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Comparison of dose rate determination using high–resolution gamma spectrometry and inductively coupled plasma – mass spectrometry

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Introduction

Determination of dose rates for luminescence and electron spin resonance (ESR) dating is possible using a variety of different analytic methods. The investigations presented here were initiated by the need to determinate the concentration of dose rate relevant elements (K, Th, U) of sediment samples from drilling cores. High resolution (HR) gamma spectrometry, predominantly used in our laboratory, was not practical due to the limited amounts of sample material available. One major advantage of inductively coupled plasma – mass spectrometry (ICP–MS) is the possibility to analyse samples as small as 10 mg. The performance of sample preparation (homogeneity, digestion) and of the measurement itself can be verified by comparison with certified reference materials (CRM).

Disequilibria within the thorium and uranium decay series is a potential error source in luminescence and ESR dating. The most suitable approach to test for disequilibria is a combination of alpha spectrometry and low-level gamma spectrometry (Krbetschek et al., 1994; Olley et al., 1996). However, the low activities of ^{232}Th and ^{238}U make these measurements rather time consuming (some days per sample) precluding regular checks in routine dating procedures. An alternative method to allow evaluation of sample secular equilibrium is to measure the mother isotope at the head (ICP–MS) and the daughters at the end of a decay chain (HR gamma spectrometry). However, it is first necessary to exclude systematic differences between the two methods caused by difficulties with analytical procedures.

The results of ICP–MS and HR gamma spectrometry are compared for a variety of samples from different geological sites. These samples are likely to be in equilibrium state due to their depositional history. For one sample, repeated measurements were carried out to obtain more information concerning the reproducibility of the results. A brief description of samples used in this study is presented in Tab. 1.

Table 1.

Description of samples analysed within this study. More information about the certified reference materials (CRM) is given by (^{*1}) Govindaraju (1994) and (^{*2}) Pszonicki et al. (2000), respectively

Sample	Origin	Sediment type	Grain-size
AJS 1–3	Oman	aeolianite	sand
BBR	Germany	house standard (basalt)	
BCR–1	USA	CRM (basalt) ^{*1}	
BGR 1–11	Argentina	loess and dune sand	silt or sand
GSD–3	China	CRM (fluvial) ^{*1}	
GSD–4	China	CRM (fluvial) ^{*1}	
HAB 1–3	Switzerland	fluvial deposit	sand or silt
HÜW 1–3	Switzerland	overbank deposit	sand or silt
NUSSY	Germany	loess	silt
PGM 1–4	New Zealand	estuary deposit	sandy silt
PIC 5–7	New Zealand	coastal deposit	sand or silt
SOIL–7	Austria	CRM (soil) ^{*2}	
WIL 1–5	Oman	desert lake and dune sand	sand

High resolution (HR) gamma spectrometry

HR gamma spectrometry was carried out using a high–purity germanium detector (Canberra GC2019–7935.2, coaxial p/n–type, 20 % relative efficiency, 1.9 keV FWHM at 1.33 MeV). After drying the samples at 50°C and determining natural water content, 800 g or 1600 g of sediment were filled into Marinelli beakers. Analyses were performed after one month of storage to build up equilibrium between radon and its daughters. Samples were measured for 20 hours. The influence of environmental radioactivity was minimised by a shielding of low–activity lead. Using large samples and measuring for a long time significantly reduces the effect of background variability. Since natural radioactivity is generally weak for the samples which had been analysed (0.5 – 2.0 % of K, 1 – 15 $\mu g\ g^{-1}$ of Th, 1 – 4 $\mu g\ g^{-1}$ of U), most of the thorium and uranium series γ–lines are close to the detection limit. Calibration was done by home standards containing known quantities of added radioactive elements (IAEA).

The results shown in Tab. 2 represent the average of 11 measurements of sample NUSSY, an Upper Weichselian loess from the Nußloch quarry near Heidelberg. All analyses were carried out during a period of two years using the same sealed container. This procedure provides accurate information of uncertainty due to peak matching and the error caused by background variability. The relative standard deviation (RSD) for different γ-lines ranges from approximately 1 % to 6 %. The poorer reproducibility is given for energy peaks where the signal/background ratio is low (e.g. for the peak of ^{212}Pb at 300.1 keV). The RSD of the average of all measurements and of all energy peaks is 2.1 % for K, 4.6 % for Th and 3.4 % for U.

Inductively coupled plasma – mass spectrometry (ICP-MS)

50 g of each sample were pulverised in a laboratory disc mill (tungsten carbide grinding barrel) and homogenised for analysis. Prior to ICP–MS analysis the sample material was dried overnight at 105°C (dry basis). All reagents used were Suprapur® grade (Merck).

Using conventional HF/HNO_3 decomposition, the recovery of Rb, Th and U will be severely restrained by selective coprecipitation with insoluble fluorides of major elements. The use of $HClO_4$ instead of HNO_3 enables an almost 100 % recovery of trace elements by completely suppressing fluoride precipitation (Yokoyama et al., 1999). Quantitative decomposition of samples, especially those containing resistant heavy minerals (e.g. Zircon), was considered using two different digestion protocols:

(1) *Conventional open system decomposition*
3 ml of 10 M $HClO_4$ and 3 ml of 22 M HF were added slowly to the weighed sample (15 ml Savilex PFA–vials, 100 mg) to prevent losses by violent carbonate reaction. After repeated sequential evaporation with 6 M HCl and 5.5 M HNO_3 the residue was dissolved with 0.5 M HNO_3, transferred to 50 ml volumetric flasks and stored in tightly closed HD-PE bottles. This procedure lasts for at least 2–3 days.

(2) *High pressure MULTIWAVE microwave digestion system*
This automated system is equipped with special designed 50 ml TFM-vessels in combination with an evaporation rotor (Anton–Paar/Perkin–Elmer 6EVAP) and an aspiration-evaporation device (Prolabo ASPIVAP) (Knapp et al., 1997). The p–T monitored microwave-powered closed system reaches maximum temperatures of 260° C (for 20 minutes) and a pressure of 70 bar. Reagents and sample quantity used are identical to the ones used in the conventional decomposition protocol. The main advantage of microwave digestion is the short time needed (ca. 7–8 hours) and a guaranteed quantitative sample dissolution (Kasper and Preusser, 2000).

The elements K, Rb, Th and U were analysed by inductively coupled plasma – quadrupole mass spectrometry (ICP–QMS, Sciex/Perkin-Elmer ELAN 6000). Special attention was focused on automatic and customised corrections for isotopic interference, interfering molecular species, specially customised resolution for K and internal standardisation.

The NUSSY sample was used for an inter–laboratory comparison and the results are shown in Tab. 3. For most of the measurements, the results are similar when the standard deviation is considered. However, the contents of U analysed with ICP–MS at the Cologne laboratory are slightly lower compared with the average results determined by the other laboratories. The concentrations of K and Th analysed by a commercial laboratory are slightly higher in comparison with the contents measured by the other laboratories.

Comparison of ICP-MS, HR-gamma spectrometry and CRM

Concentrations of dose rate relevant elements of 34 samples have been determined using ICP–MS and HR gamma spectrometry, respectively (Fig. 1–3).

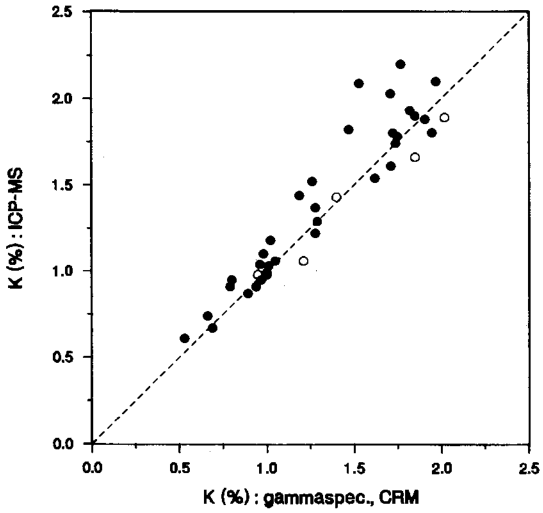

Figure 1.
Comparison of concentration of K determined by HR gamma spectrometry (closed circles) and CRM (open circles), respectively, versus ICP-MS.

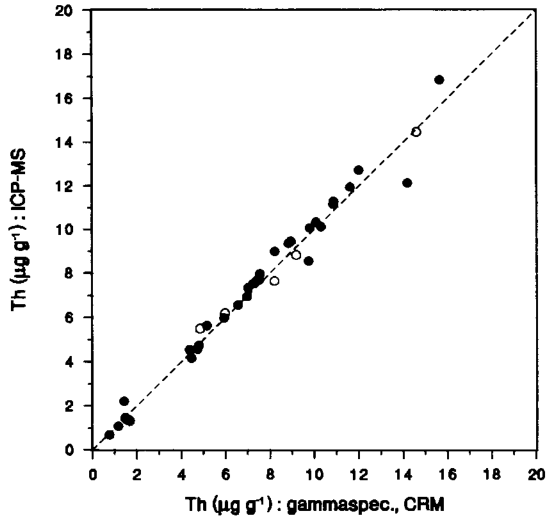

Figure 2.
Comparison of concentration of Th determined by HR gamma spectrometry (closed circles) and CRM (open circles), respectively, versus ICP-MS.

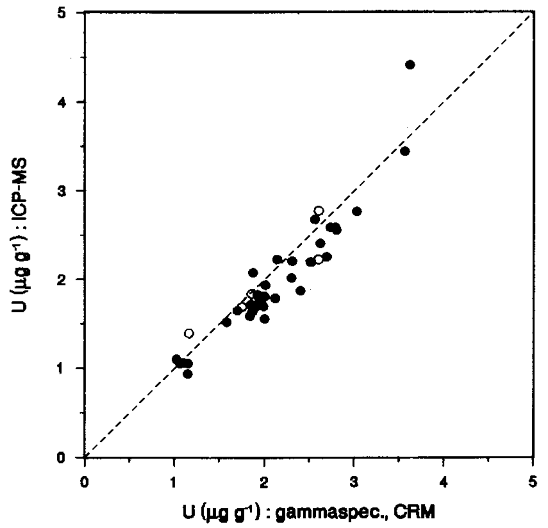

Figure 3.
Comparison of concentration of U determined by HR gamma spectrometry (closed circles) and CRM values (open circles), respectively, versus ICP-MS.

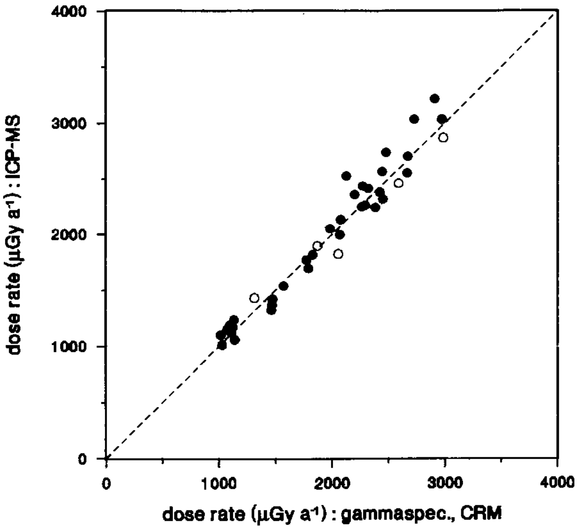

Figure 4.
Plot of dose rates calculated for HR gamma spectrometry (closed circles) and CRM values (open circles), respectively, versus dose rates determined using the ICP-MS results.

Table 2.
HR gamma spectrometry results for the different energy peaks of potassium and of isotopes from the thorium and uranium series of the NUSSY sample. The averages (n = 11) of the deduced contents of dose rate relevant elements, standard deviation (SD) and relative standard deviation (RSD), and the signal to background (BG) ratio with standard deviation are shown for repeated measurements.

Element	Peak (keV)	Content	SD	RSD	signal/BG
Potassium (%)					
K–40	1460.0	0.96	0.02	2.1	26.3 ± 1.9
Thorium (μg g^{-1})					
Tl–208	583.2	7.29	0.18	2.5	3.5 ± 0.2
Tl–208	2614.5	7.25	0.27	3.7	40.2 ± 7.3
Pb–212	238.6	7.37	0.08	1.1	3.8 ± 0.1
Pb–212	300.1	7.43	0.47	6.3	0.37 ± 0.03
Bi–212	727.3	7.30	0.44	6.0	1.0 ± 0.1
Ac–228	338.3	7.67	0.35	4.6	1.3 ± 0.2
Ac–228	911.1	7.58	0.25	3.3	4.2 ± 0.2
Mean	–	7.41	0.34	4.6	–
Uranium (μg g^{-1})					
Pb–214	295.2	2.67	0.06	2.2	2.3 ± 0.1
Pb–214	351.9	2.70	0.04	1.5	4.6 ± 0.4
Bi–214	609.3	2.70	0.03	1.1	6.3 ± 0.6
Bi–214	1120.3	2.69	0.09	3.3	2.0 ± 0.2
Ra–226, U–235	186.0	2.61	0.16	6.1	0.53 ± 0.04
Mean	–	2.68	0.09	3.4	–

Table 3.
Comparison of analyses determining the dose relevant elements (RSD) for the NUSSY sample carried out by different laboratories using ICP–MS and HR gamma spectrometry, respectively.

Laboratory		K (%)	Rb (μg g^{-1})	Th (μg g^{-1})	U (μg g^{-1})
Cologne (γ–spec.)	(n = 11)	0.96 (2.1)	–	7.4 (4.6)	2.7 (3.4)
Cologne (ICP–MS)	(n = 10)	1.04 (8.9)	51.8 (2.3)	7.7 (2.1)	2.3 (4.4)
GFZ (ICP–MS)	(n = 3)	–	51.6 (1.5)	7.7 (5.3)	2.6 (0.8)
Commercial (ICP–MS)	(n =1)	1.14	–	8.8	2.7

Generally, the results for both methods are in good agreement.

For some samples significantly higher K contents were determined using ICP–MS (Fig. 1). This is due to the atomic weight of K and hence the massive isotopic interference of Argon from the plasma source. With respect to reproducibility and accuracy of the ICP–MS results, we intend to carry out further tests using alternative analytical methods such as atomic absorption spectrometry (AAS) or flame emission spectrometry (FES). Additionally, the remarkable covariance of Rb and K might be used for cross-checking the results.

Slightly lower U contents in comparison with HR gamma spectrometry were measured using ICP–MS (Fig. 3) as it has already been shown in the laboratory inter–comparison test (Tab. 3). It is possible that the conventional digestion protocol might not always guarantee complete dissolution of samples due to chemically resistant minerals such as Zircon. Thus, we favour the use of high–pressure microwave digestion in future research.

A comparison of dose rates calculated from the concentration of radioactive elements as determined by the two different methods is shown in Fig. 4. Dose rates have been calculated for 150 µm quartz grains assuming an alpha efficiency of 0.1 and a sediment moisture of 20 %. Neither cosmic rays nor internal dose rate contribution have been considered.

Calculations were carried out using the AGE program developed by R. Grün which uses the conversion factors of Nambi and Aitken (1986). The differences in dose rates of the two different methods is generally less than 10 % but it has to be considered that some of the ICP–MS results may be affected by methodological difficulties.

Conclusions

Determination of the concentration of dose rate relevant elements analysed by ICP–MS and HR gamma spectrometry yield consistent results for most of the samples. The ICP–MS results are in good agreement with values of analysed CRM. However, digestion of samples and the custom resolution technique used for the determination of K have to be considered carefully. Methodological improvements may further increase the accuracy of ICP–MS analyses, in particular for K. It is emphasised that a combination of ICP–MS and HR gamma spectrometry may reduce the uncertainties in dose rate determination by the ability to routinely check for secular disequilibria within the thorium and uranium decay series.

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Reviewer

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