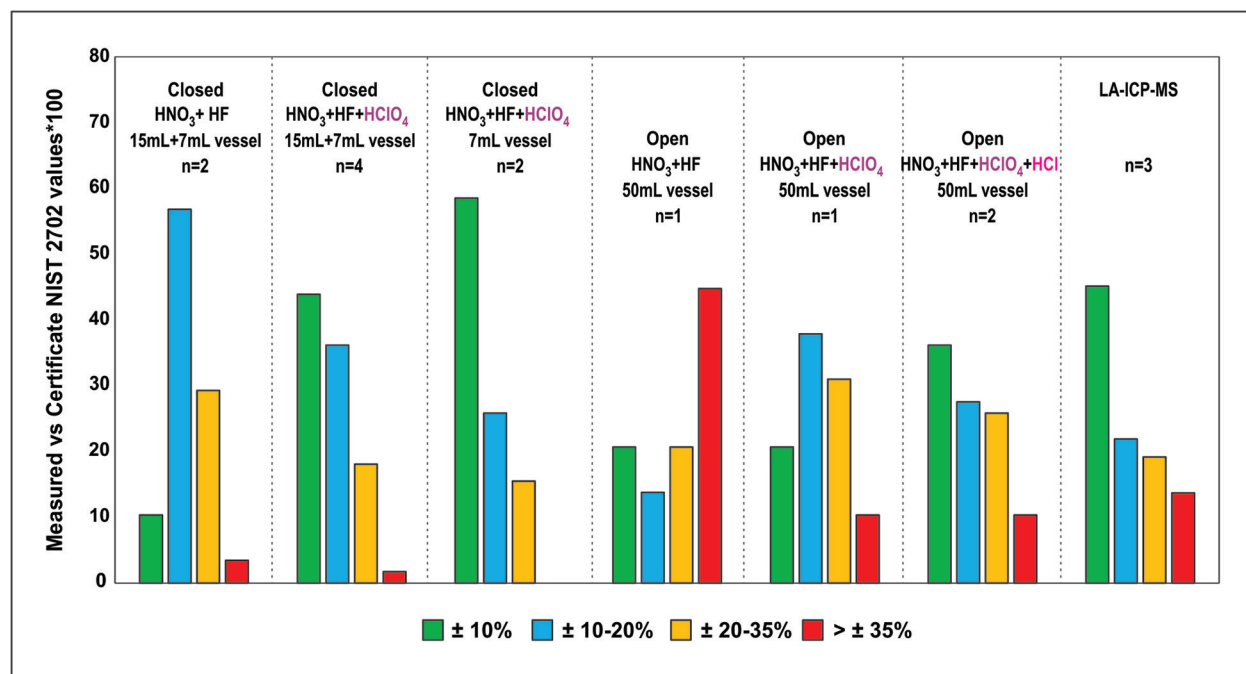


Fig. 1. Histograms showing the percentage of measurements within each digestion series that fall within $\pm 10\%$, $\pm 10-20\%$, $\pm 20-35\%$ and outside the $\pm 35\%$ deviation from NIST 2702 certificate values; all calculations are based on TAB corrected values; n = number of replicate samples tested for each procedure

close versus open vessel digestion procedure, we conclude that the most efficient digestion among the studied procedures, was decomposition in a mixture of $\text{HNO}_3 + \text{HF} + \text{HClO}_4$ in a closed (tightly screw-capped) vessel. We note that these are preliminary results, since the number of digestions and ICP-MS measurements for each procedure is insufficient to fully characterize the digestion efficiency. Further tests using the same setup and perhaps additional variables (such as the volume of acid, particularly in the larger vessels), combined with improved ICP-MS measurement protocols are needed for a more detailed characterization. Nevertheless, these new data clearly highlight the advantage of closed vessel benchtop $\text{HF} + \text{HNO}_3 + \text{HClO}_4$ digestion of organic-rich sediments compared with other tested benchtop digestion techniques.

Acknowledgements: This work is funded by project № КП-06-ДВ/6 of the Bulgarian National Science Fund. We thank Valentina Lyubomirova, Nadezhda Lihareva, Elitsa Stefanova, Valentin Ganey, Tanya Ilieva and Petya Boteva for helping with various aspects of the analytical work.

References

- Balaram, V., S. L. Ramesh, K. V. Anjaiah. 1995. Comparative study of the sample decomposition procedures in the determination of trace and rare earth elements in anorthosites and related rocks by ICP-MS. – *Fresenius' J. Analytical Chemistry*, 353, 176–182; <https://doi.org/10.1007/BF00322955>.
- Brumsack, H. J. 2006. The trace metal content of recent organic carbon-rich sediments: implications for Cretaceous black shale formation. – *Palaeogeography, Palaeoclimatology, Palaeoecology*, 232, 2–4, 344–361; <https://doi.org/10.1016/j.palaeo.2005.05.011>.
- Cotta, A. J., J. Enzweiler. 2012. Classical and new procedures of whole rock dissolution for trace element determination by ICP-MS. – *Geostandards and Geoanalytical Res.*, 36, 1, 27–50; <https://doi.org/10.1111/j.1751-908X.2011.00115.x>.
- Georgiev, S. V., H. J. Stein, J. L. Hannah, G. Yang, R. J. Markey, C. E. Dons, J. H. Pedersen, R. Di Primio. 2019. Comprehensive evolution of a petroleum system in absolute time: the example of Brynhild, Norwegian North Sea. – *Chem. Geol.*, 522, 260–282; <https://doi.org/10.1016/j.chemgeo.2019.05.025>.
- Hu, Z., L. Qi. 2014. 15.5 – Sample digestion methods. – In: Holland, H. D., K. K. Turekian (Eds.), *Treatise on Geochemistry* (Second edition). *Reference Module in Earth Systems and Environmental Sciences*, 15, 87–109; <https://doi.org/10.1016/B978-0-08-095975-7.01406-6>.
- Mihaylova, V., V. Lyubomirova, R. Djingova. 2013. Optimization of sample preparation and ICP-MS analysis for determination of 60 elements for characterization of the plant ionome. – *Intern. J. Environmental Analytical Chemistry*, 93, 13, 1441–1456; <https://doi.org/10.1080/03067319.2012.736978>.
- Peytcheva, I., A. von Quadt, V. Kostov-Kytin, M. Kadiyski, M. Stavrev. 2021. U–Pb dating and composition of columbite from Vishteritsa: Implication for timing of granite magmatism and rare-element granitic pegmatites in the Western Rhodopes, Bulgaria. – *Geologica Carp.*, 72, 3, 195–212; <https://doi.org/10.31577/GeolCarp.72.3.2>.
- Smirnova, E. V., I. N. Fedorova, G. P. Sandimirova, L. L. Petrov, N. G. Balbekina, V. I. Lozhkin. 2003. Determination of rare earth elements in black shales by inductively coupled plasma mass spectrometry. – *Spectrochimica Acta, Part B: Atomic Spectroscopy*, 58, 2, 329–340; [https://doi.org/10.1016/S0584-8547\(02\)00152-0](https://doi.org/10.1016/S0584-8547(02)00152-0).
- Xu, G., J. L. Hannah, B. Bingen, S. Georgiev, H. J. Stein. 2012. Digestion methods for trace element measurements in shales: Paleoredox proxies examined. – *Chem. Geol.*, 324, 132–147; <https://doi.org/10.1016/j.chemgeo.2012.01.029>.
- Yokoyama, T., A. Makishima, E. Nakamura. 1999. Evaluation of the coprecipitation of incompatible trace elements with fluoride during silicate rock dissolution by acid digestion. – *Chem. Geol.*, 157, 3–4, 175–187; [https://doi.org/10.1016/S0009-2541\(98\)00206-X](https://doi.org/10.1016/S0009-2541(98)00206-X).