

## Application Note

# Ultra trace level measurement of barium by ICP-MS after application of alkaline sodium fusion

23/11/2022

### Authors

J.L. Mas<sup>1</sup>, J. Mantero<sup>2</sup>, M. Villa-Alfageme<sup>2</sup>, A. Calleja<sup>3</sup>, E. Alonso<sup>4</sup>.



<sup>1</sup> Dpto. Física Aplicada I, Avda. Reina Mercedes s/n. Universidad de Sevilla.

<sup>2</sup> Dpto. Física Aplicada II, Avda. Reina Mercedes s/n. Universidad de Sevilla.

<sup>3</sup> Servicio de radioisótopos, CITIUS, Avda. Reina Mercedes 4B, Universidad de Sevilla.

<sup>4</sup> Dpto. Química Analítica, C/Virgen de África 7, Universidad de Sevilla.



## 1. Introduction

The analysis of biogenic Ba in ocean particulate material has been proposed as a proxy to calculate the remineralization rate of particulate organic carbon (POC) at the mesopelagic zone. Micro-crystals of biogenic Ba (Ba "in excess", Ba<sub>xs</sub>) accumulate in the twilight zone as barite (BaSO<sub>4</sub>) that precipitate inside biogenic aggregates and pellets. The concentration of Ba in these particles can exceed the range 100-1000 ppm (Dehairs et al., 2000).

The first analytical problem deriving from this proxy is that open ocean samples contain very scarce mass amount, usually in the range of a few tenths of milligrams. This fact limits the use of well-established techniques for the quantification of Ba, such as XRF that requires a large amount of mass. As an alternative, high sensitivity instruments such as ICP-OES or ICP-MS have been proposed for these analyses after digestion of the samples.

The second problem associated to this analysis is the lack of appropriate certified reference materials for ocean particles to implement alternative methods.

The third analytical problem, and the most important for using this proxy with a destructive technique such as ICP-MS, it is related to the use by many authors of mineral acids such as HNO<sub>3</sub>, HCl, HF and even HClO<sub>4</sub> for sample digestion, despite the well-known fact that BaSO<sub>4</sub> cannot be completely dissolved in such media, where it has extremely low solubility (Tian et al., 2020). This fact leads to uncontrolled, incomplete sample digestion, random underestimating of Ba concentrations, and it raises some questions regarding some of the conclusions published in the literature about oceanographic Ba.

We propose the use of alkali fusion with KHSO<sub>4</sub> as an alternative; a robust complete dissolution procedure to be used for transferring biogenic Ba to a solution, analyzable by ICP-OES or ICP-MS techniques.

Alkali fusion with KHSO<sub>4</sub> has been successfully applied to the total digestion of refractory matrices including industrial sludges and sulfates (Mantero et al., 2010). This approach, however, presents two main drawbacks: 1) the large amount of salt required for alkali fusion implies high Total Dissolved Solid contents (TDS), hence the produced solutions require the use of high dilution factors (DFs) before the analysis. 2) The presence of HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> anions in the produced solutions introduce severe sample matrix effects in the plasma, affecting the quality of the results. A time-consuming analyte separation could be applied to avoid those matrix effects. Alternatively, additional DFs could be applied; however, this approach could lead to analyte concentrations falling below the limit of detection of the technique.

This note tests the potential of alkali fusion for the analysis of Ba<sub>xs</sub> using an ICP-MS coupled to a new high efficiency nebulizer. The aim of this work is finding DFs high enough as to provide analytical quality results, and low enough as to allow a proper quantification of the Ba resulting concentrations.

## 2. Experimental

### Instrumentation

The measurements were performed with an Agilent 8800 ICP-MS/MS instrument (Servicio de Radioisótopos, CITIUS, Univ. of Seville, Spain). The general operating conditions are provided in Table 1.

Nebulization was carried out using the new MassNeb<sup>®</sup> nebulizer (Ingeniatrics, Camas, Seville, Spain), which is specifically designed for its use in ICP-MS instruments. This nebulizer allows high TDS levels (100 g/L) and provides an inert sample pathway. Its size fits to conventional endcaps, and the Super Flangeless Ferrules<sup>™</sup> allows a direct and fast connection of the nebulizer to the Teflon-T used for online mixing of the sample and the internal standard solutions. Excepting certain tests, the samples were introduced using a CETAC ASX-560 autosampler.

Parameter	Conditions
Carrier gas flow rate	0.71 mL/min
Make up gas	0.37 mL/min
Uptake/Peristaltic pump stabilization	45 s, 0.3 rps / 20s, 0.1 rps
Wash-out program	1% HNO <sub>3</sub> , 65 s, 0.3 rps
Sample uptake during analysis	0.25 mL/min (0.13 rps)
ORS	Off (no gas)
Measurement mode	SingleQuad
Internal standard	<sup>103</sup> Rh (online)
Detection	1 peak per mass, 4 replicates, 1000 sweeps
Counting times:	Ba (135, 137, 138): 1.2 ms. 67, 69, 97, 101, 105, 118, 121, 125, 131: On demand, ranging 0.21-0.26 ms.

**Table 1.** Operating conditions for the Agilent 8800 ICP-MS/MS coupled to MassNeb<sup>®</sup> nebulizer.

## Standards and sample preparation

Instrument was tuned with a solution containing 0.5-1.0 ng/mL of <sup>7</sup>Li, <sup>89</sup>Y, <sup>140</sup>Ce and <sup>205</sup>Tl (Spex Certiprep, NJ, USA). Ba was measured using a standard solution at 1024 ppm subsequently diluted (SCP-Science, Quebec, Canada). All the dilutions were performed by using fresh milliQ water and 1% HNO<sub>3</sub> derived from 69% HNO<sub>3</sub> (Sigma Aldrich, Darmsdadt, Germany) after double distillation (Savillex DTS-100, MN, USA).

The procedural blanks were prepared using reagent grade HKSO<sub>4</sub> (Merck, Germany), 25 g of this salt, per replicate, were used to prepare procedural blanks equivalent to the analysis of 200 mg of solid sample; the possibilities and constrains of downscaling these mass amounts are shown further on.

The sample is added to the HKSO<sub>4</sub> salt melted at a Bunsen burner; after thorough mixing and new melting, the crucible is heated inside an oven at 800 °C. The sample is collected using ~ 200 mL of 8M HNO<sub>3</sub>. Details of the procedure can be found in (Mantero et al., 2010)

As the solution cannot be directly introduced into the ICP-MS on a routine way, different DFs were applied by using milliQ water and HNO<sub>3</sub>, being the final HNO<sub>3</sub> concentration in the range of 1-2 %.

Each of these diluted replicates was spiked with Ba to achieve a resulting concentration equivalent to analyzing 200 mg of particles containing 50 ppm (i.e., conservative approach for concentration, optimistic approach for mass sample amount) of Ba by alkali fusion and diluting the resulting solution to levels DF ~ 50 – 400 m:m. That provides solutions with nominal Ba concentrations ([Ba]<sub>nominal</sub>) in the range of 0.1-2.3 ppb. From each of those spiked samples, an aliquot was taken and spiked again to increase the Ba concentration by ~ 20-30 % regarding [Ba]<sub>nominal</sub>. Then we define a recovery as:

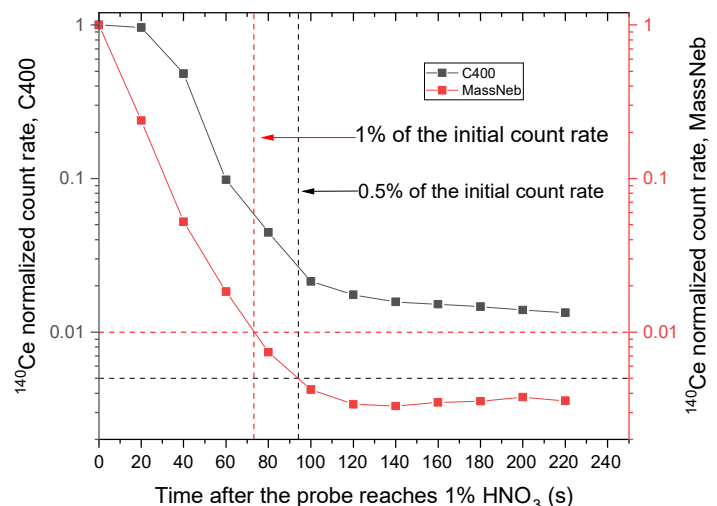
$$R = 100 \frac{[Ba]_{2-spike,measured} - [Ba]_{1-spike,measured}}{[Ba]_{2-spike,nominal} - [Ba]_{1-spike,nominal}}$$

Both solutions were analyzed by external calibration. According to USEPA 200.8 quality guidelines should R result within a range 85-115 % (within the uncertainty intervals), that would pass the quality control test for matrix-matched samples, meaning that no important sample matrix effects are being detected.

Additionally, a QC-sample (blank) was analyzed both at the end of the calibration line and replicated every 2-3 measurements to provide that no important memory effects are being detected. The USEPA-200.8 suggests some other QC-samples such as replicate standards, replicate samples, etc. Being those tests routinely passed at this lab, the results are not included in this note for the sake of brevity.

## 3. Results and discussion

Many of the problems associated with sample matrix and memory effects depend on the used nebulizer and its configuration. The design of MassNeb<sup>®</sup> minimizes the dead spaces, resulting in good performances for washing and minimizing memory effects, as can be found in Figure.1 that compares performance with the default system frequently used in this laboratory.



**Figure 1.** Normalized count rates after nebulizing 1 ppb of Ce for ~ 15 min subsequently nebulizing 1% HNO<sub>3</sub> (0.1 rps, please note that no autosampler was used in this test, hence increasing the tubing length will increase the wash-out times unless a higher peristaltic pump rate is applied)

The signal drops to 1% of the initial value after just ~ 70 s, and to 0.5 % of the initial value after just ~ 90 s. This feature could be extremely useful for the analysis of complicated matrices like the one this note is analyzing. Also for persistent analytes such as I, Hg or Th

On the other hand, and after an appropriate tuning of the nebulizer working conditions, we did find high sensitivities, in the range of 1.86 Mcps/ppb, 3.8 Mcps/ppb and 2.7 Mcps/ppb for <sup>59</sup>Co, <sup>140</sup>Ce and <sup>205</sup>Tl, respectively (background corrected). These performances ensure sensitivity high enough as to provide a convenient count rate at the most difficult Ba concentration level, circa 0.1-0.2 ppb.

The external calibration is presented for <sup>138</sup>Ba in Figure 2. This one is the highest abundance isotope of barium although it is overlapped by La and Ce isotopes; the reason why we used this isotope for this technical note is that, unexpectedly, La and Ce count rates in the samples were several orders of magnitude less than those of Ba isotopes. The same situation was found for the other potential interferences monitored, shown in Table 1.

For true real-natural samples, where Ce or La could be expected at high concentrations, 135-137 isotopes should be considered: according to the respective natural abundances, MassNeb® nebulizer would still provide sensitivity enough as to perform the analysis while obtaining high count rates and statistically significant results.

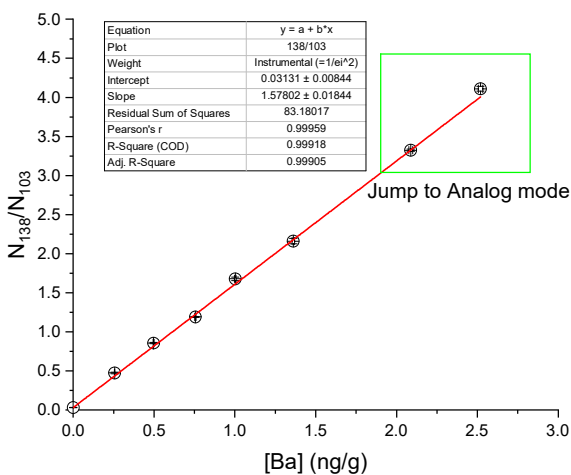


Figure 2. Figure 2: External calibration line used in this work with MassNeb®

Figure 3 shows the values of R obtained as a function of the applied DF. The results show that after applying a DF of ~ 175, the coupled performances of MassNeb® nebulizer and the applied procedure allows quantifying Ba concentrations by using an external calibration line and alkali fusion of samples while overcoming the exigent requirements of USEPA 200.8 procedure for the detection of sample matrix effect.

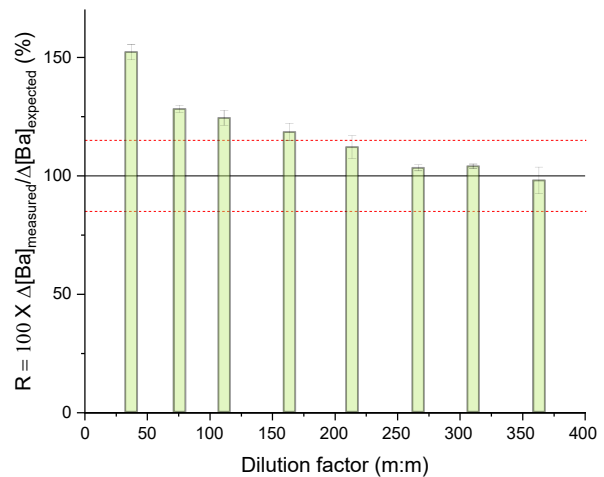
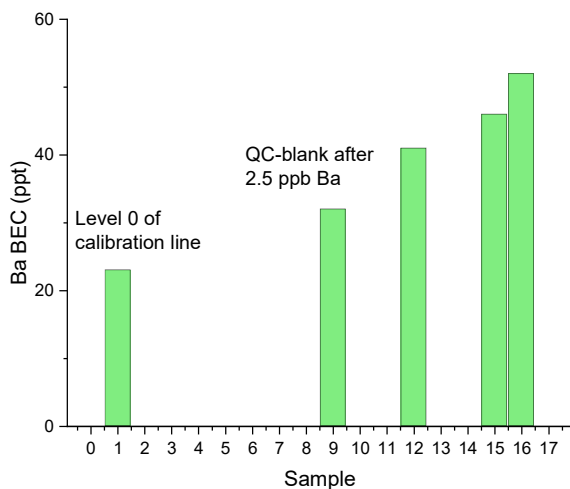


Figure 3. Obtained recoveries for Ba spiked concentrations as a function of the applied dilution factors. Red lines mark the usual confidence intervals suggested in USEPA 200.8. Expanded uncertainties for R are expressed in terms of k = 1 significance level according to GUM-2009 guidelines.

As expected, higher DFs imply smaller Ba concentrations and therefore higher relative uncertainties in the calculation of R. However, the performances of the system are good enough as to provide a robust and reliable procedure as to perform the required analyses with the higher standards of quality that would be required for any chemical laboratory.

Figure 4 shows the background equivalent concentration (BEC) obtained for the previously mentioned QC-blanks during the analytical running. Bearing in mind that the solutions were analyzed in increasing Ba concentrations (i.e., decreasing DFs), it is not strange to find that BEC increases. However, as can be seen for points 3-4, the application of a DF in the range of 150-200 does not increase the corresponding BEC in a proportion that would preclude the measurement of Ba concentrations in the range of 0.4-0.8 ppb (the expected concentration for low-concentration Ba particles).



**Figure 4.** Ba-BEC (ppt) for different replicates of a blank solution.

Finally, we could consider what happens in cases where not even 0.2 g of sample are available for analysis. The results suggest that if downscaling sample and salt mass amounts, the alkali fusion procedure would still be affordable for the analysis of ocean particles: decreasing mass sample amount to, for example, 0.02 g, would require decreasing salt mass to 2.5 g,

although the DF to be applied to the sample solution should be chosen with care.

## 4. Conclusions

We have shown that alkaline fusion, together with an appropriate choosing of DF, could be a good alternative to mineral acid digestion for the analysis of Ba<sub>xs</sub>.

The use of MassNeb® nebulizer with ICP-MS allows overpassing the exigent Quality-checks of USEPA-200.8 method in complicated matrices such as those resulting from alkali fusion.

Furthermore, MassNeb® small memory effects suggests that its application could be useful for other complicated matrices and persistent analytes such as I, Hg or Th.

Finally, this nebulizer's high transport efficiency and high sensitivity allows quantification of analyte below the sub-ppb level.

## References

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# Ingeniatrics



*Nebulizers and Nozzles*

P.I. Parque Plata  
C/ Camino Mozárabe, 41  
41900 Camas, Seville  
(Spain)

(+34) 954 08 1214  
[info@ingeniatrics.com](mailto:info@ingeniatrics.com)

[www.Ingeniatrics.com](http://www.Ingeniatrics.com)