

**European Mountain lake Ecosystems: Regionalisation,
diaGnostics & socio-economic Evaluation**

EMERGE

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**CHARACTERIZATION OF LAKE SEDIMENTS – EXTRACTION
METHOD OF ELEMENTS SOLUBLE IN AQUA REGIA**

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Characterization of lake sediments – Extraction method of elements soluble in aqua regia.

Extraction method of elements soluble in aqua regia. European Standard CEN/TC 308/WG 1/TG 1 (Method C, microwave oven)

Definition .-

Aqua regia : Digestion solution obtained by mixing 1 volume of nitric acid and 3 volumes of hydrochloric acid.

Reagents.-

Concentrate HCl and HNO₃, “Baker RA”.

Deionized water “Milli-Q”.

The reagents used shall be of sufficient purity as not introduce a significant error into the subsequent analysis. A reagent blank comprising the same quantity of acid shall be taken through the entire procedure with each batch of analysis.

Apparatus .-

A calibrated microwave oven “Milestone Mega-MLS-1200” with programmable power and 6 closed PFA 100 ml high pressure vessels (110 bar) equipped with a system capable of controlling surpression in order to avoid explosion of the vessel.

Pressure vessels cleaned by aqua regia digestion in the same condition as sample attack.

All glassware and plasticware cleaned with HNO₃ 1/10 soaking during 24 hours.

Procedure .-

Weigth approximately 0,5 g, to the nearest 0,001 g, of the wet sample and transfer to the PFA vessel. Add 1 ml HNO₃ and 3 ml HCl. Place cover and spring on the top of the vessel. Place it in the rotor. Place the loaded rotor in the microwave and start the digestion program:

- | | |
|----------|-----------------|
| Step 1 - | 2 min. at 250 W |
| Step 2 - | 2 min. at 0 W |
| Step 3 - | 5 min. at 250 W |
| Step 4 - | 5 min. at 400 W |
| Step 5 - | 5 min. at 500 W |
| Step 6 - | 15 min. vent. |

At the end of the programme, cool the rotor to room temperature. Check vessels for surpression and open the vessels slowly under fume extraction, then transfer the digested sample into a 50 ml volumetric flask, filtering through acid washed paper and dilute to the mark with water.

A blank test shall be carried out in parallel by the same extraction procedure in every rotor.

Measurements.-

Apparatus .-

Inductively Coupled Plasma (ICP-OES) "Thermo Jarrell-Ash, model 61E Polyscan".

Inductively Coupled Plasma (ICP-OES) "Perkin Elmer, model Optima 3200 RL".

Mass Spectrometry Inductively Coupled Plasma (ICP-MS) "Perkin Elmer ELAN 6000".

Extracts and blanks diluted 1/5 and 1/20 with deionized water.

Calibration with 5 standards in aqua regia.

Rhodium used as internal standard in ICP-MS.

Analysis of As, Se and Hg by hydride generation ICP-MS, if necessary.

Quantification limits based on wet original sample, in $\mu\text{g/g}$ (ppm), depending on matrix:

Fe	5 - 10 ppm
Mn	2,5 - 5 ppm
Al	50 - 100 ppm
Ti	0,2 – 1 ppm
Cu	0,2 – 1 ppm
Zn	1 – 5 ppm
Pb	0,2 – 0,4 ppm
Cd	0,1 – 0,2 ppm
As	0,1 – 0,2 ppm
Se	0,1 – 0,2 ppm
Hg	0,4 ppm

Method Validation.-

Aqua regia extraction and analysis validated with Reference Material CRM 144R.

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Will be updated by Lluís Camarero

Comments on trace metal analysis for EMERGE.

About reporting detection levels:

Before going into the analytical procedures themselves, some precisions on the detection limits are needed. In ICP-MS technique the detection limit largely depends on the composition of the matrix (all extracted elements that are not to be analysed and can be in high concentration). It is difficult to say a priori what interferences due to the matrix will be found, and the right way to establish accurately the detection levels is by addition of several internal standards to the sample. The detection levels reported by the U. Barcelona lab (SCT) are estimations based on the standard deviation of blanks: by definition, the reporting (or quantification) detection limit (RDL) is 10 times this std. dev., while the method detection limit (MDL) is 3 times the std. dev. The values indicated by the SCT are rather conservative estimates of the RDL, as they do not want to promise something that will be later impossible in practice. Nevertheless, if we look at the MDL, these will be at least 3 times lower, and possibly (hopefully) better when established by standard addition, than RDL. Standard addition will not be performed for all samples, since this would multiply the work by 4 or 5, but in a set of samples enough to get a good idea of the performance of the method.

Detection levels.

In the table below there is a comparison of the detection levels for trace metal analysis in sediments reported by the Trace Metal Section of the Department of Natural Resources of the EPA (as a reference lab; http://dnr.metrokc.gov/wlr/envlab/Sections/MET/met_intr.htm) and by the SCT, in ppm referred to dry weight (note that previously it were referred to wet weight by the SCT, assuming a solid content of 50%).

element	MDL (EP)	RDL (EPA)	RDL (SCT)
Cd	0.08	0.8	0.2 - 0.4
Pb	0.2	0.8	0.4 - 0.8
As	0.2	0.8	0.2 - 0.4
Se	0.4	2	0.2 - 0.4
Hg	0.02	0.1	0.8

In all cases the RDL at the SCT are better, with the exception of Hg. Hg at the EPA lab is analysed separately in a dedicated CVAA analyzer, while the rest of metals are done by ICP-MS.

Improving the detection level for Hg.

The factor that determines the detection level is the dilution at which the extract has to be brought in order to make it acceptable for injection into the instrument. In the case of concentrated acids (as aqua regia is) the extract has to be diluted by 20 times. Weaker extractants may do not need to be diluted that much, but then the extraction capacity is much lower. As an example, the following table shows the Pb extraction capacity of different extractants in a stepwise extraction and an extraction with concentrated HNO₃ + H₂O₂ on surface sediments of lake Redó (concentration in ppm dry weight):

						nitric acid
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step 1	step 2	step 3	step 4	step 5	step 6	extraction
11	86	141	51	26	9	298

step 1: 1 M ammonium acetate

step 2: 1 M ammonium acetate + acetic acid

step 3: 0.04 M hydroxylamine hydrochloride in 25% acetic acid

step 4: 30% H₂O₂ + 1.4 ammonium acetate in 9% HNO₃

step 5: 0.2 M sodium hydroxide

step 6: concentrated hydrofluoric + nitric acids

Upon a total of 325 ppm (sum of step 1 to 6), the concentrated nitric extraction would extract 92% of Pb, whereas a mild acid extraction (equivalent to step 1 + 2) would extract an amount as low as 30%. In the case of Hg, which is largely found in organic forms, could be even worse.

Hydride generation does accept higher acid concentration in the samples and this could improve the detection limit by 4 or 5 times, but only inorganic Hg susceptible to be reduced to hydride is then determined. That means that since organic matter is not 100% mineralized with aqua regia, the remaining methyl-Hg (for instance) is not measured. An alternative is to use an extraction with nitric acid and hydrogen peroxide as mentioned above, which digests organic matter more efficiently. The point with this method is that, although quite commonly used, it seems that is not a so well standardised method and may be more difficult to find reference materials certified for this extraction (but I am still trying to find out more about this).

A third alternative is to use CVAA or GFAA, which accept also quite concentrated acid solutions, but it is more time consuming and would increase significantly the costs of analyses since it is a completely different technique. The detection limit would be comparable to analysing Hg by hydride generation, anyway.

These are the possibilities that the SCT may offer. I do not think there are many others, with the exception of very specialised and rare methods (e.g. CVAA on solid samples by calcination) which we can not likely afford with EMERGE budget.

Desirable - realistic detection levels for Hg

In view of the available methods, I do not think we may expect a priori a RDL much lower than 0.1-0.2 ppm dry weight for sediment samples (and MDL perhaps 3 times lower) extracted with a nitric acid + H₂O₂ and using hydride generation. I have asked to the SCT to process a sample from lake Redo, so they can more accurately determine the detection level and see if it can be still improved. The alternative would be using a weaker extraction, which I would prefer to avoid if possible by the reasons exposed above.

On the other hand, I don't know what levels of Hg should we expect in our sediments. Studies focuss more on polluted sediments. Perhaps someone else have an idea on the range and may help to decide whether these detection levels are good enough. I do not think that Stan's suggestion of 0.06 ppb is realistic. Although ICP-MS determinations on pure water are in this range, all the process of solubilising the elements plus the effect of the matrix lead to much higher detection limits. Even ultra sophisticated methods for methyl-Hg determination in sediments, for instance, are in the range of 0.025 ppm (Falter, R., Ilgen, G (1997): Determination of trace amounts of methylmercury in sediment and biological tissue by using water vapor distillation in combination with RP C18 preconcentration and HPLC-HPF/HHPN-ICP-MS. *Fresenius J. Analytical Chemistry* 358, 401-406)