

# Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) for dose rate determination: some guidelines for sample preparation and analysis

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## Background

We have recently started using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) as a part of our evaluation of environmental dose rates and report our method here for the benefit of others who may wish to use this promising technique. As with most analytical procedures, there are a combination of advantages and disadvantages to this method (Table A1). The method allows high precision determination of radionuclides from relatively small samples (>10mg), which is clearly advantageous if sample size is limited. Further, owing to the short range (c. ~2mm) of  $\beta$ -particles, the calculation of  $\beta$ -dose from small (representative) samples is likely to be more accurate than that calculated from in situ  $\gamma$ -spectrometry, as the  $\gamma$ -range (>50cm) far exceeds the  $\beta$ -range. Conversely, the  $\gamma$ -dose calculated from a small sample will only be accurate if the sample measured is representative of the burial sediment for ~50cm in all directions (both in elemental composition and moisture content). A further potential drawback is that disequilibrium in the U and Th decay chains cannot be evaluated using ICP-MS. While it is unlikely that ICP-MS will supersede all other approaches, and indeed the most sensible strategy will be to continue a multi-techniques assessment approach, it does represent a potentially powerful complement to other methods of dose rate assessment (Aitken, 1998).

## Analysis via ICP-MS

Problems have previously been associated with ICP-MS measurement of U, Th and K in sediment samples. Firstly, the instrument sensitivity required to measure K has been a long standing issue in ICP-MS research and interference from the background spectrum of the  $^{40}\text{Ar}^+$  carrier gas has frequently limited the quality of analysis of K (Potts, 1987). Secondly, problems have been described in silicate mineral sample digestion. Specifically, it is reported (Preusser and Kasper, 2001; Yokoyama et al., 1999)

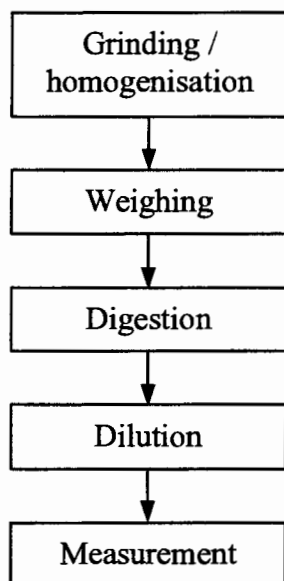
that the use of hydrofluoric (HF) and nitric ( $\text{HNO}_3$ ) acid digestion may result in the formation of fluoride precipitates, which inhibit the full recovery of certain elements (particularly the highly insoluble ThF groups).

Recently, results were presented by Preusser and Kasper (2001) showing good correlation between U, Th and K concentrations derived from  $\gamma$ -spectrometry and ICP-MS measurements. Potential inaccuracies introduced by incomplete sample digestion (as described above) were avoided by using a 22M HF and 10M  $\text{HClO}_4$  (perchloric acid) solution in the digestion procedure ( $\text{HNO}_3$  being used to suppresses the formation of insoluble fluoride precipitates). The sample was subsequently evaporated in a 6M HCl and 5.5M  $\text{HNO}_3$  solution and finally dissolved in  $\text{HNO}_3$  prior to measurement. While a perchloric acid digestion ensures complete digestion, its potentially explosive character (e.g., on contact with organic material; Schumacher (1960)), and the limited availability of perchloric acid-safe fume hoods, in our view make it less preferable to alternative strategies.

Over the past few months we have experimented with various sample preparation methods and have converged to what we believe is a more convenient and successful method. We have chosen to use the more conventional HF and  $\text{HNO}_3$  digestion rather than perchloric acid because of the difficult safety issues it presents (Schumacher, 1960). In order to avoid problems associated with fluoride precipitation our digestion procedure incorporates a final stage in which a small quantity of high purity concentrated Al solution (aluminium nitrate,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in a matrix of  $\text{HNO}_3$ ) is added to the sample. The mass action effect of Al, preferentially binding to the fluoride complexes, results in full dissolution of the otherwise acid insoluble fraction. For the sake of convenience we list our approach below.

### Stages of preparation

Figure 1 shows the five key stages of the ICP-MS procedure. These stages are described further in the remainder of this paper.



**Figure 1.**  
Stages of the ICP-MS procedure

### Grinding and weighing

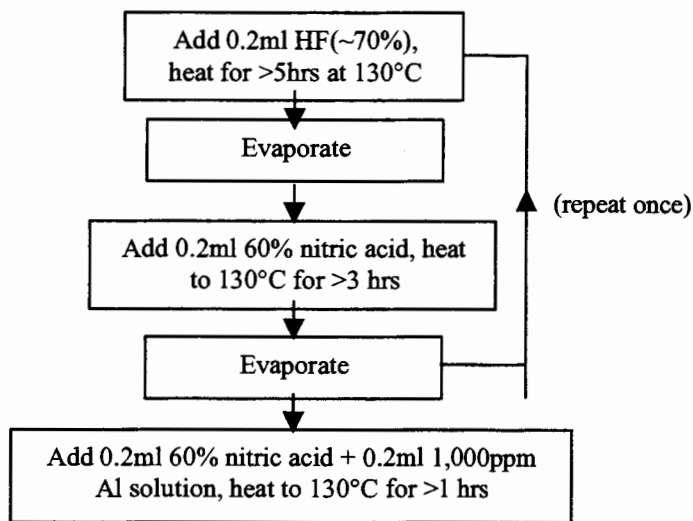
Approximately 20g of raw (dry) sediment is ground in a ball mill for a 3 minutes (we use an MM200 ball mill supplied by Christison Scientific, operated at 25Hz) to reduce the sediment to a fine (<10 $\mu$ m) homogenised powder. Approximately 50mg of the powder is then sampled for digestion (to a precision of 0.001 mg).

### Digestion

The digestion procedure is shown schematically in Figure 2 and described in detail below.

The powdered sample is placed into sealable, Teflon containers ('Teflon bombs' vol ~ 6 ml). 1.5 ml of concentrated Aristar HF (60-75%) is added to each, and the bombs are sealed and heated to 130 $\diamond$ C using thermostatically-controlled laboratory hot-blocks. The samples remain held at this temperature for at least 5 hours (typically overnight). After the bombs have returned to room temperature the lids are removed and the bombs re-heated at 130 $\diamond$ C (>100 $\diamond$ C being required for the formation and evaporation of SiF<sub>4</sub>). After 2-3 hours the sample solutions is dried. Following evaporation, 0.2ml of concentrated (~60%) Aristar or other higher (i.e. double distilled) purity nitric acid (HNO<sub>3</sub>) is then added to the sample. The lid is replaced and the bomb re-heated at 130 $\diamond$ C for >3 hours. Following subsequent cooling, the lid is removed and the sample heated at 130 $\diamond$ C to allow a

further evaporation to take place. This entire procedure is then repeated.



**Figure 2.**  
Sample digestion

To the dry residual, 0.2ml of concentrated (~60%) high purity nitric acid, plus 0.6ml of high purity aluminium solution (10,000 ppm) (or equivalent) is added. The bomb is then heated (whilst sealed) at 130 $\diamond$ C for ~ 1 hour. In the presence of aluminium, fluoride precipitates are broken down as the fluorine preferentially bonds to the aluminium and releases other elements (predominantly K and Th) back to solution. Following heating, the sample solution should be clear. If any residue remains, further heating and/or additional aluminium solution may be necessary to ensure full dissolution, although this has not, in our experience, been necessary.

Using 1% nitric acid (high purity acid diluted with high purity [18 $\mu$  $\Omega$ , Millipore] water), the solution can then be washed out of the Teflon bomb in to a sample tube. It is essential that a full procedural blank (full preparation, but with no powdered sample present) is measured with each batch of samples, in order to check for contamination (from, for example, impure acid). It is also good practice to measure both an internal standard (as a supplement to machine stability checks) and an external standard containing known concentrations of each measured isotope.

<sup>1</sup> Stoichiometrically 1g SiO<sub>2</sub> requires 2g HF ie ~2ml 14M HF, but an excess is required to ensure complete attack of sample. 0.5-1ml 28M HF should provide a large excess.

### Sample dilution and spiking

The sample is then diluted according to the requirements of the ICP mass-spectrometer being used and a 'spike' is added to the solution (in Oxford we have been using Indium) prior to measurement in order to check for unexpected matrix effects and for instrument instability.

### ICP-MS Measurement

The instrument used for ICP-MS analysis was an Elan 6100 DRC Quadropole ICP-MS, which has minimum detection limits for U, Th & K of ~1 ppt ( $10^{-12}$ ). The concentrations reported here were measured at ppb ( $10^{-9}$ ) levels.

### Testing the method

In order to test our methods, we prepared and measured a geological standard, JB1 (Japanese Basalt) using the procedures outlined above. The published values for U, Th and K concentrations of sample JB-1 are given in Table 1; our measured concentrations (the mean and standard deviation of five independent measurements) are shown for comparison. These values are shown graphically in Figure 3. As can be seen, the values obtained for JB-1 using our method agree well with the quoted values.

	U (ppm)	Th (ppm)	K (%)
Imai <i>et al.</i> (1995)	1.67 ± 0.28	9.30 ± 0.71	-
Makishima and Nakamura (1997)	1.75 ± 0.04	9.66 ± 0.23	-
Terashima <i>et al.</i> (1996)	-	-	1.19 ± 0.01
ICP-MS estimate	1.70 ± 0.04	9.72 ± 0.14	1.20 ± 0.02

**Table 1:**

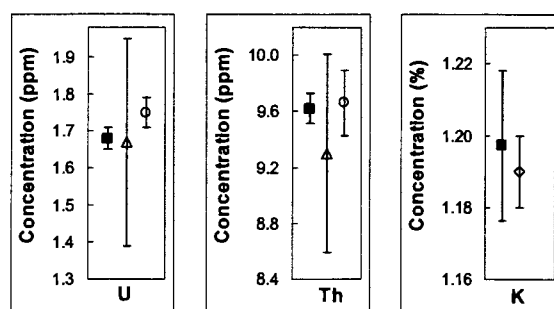
ICP-MS results of measurements of standard JB1. Consensus values for sample JB1 were taken from (A) Imai *et al.* (1995), (B) Makishima and Nakamura (1997) and (C) Terashima *et al.* (1996)

### Conclusion

Using the method described above it is possible to obtain accurate and highly precise estimates of U, Th and K via ICP-MS. While our approach requires the use of HF, it avoids the potentially even more dangerous perchloric acid treatment most recently described by Preusser and Kasper (2001). Dose rate analysis remains a key part of luminescence dating. We believe that an ICP-MS approach offers us some advantages over and above the use of nuclear

spectrometric methods such as INAA which is presently used widely.

However, as emphasized earlier, it is also helpful if dose rate estimates are based on a multi-technique strategy which allows some corroboration of results, some checks on disequilibrium, and some scope for direct measurement of  $\alpha$ -,  $\beta$ - and  $\gamma$ -dose rates. In the absence of alternatives, and as long as samples are analysed from a homogeneous sediment context which is assumed to be in secular equilibrium with respect to U, ICP-MS provides an extremely efficient method of obtaining estimates of environmental dose rate estimates.<sup>2</sup>



**Figure 3.**

The concentrations of U, Th and K measured in this study are shown as black squares. Open triangles indicate the values of Imai *et al.* (1995), open circles are from Makishima and Nakamura (1997); open diamond (K only) is from Terashima *et al.* (1996).

2

The School of Geography and the Environment offers a commercial ICP-MS service which provides analysis of U, Th & K. Costs and other details for this service are as follows:

School of Geography and the Environment  
University of Oxford

ICP-MS analysis – Standard Sample analysis (assuming sampled provided ground and homogenised)

- Minimum No. of samples = 10
- Expected turn around time 4 weeks
- Analyses for U, Th & K (including duplicate runs on blanks and geological standards)
- £13 per sample

Notes:

1. Additional cost of £5 per sample if grinding is required.
2. Running smaller batches of samples or more rapid turn around periods requires negotiation

### Acknowledgements

We thank Dr John Arden (Department of Earth Sciences, University of Oxford) for technical assistance with ICP-MS measurements and advice on silicate preparation. We are also grateful to Dr Andrew Murray for his helpful comments during the reviewing stage.

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### Reviewer

A. Murray

## Appendix A

Technique	Quantity measured/ Result	Effective sample size	Relative cost <sup>a</sup>	Precision	Vulnerable to dis-equilibrium	Potential limiting factors
<i>Direct</i>						
Portable (4 Ch) $\gamma$ Spectroscopy	$\gamma$ rays/[U], [Th], [K], <sup>D</sup> cosmic	50-60 kg	Low	Moderate-high	Yes-measures low proteges	Temp. stability, calibration
High Resolution $\gamma$ Spectroscopy (HRGS)	$\gamma$ rays/[U] - most isotopes, [Th] - most isotopes, [K]	30-60g	Very high	High	Disequ. directly measured	Calibration
Low Resolution $\gamma$ Spectroscopy (LRGS)	$\gamma$ rays/[U], [Th], [K]	500g	Low	Low	Yes	Temp. stability, calibration
Thick source $\alpha$ counting (TSAC)	$\alpha$ particles/[U], [Th]	2-3g	Very low	High	Yes-calculations assume equilibrium	Overcounting, sample representativeness
$\beta/\gamma$ TLD	$\beta$ particles or $\gamma$ rays/ $D_{\beta}$ or $D_{\gamma}$	Up to 50-60kg	Low-moderate	Moderate-high	Yes	Labour (during TL read out)
Thick source $\beta$ counting (TSBC)	$\beta$ particles / $D_{\beta}$	2-3g	Low-moderate	Moderate-high	Yes	Labour (during prep.) sample representativeness
<i>Indirect</i>						
Flame photometry (FP)	[K]	2-3g	Very low	High	-	Calibration, sample representativeness
Neutron activation (NAA)	[U], [Th], [K]	2-3g	High (non-recurrent)	Moderate	Yes-measures parents	sample representativeness
Inductively-coupled plasma mass spectroscopy (ICP-MS)	[U], [Th], [K]	2-3g	High (non-recurrent)	Very high	Yes-measures parents	sample representativeness

**Table A1**

*Some important factors in the selection of some commonly used dosimetric techniques*

<sup>a</sup>The relative cost is frequently at least in part dependent upon equipment availability, purchase/maintenance and incorporates a weighting factor for duration of measurement and degree of required operator specialisation.

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