Trace element and multi-isotope analysis of human head hair samples

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Introduction: In cooperation with the BKA Wiesbaden, this project is dealing with the investigation of human head hair. The aim of these examinations is to obtain information about the travelling behaviour of a person using spatially resolved analysis of biological samples. The question to be answered is whether it is possible to see a change of someone's habitat through the elemental or isotopic composition of his hair.
For the elemental analysis, several methods are applied: inductively coupled plasma mass spectrometry (ICP-MS), laser ablation-ICP-MS (LA-ICP-MS) and instrumental neutron activation analysis (INAA). Isotope ratio mass spectrometry (IRMS) and thermal ionization mass spectrometry (TIMS) are used for measuring the isotopic composition of carbon, nitrogen, hydrogen, oxygen, strontium and lead in the hair.
For each analysis, appropriate sample preparation methods are needed. In the following, only the INAA method is described in more detail.

Experimental: For INAA, the hair samples were irradiated without further washing procedure in order to avoid loss of soluble elements in the first tests. The samples were ground and homogenised using a vibrating mill. Two different irradiation programmes (long and short) and three different γ - spectrometry measurement routines were applied. Irradiation was performed at the research reactor TRIGA Mark II in Mainz [1]. These programmes were matched with the different radioactive half-lives of the elements [2].
During the long irradiation programme, samples of 70 mg were irradiated in the rotary specimen rack for six hours (thermal neutron flux $0.7 \cdot 10^{12} cm^{-2} s^{-1}$). After a waiting time of one to two days, the samples were measured with a high purity germanium (HPGe) semiconductor detector for one hour, followed by measurements of eight hours.
For the short irradiation of one minute, a 30 mg aliquot of each sample was taken. This irradiation was carried out in the pneumatic specimen tube with a thermal neutron flux of $1.6 \cdot 10^{12} cm^{-2} s^{-1}$. The samples of this short irradiation were measured for ten minutes after a decay time of approx. two minutes.
High purity liquid standards were used for the quantification. These standards were irradiated in the same procedures as the hair samples. For data evaluation, the software Genie 2000 Version 3.0 (Canberra Eurisys) was used.

Results of the first INAA tests: To test the ability of this analytical method to accurately determine element concentrations, two standard human hair reference materials of the *China National Analysis Center for Iron and Steel* [NCS DC 73347 and NCS ZC 81002b] and two hair standards of the *International Atomic Energy Agency* (Wien, Austria) [IAEA-085 and IAEA-086] were analysed.
For these four standards, good recoveries were achieved. A comparison of some experimental results of NCS DC 73347 with the values given in the certificate is listed in Table 1. The concentrations of Ca, Mn, Na, Zn and As are in good agreement with the certified values. The concentrations found for K and Br are close to the information values given in the certificate. For Al, no concentration is specified in the certificate. The Cu content is below the limit of quantification. For Zn, two nuclides were measured. The precision for Zn-69m is significantly better than for Zn-65. The results achieved by the measurement sequences 6h-1h and 6h-8h are very similar. Therefore, it may only be necessary to concentrate on one of these two measurement routines in the future.

1min - 10min	DC73347 [µg/g]	certificate [µg/g]
Al	17181 ± 871	-
Ca	2933 ± 578	2900 ± 300
Cu	-	10,6 ± 1,2
Mn	5,90 ± 0,53	6,3 ± 0,8

6h - 1h	DC73347 [µg/g]	certificate [µg/g]	6h - 8h	DC73347 [µg/g]	certificate [µg/g]
Na	139,4 ± 3,7	152 ± 17	Na	139,7 ± 5,1	152 ± 17
K	15,7 ± 2,2	[20]	K	17,6 ± 2,2	[20]
Zn-65	196,0 ± 54,46	190 ± 9	Zn-65	157,5 ± 18,6	190 ± 9
Zn- 69m	173,2 ± 6,6	190 ± 9	Zn- 69m	175,4 ± 6,8	190 ± 9
As	0,23 ± 0,02	0,28 ± 0,05	As	0,23 ± 0,02	0,28 ± 0,05
Br	0,24 ± 0,06	[0,36]	Br	0,29 ± 0,03	[0,36]

Table 1. Element concentrations of human hair reference material NCS DC 73347 determined by using INAA and compared with the certificate (right column). Concentrations in brackets [] are information values.

Conclusion: For all analytical techniques mentioned above, sample preparation methods were developed and first tests were realised. By using ICP-MS, LA-ICP-MS and INAA, the elemental composition of hair samples could be determined. Also, the results of IRMS and TIMS are promising. Thus, these analytical methods seem to be suitable for the investigation of human head hair.
In the future, further analyses of more hair samples will be performed. Still, the development of an adequate interpretation method for the results will be a major task.

References

[1] Hampel, G., Eberhardt, K., Trautmann, N., 2006. Der TRIGA Forschungsreaktor Mainz, atw internationale Zeitschrift für Kernenergie 51 (5), 328-330.
[2] Reus, U., Westmeier, W., 1983. Catalog of gamma rays from radioactive decay part II. At. Data Nucl. Data Tables 29 (1), 193-406.

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