CPT/Inf (2008) 13 Addendum

Addendum to the report on the visit to Turkey carried out by the European Committee for the Prevention of Torture and Inhuman or Degrading Treatment or Punishment (CPT)

from 19 to 22 May 2007

(transmitted to the Turkish authorities by letter of 22 February 2008)

The Turkish Government has requested the publication of the report on the CPT's May 2007 visit to Turkey, including this Addendum, and of its response (document CPT/Inf (2008) 14).

Strasbourg, 6 March 2008

1. The report on the CPT's ad hoc visit to Turkey from 19 to 22 May 2007 was adopted by the Committee at its 63rd meeting, held from 2 to 6 July 2007, and forwarded to the Turkish authorities on 23 July 2007 (see document CPT/Inf (2008) 13). This Addendum to the visit report relates, inter alia, to the allegations of intoxication by heavy metals referred to in paragraphs 29 and 30 of the visit report.

2. The hair samples taken from Abdullah Öcalan by the CPT's delegation during the May 2007 visit were subsequently analysed for heavy metal content by Professor Thomas Prohaska, Professor for Analytical Chemistry at the University of Natural Resources and Applied Life Sciences in Vienna (Austria)[*]. The results of the analysis, together with information in the CPT's possession concerning the prisoner's state of health, were then forwarded for their opinion to Professor Patrice Mangin and Doctor Frank Sporkert of the University Institute of Forensic Medicine in Lausanne (Switzerland).

   The report drawn up by Professor Prohaska is set out in Appendix 1 to this Addendum, and the conclusions of the forensic opinion drawn up by Professor Mangin and Doctor Sporkert in Appendix 2.

3. The findings of the experts appointed by the CPT indicate that the prisoner has not been the subject of intoxication by heavy metals.

   As regards the elevated levels of barium, magnesium and strontium detected in the hair samples, the experts consider that they are probably linked to environmental factors. In any event, the view is expressed that the levels found are not dangerous for the prisoner's health.

   Nevertheless, the CPT shares the opinion that, as a precautionary measure, it would be appropriate for the levels of barium, magnesium and strontium in the prisoner's blood and urine to be monitored for some time on a three-monthly basis. **The CPT recommends that, subject to the consent of the prisoner, such quarterly tests be carried out for a period of twelve months. The Committee would like to receive the results of each test.**

4. Reference should also be made to two recommendations concerning medical matters formulated by the CPT in its report on the May 2007 ad hoc visit, namely that the prisoner immediately receive : i) a comprehensive ear, nose and throat (ENT) examination, including an endoscopic examination; and ii) an X-ray examination of the thorax. These examinations were finally carried out at the end of November 2007.

   The results of the X-ray examination of the thorax are reassuring.

   As regards the results of the ENT endoscopic examination, they indicate that the prisoner is suffering from a condition linked to surgery performed prior to his imprisonment that will require continuous care. This question will be discussed further in separate correspondence with the Turkish authorities.

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[*] At the request of the Turkish authorities, the analysis of the hair samples was carried out in a laboratory in Turkey. During the time required to arrange for a suitably-qualified expert to carry out the analysis in Turkey, the hair samples remained subject to a strict chain of custody under the control of the CPT.

APPENDIX 1

1 Introduction

The following work was carried out at TÜBITAK Ulusal Metroloji Enstitüsü from 29.10.2007 – 06.11.2007 under the supervision of Prof. Dr. Thomas Prohaska, Analytical Chemist and Analytical Consultant, and DI Patrick Galler. The work comprised the setting up and installation of an analytical method to analyze hair samples on heavy metal content both by liquid digestion analysis (ICP-MS – inductively coupled plasma mass spectrometry) and laser ablation (LA-ICP-MS) analysis for the following set of elements, which were agreed on in Gebze, 01.11.2007: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Hg, Li, Mg, Mn, Mo, Na, Ni, Pb, Pd, Pt, Rb, Sb, Se, Sn, Sr, Te, Th, Ti, Tl, U, V, W, Y, Zn and Zr. A major goal was the investigation of Sr and Cr in the corresponding hair samples. These elements will be discussed in more detail in the following report. For the other elements, the concentrations within the hair and literature ranges are given.

2 Analytical protocol

2.1 Materials and method

All materials (i.e. reagents, laboratory ware and instrument spare parts) have been ordered and prepared within the clean room facilities of the University of Natural Resources in Vienna. All handling was performed with maximum precautions in order to avoid any contamination. Therefore, sample handling was performed by using disposable PE (polyethylene) gloves solely. All lab ware used for sample preparation, digestion, dilution and measurement was pre-cleaned using the following standard procedure:

Cleaning Step	reagent	duration	loc
soaking	10 % HNO_3	3 days	clean bench class 10
rinsing	reagent II grade water	-	clean bench class 10
soaking	1 % HNO_3	1 day	clean bench class 10
rinsing	reagent II grade water or subboiled water	-	clean bench class 10
drying	-	1 day	clean bench class 10

Table 1: cleaning procedure

LDPE (low density PE) bottles (Semadeni, Ostermundingen, Switzerland) were used for storage of standard solutions and concentrated HNO_3. Nitric Acid was prepared by double sub-boiling distillation (Milestone-MLS GmbH, Leutkirch, Germany) of analytical reagent grade acid (Merck KGaA, Darmstadt, Germany). Water, pre-treated by reverse osmosis, was further purified by a laboratory-reagent grade water system (F+L GmbH, Vienna, Austria) followed by sub-boiling distillation (Milestone-MLS GmbH, Leutkirch, Germany). All standard solutions were prepared from certified single 1000 µg/g stock solutions (Merck).

The following reference materials were investigated along with the hair material in order to prove the validity of the results: BCR-397 (IRMM, Belgium) was taken as reference material for method validation. Since the material is only certified for a limited number of elements, an in-laboratory certified reference material (TP-IAEA, BOKU, Vienna, Austria) was used for further validation. Especially Cr is not certified in the BCR-397 hair material. Only an informative value is given, which is about 1000 times higher compared to normal Cr levels in hair material and it is further reported that especially the Cr values are heterogeneously distributed within the reference material. Therefore, Cr values of the BCR-397 cannot be taken for validation purposes (which was also proven within this work). Similar (inhomogeneity) is true for Ni. Therefore, a certification of the TP-IAEA hair material was undertaken for Cr using isotope dilution mass spectrometry.

2.2 Sample description

The samples under investigation consisted of two sets of hair material. The first set was hair material from the scalp and the second set was hair from the thorax region of the individual concerned (Table 2). Both sets of hair samples were handed over in the laboratory by CPT and Turkish Authority representatives. Strict precautions were taken that no alteration of the hair material took place at any step of the investigation.

The 4-eyes principle was followed during each single step of the analytical protocol.

Sample	Color	Length	Total weight
scalp hair	black/white	20 – 50 mm	~ 293 mg
thorax hair	black/white	25 – 65 mm	~ 82 mg

Table 2: sample description

2.3 Sample preparation

The hair samples of both sets were weighed prior to further investigation in order to have an estimate of the available material for the successive investigation. After weighing, both sets of hair samples were washed according to a procedure proposed by the IAEA[1] (Table 3). This procedure is the best validated procedure available at the moment. It is used to remove possible surface contaminants of the hair material. Even though it has the potential of removing surface contaminants, it is not able to remove exogenous contamination which diffuses into the inner structure of the hair by e.g. prolonged contact with aqueous solutions containing elevated levels of minerals. On the other hand, several investigations propose the opinion that endogenously incorporated elements can be removed to a non significant extent from the hair material. Nonetheless, the IAEA procedure provides the only standardized washing procedure which allows comparability of data. Therefore information stored in the hair has to be extracted additionally by means of laser ablation analysis, which gives information about surface layers and the inner core of a hair material. This information cannot be extracted by conventional liquid nebulisation bulk analysis.

Cleaning Step	Reagent	Replicates	Loc
washing	TritonX-100 1:200 with double subboiled H_2O	4	laboratory UME
de-fatting	Acetone ultrapure	1	laboratory UME
rinse	double subboiled H_2O	2	laboratory UME
de-fatting	Acetone ultrapure	2	laboratory UME
rinse	double subboiled H_2O	3	laboratory UME
drying	75°C +/- 5	-	laboratory UME

Table 3: applied washing procedure

The blank contribution caused by the washing reagents was insignificant as could be proven both by blank analysis as well as by LA-ICP-MS investigation of washed and unwashed hair samples. After washing of the hair samples, the samples were dried in a conventional convection dryer at approximately 70-75 °C until a constant weight was reached, indicating successful removal of all excess humidity.

2.4 Liquid digestion analysis

2.4.1 Sample digestion

The digestion was performed using a micro- digestion method in two series on two different days. In order to prove the validity of the method and to avoid erratic results by sample inhomogeneity, a larger sample amount was digested using microwave assisted digestion, as well.

2.4.1.1 Micro-digestion using PFA screw cap vessels

Based on the assumption that no more than 50 hair strands in total would be available for analysis, a micro-digestion method for sample amounts ranging from 1-10 mg sample material was developed. A comparable method has already been described and successfully applied for bio-monitoring purposes [2]. The micro-digestion was performed in the following way: a defined amount of sample was weighed on an analytical balance and transferred to a PFA vessel. 1.2 – 1.5 mL of nitric acid and 0.6 mL of hydrogen peroxide were added to the PFA vessel, which was then covered with a screw cap. The screw cap was not placed tightly on the PFA vessel in order to allow excess pressure to be removed from the PFA vessel. The PFA vessel was then placed at 80-120 °C on a hot plate. Samples were typically left for 60-120 minutes on the hot plate, depending on the visually perceivable status of digestion of the hair samples under investigation. Moderate shaking was used from time to time in order to remove single strands of hair adhering to parts of the PFA vessel not covered with digestion reagent. The PFA vessels were left on the hot plate until the digestion solution could be observed through the transparent walls of the PFA vessels to be clear and colorless. Then the screw caps were removed from the PFA vessels and samples were evaporated to near-dryness at slightly increased temperatures and finally dissolved in 3-5 mL of 1% nitric acid. The resulting amount of sample solution was determined gravimetrically.

Digestion date	Sample code	Sample origin	Amount of sample [µg]	Final dilution weight [g]
30.10.2007	TP-IAEA_1	reference material - BOKU	1000.2	3.2207
	TP-IAEA_2	reference material - BOKU	1080.2	3.2726
	TP-IAEA_3	reference material - BOKU	1399.5	3.8189
	BCR_397_1 (VIRIS)	IRMM, Belgium	1002	3.2508
	BCR_397_2 (VIRIS)	IRMM, Belgium	997.7	4.1775
	BCR_397_3 (VIRIS)	IRMM, Belgium	992.4	3.5583
	BCR_397_(UME)	IRMM, Belgium	934	3.068
	blank		0	3.6203
	blank		0	3.5954
	blank		0	5.0168
31.10.2007	BCR_397 (VIRIS)	IRMM, Belgium	2059.8	3.815
	BCR_397 (UME)	IRMM, Belgium	2124.8	3.9105
	TP-IAEA_1	reference material - BOKU	2340.1	3.7077
	TP-IAEA_2	reference material - BOKU	2024.4	3.5353
	blank		0	3.5207
	blank		0	3.7074
1.+2.11.2007	BCR_397_1 (VIRIS)	IRMM, Belgium	3953.6	3.7894
	BCR_397_2 (VIRIS)	IRMM, Belgium	4464.9	3.9248
	BCR_397 (UME)	IRMM, Belgium	4125.6	4.2991
	TP-IAEA_1	reference material - BOKU	4103.6	3.6385
	TP-IAEA_2	reference material - BOKU	4623.9	3.2466
	POILS_THORAX_1	person concerned	4248.4	4.3532
	POILS_THORAX_2	person concerned	4404.4	3.6255
	POILS_THORAX_3	person concerned	4457.3	3.5090
	SCALP_CHEVEUX_1	person concerned	4154.7	3.8634
	SCALP_CHEVEUX_2	person concerned	4160.5	3.294
	SCALP_CHEVEUX_3	person concerned	3932.6	4.1062
	blank		0	3.7804
	blank		0	3.6124
	blank		0	3.8392
2.+3.11.2007	BCR_397 (VIRIS)	IRMM, Belgium	4192.3	4.0765
	BCR_397 (UME)_1	IRMM, Belgium	4477.9	4.0179
	BCR_397 (UME)_2	IRMM, Belgium	4090.9	4.9907
	TP-IAEA_2, recovery	reference material - BOKU	4572.9	3.9717
	TP-IAEA_1, recovery	reference material - BOKU	4149.3	4.2389
	POILS_THORAX_1	person concerned	4464.7	4.1154
	POILS_THORAX_2	person concerned	4410.8	4.0064
	POILS_THORAX_3	person concerned	4266.9	4.6336
	SCALP_CHEVEUX_1	person concerned	3683.2	3.8234
	SCALP_CHEVEUX_2	person concerned	4727	3.7858
	SCALP_CHEVEUX_3	person concerned	4268.4	3.8152
	TP-IAEA_3, recovery	reference material - BOKU	4555.6	4.1425
	blank		0	4.7521
	blank		0	4.5786
	blank		0	3.9394

Table 4: Samples for micro-digestion using PFA screw cap vessels

At least 2 blank digestions were performed for each digestion batch with PFA vessels containing no sample material at all, in order to monitor background contamination levels resulting from reagent impurities or the environment of the laboratory. A certified reference material (BCR-397) and an in-house reference hair material (TP-IAEA) from the VIRIS laboratory at the BOKU Vienna have been used for validation of the digestion procedure. The BCR-397 hair reference material has been provided from the VIRIS laboratory as well as from the UME facility in Gebze. Both batches of material were used in order to enable cross checking of the different batches. In some cases the digestion had to be performed on 2 subsequent days, due to the time required. A compilation of digestions performed including the corresponding sample weights is presented in table 4.

2.4.1.2 Microwave assisted digestion

The actual amount of sample available by far exceeded the expectations of the analytical consultants, resulting in the possibility of application of a further digestion method. The method concerned is a conventional microwave assisted, closed vessel digestion which allows effective dissolution of large amounts of sample at harsher conditions than available in the digestion procedure described in section 2.4.1.1.. A “Start 1500” microwave digestion system from Milestone MLS (Leutkirch, Germany) was used for sample digestion. A written agreement was signed on the parameters of the microwave assisted digestion procedure by the Turkish expert present, Ao. Prof. Thomas Prohaska and DI Patrick Galler. It was agreed to digest a sample amount of approximately 50 mg hair material in a mixture of 4 mL nitric acid and 0.5 mL hydrogen peroxide. Due to the amount of sample available, approximately 40 mg of sample were digested, so that enough sample material for an exact reproduction of the described procedure will be available for future purposes. Furthermore it was agreed to keep the digestion conditions under temperature control and to use a maximum energy of 700 W. The temperature program used for the digestion of the hair samples is depicted in figure 1. The maximum temperature for the plateau is 145 °C, which is reached via a linear ramp over 15 minutes starting from room temperature. After digestion the vessels were left for cooling over night.

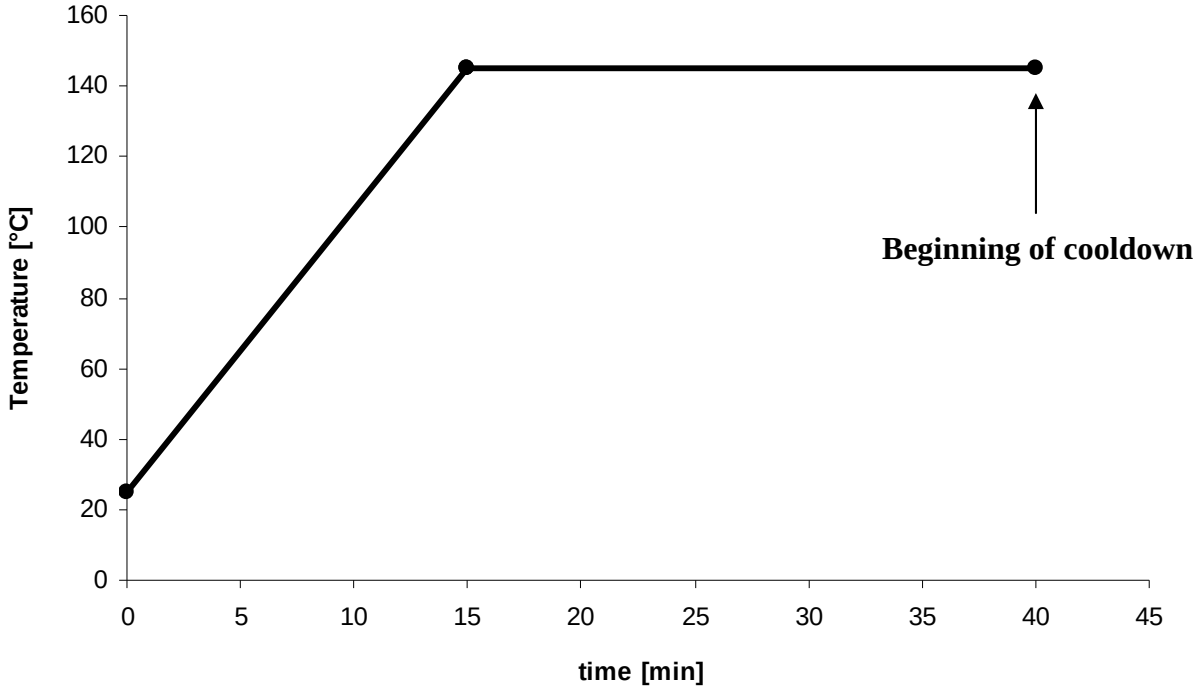

Figure 1: Temperature Program used for microwave assisted digestion

After the samples had cooled down to room temperature the content of the digestion vessels was transferred to PFA vessels for evaporation to near dryness on a hot plate. Finally the residue was dissolved in 5-6 mL of 1% nitric acid.

With respect to the large amount of sample used for microwave digestion and the wish to leave a quantity of sample for potential future investigations, the procedure could be applied exclusively to the scalp hair of the person concerned (see table 2) and not be repeated a second time. A summary of all microwave assisted digestions performed can be found in table 5.

Digestion date	Sample code	Sample origin	Amount of sample [µg]	Final dilution weight [g]
3.11.2007	SCALP_CHEVEUX_1	person concerned	42.3	4.9570
	SCALP_CHEVEUX_2	person concerned	36.65	6.4339
	SCALP_CHEVEUX_3	person concerned	36.88	5.9780
	TP-IAEA_1	reference material - BOKU	39.13	5.5761
	TP-IAEA_2	reference material - BOKU	37.89	5.9160
	TP-IAEA_3	reference material - BOKU	40.66	5.0913
	BCR_397 (us)_1	IRMM, Belgium	39.47	6.0227
	BCR_397 (us)_2	IRMM, Belgium	39.67	5.1330
	BCR_397 (Tübitak)	IRMM, Belgium	38.18	5.4283
	blank		0	5.7925
	blank		0	5.7593
	blank		0	6.5481

Table 5: Samples for microwave assisted digestion

2.4.2 Sample analysis

After digestion of the samples, evaporation of the strong acid matrix to near dryness and dissolution of the sample residues in 1 % nitric acid, mass spectrometric investigation of the elemental contents of the obtained sample solutions could be performed. Samples were analyzed by means of an Elan DRC-e (PerkinElmer, Waltham, Massachusetts, USA) inductively coupled plasma-mass spectrometer (ICP-MS). Quantification of the sample content was performed via external calibration. Due to the immanent characteristics of elemental analysis by ICP-MS, quantification for some isotopes (e.g. ^{53}Cr, ^{54}Cr, ^{40}Ca,…) is potentially biased due to isobaric interferences. The mass spectrometer employed for this work allows use of a so-called dynamic reaction cell (DRC), which can effectively suppress occurrence of certain interferences. For example it may be used in order to eliminate interferences for e.g. the isotopes ^{53}Cr and ^{54}Cr; which are interfered by the molecular species $^{13}C^{40}Ar$ as well as $^{14}N^{40}Ar$. The method according to W.J. McShane et al. [3] was used for the quantification of the Cr content of a major part of the samples. All samples from the person concerned have been quantified via this approach, as the Cr quantification was found to yield inconsistent results in the so called standard mode.

A low-flow PFA nebuliser with an approximate solution uptake of 100 µL/minute was used in combination with an un-cooled cyclonic quartz spray chamber for sample introduction into the ICP-MS. Essentially all parts of the ICP-MS sample introduction system: including torch, injector, interface cones and spray chamber have been exchanged to completely new components that have never been used before. In this way contamination effects resulting from previous measurements on the same ICP-MS can be excluded as a potential source of error.

2.4.3 Data evaluation

External calibration standards were gravimetrically prepared from single element stock solutions in the following concentrations: 0, 0.005, 0.01, 0.05, 0.1, 0.5, 1, 5, 10, 20, 30, 40, 50, 60, 80, 100, 200 ng/g. Elements contained are: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Hf, Hg, Ir, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Pd, Pt, Rb, Rh, Sb, Se, Sn, Sr, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr (see section 1.). All calibrations performed during this work have been prepared from these stock solutions. A defined amount of an Indium (In) solution of known In content was added to every sample and standard in order to compensate for signal intensity variations and drifts during the measurement. Measured signal intensities for all isotopes of interest are routinely normalized to the signal intensity of the internal standard In. Measured calibration solutions yield a linear increase of the measured and normalized signal intensity with increasing concentration. A linear equation may be fitted to the resulting data points which subsequently may be used for calculation of the elemental concentrations in the investigated sample solutions.

2.5 Laser ablation analysis

2.5.1 Sample preparation

Single hair samples were affixed on pre-cleaned microscopic slides by using UHU® glue-it. A thin film of the liquid glue was evenly distributed on a thin glass slide. Attention has to be paid to the problem that a surplus of glue can cover the hair surface. An un-washed hair sample is affixed in addition to any washed hair samples in order to prove that no contamination has taken place during the washing procedure. Background levels of the analyzed glue were at gas blank levels for all elements under investigation.

2.5.2 Sample analysis

LA-ICP-MS was performed according to the method applied earlier in the VIRIS laboratories in Vienna.[4] Laser ablation was performed by using a New Wave UP 266 nm laser ablation system (New Wave Research, USA). Hair material is ablated by means of a laser beam (actual diameter 50 µm; energy level 40 %) along a single hair in order to retrieve time resolved quantitative information of the hair surface. Subsequently, a second line is ablated in the 50 µm trench of the first ablation using a nominal spot size of 8 µm (50 % energy level) in order to retrieve the information of the inner hair. Scan lines were set between 500 and 10 000 µm in length using a scan speed of 10 and 25 µm/s, respectively.

ICP-DRCMS analysis was performed by choosing sulfur as internal standard. Sulfur is found in almost 100 proteins of the hair and amounts to approximately 5 % of the elemental concentration in the hair. The sulfur concentration is reported to be stable with respect to hair samples and length of a single strand.[5]

Nevertheless, sulfur is spectrally superposed by a O_2^+ interference. Thermo-chemistry is unfavorable for charge transfer reaction for elimination of O_2^+ since the interfering ion has a similar ionization potential as the analyte. A recent study employed Xe for partial removal of the O_2^+ interference. [6] As alternative approach, oxygen was used successfully to convert S-ions into the molecular ion of $^{32}S^{16}O^+$ (m/z 48) via an exothermal reaction. [7] Generally, the variation of the gas flow in the DRC is not possible, when a transient signal needs to be analyzed within a short period of time. Therefore, all isotopes of interest were analyzed with DRC mode. Most elements undergo a signal reduction of about 10 – 50%, which does not influence the final results except for deterioration of LOD (limits of detection).

2.5.3 Data evaluation

All elemental intensities are blank corrected (by a gas blank which is acquired directly before measurement) and subsequently normalized to the intensity of $^{32}S^{16}O^+$ (m/z 48) which acts as internal standard. Hg results were quantified using BCR 397 as calibration standard. All other normalized signal intensities were compared relative to the laboratory reference standard (TP-IAEA).
(N.B.: 9 – 30 single hairs are required for analysis).

2.6 Method validation and uncertainty calculation

2.6.1 Reference materials and reference ranges

The reference values of BCR 397 and TP-IAEA are given in the following table in µg/g.

Element	BCR 397 – Uncertainty in ( )	Type of value	TP-IAEA	uncertainty	method
Ag			0.350	0.090	ICP-MS
Al			7.800	2.100	ICP-MS
As	0.31 (0.02)	Indicative	0.115	0.020	ICP-MS
Au			0.035	0.010	ICP-MS
B	2.8 (0.3)	Informative	3.000	0.500	ICP-MS
Ba			0.150	0.070	ICP-MS
Be			nd	nd	
Bi			0.020	0.050	ICP-MS
Ca	1560 (40)	Informative	180.000	50.000	ICP-MS
Cd	0.521 (0.024)	Certified	0.100	0.050	ICP-MS
Co	0.55 (0.03)	Informative	0.015	0.005	ICP-MS
Cr	91 (33)	Informative	0.099	0.037	
Cs			<LOD		ICP-MS
Cu	110 (5)	Indicative	15.300	2.000	ICP-MS
Fe	580 (10)	Informative	24.000	10.000	ICP-MS
Ga			0.020	0.020	ICP-MS
Hg	12.3 (0.5)	Certified	1.46		LA-ICP-MS (indicative)
Li			0.040	0.020	ICP-MS
Mg	200 (5)	Informative	15.000	6.000	ICP-MS
Mn	11.2 (0.3)	Informative	0.400	0.150	ICP-MS
Mo	6.6 (0.2)	Informative	0.050	0.020	ICP-MS
Na			51.000	16.000	ICP-MS
Ni	46.0 (1.4)	Indicative	0.246	0.080	ICP-MS
Pb	33.0 (1.2)	Certified	1.750	0.200	ICP-MS
Pd			nd	nd	ICP-MS
Pt			nd	nd	
Rb			0.112	0.080	ICP-MS
Sb			nd	nd	
Se	2.00 (0.08)	Certified	0.912	0.240	ICP-MS
Sn			0.843	0.281	ICP-MS
Sr	5.25 (0.07)	Informative	0.270	0.070	ICP-MS
Te			nd	nd	
Th			<0.005		
Ti	14.1 (0.5)	Informative	0.070	0.050	ICP-MS

Tl	0.004 (0.001)	Informative	0.010	0.005	ICP-MS
U			<0.005		
V			0.050	0.020	ICP-MS
W			<0.1		ICP-MS
Y			<0.1		ICP-MS
Zn	199 (5)	certified	195.000	45.000	ICP-MS
Zr			0.241	0.152	ICP-MS

Table 6: Reference values for BCR-397 and TP-IAEA reference material

2.6.2 Liquid analysis

LOD of the methods are given in the following table. The LOD are calculated for µg g^{-1} hair material and take into consideration the different sample weights used for digestion.

	PFA	digestion		MW digestion
	1 mg	2 mg	4 mg	40 mg
Element				
Ag	0.366	0.196	0.035	0.001
Al	2150.816	1151.009	203.379	3.525
As	0.026	0.014	0.002	0.002
Au	0.111	0.059	0.010	0.014
B	2.353	1.259	0.222	0.539
Ba	0.094	0.050	0.009	0.013
Be	0.024	0.013	0.002	0.001
Bi	0.005	0.003	0.000	0.000
Ca	50.169	26.848	4.744	2.274
Cd	0.076	0.041	0.007	0.001
Cd	0.071	0.038	0.007	0.002
Co	0.020	0.011	0.002	0.003
Cr	1.325	0.709	0.125	0.029
Cr	0.810	0.434	0.077	0.036
Cs	0.003	0.002	0.001	0.001
Cu	4.532	2.425	0.429	0.924
Fe	29.910	16.006	2.828	1.856
Ga	0.006	0.003	0.001	0.001
Hg	0.250	0.134	0.024	0.068
Li	0.092	0.049	0.009	0.018
Mg	3.990	2.135	0.377	0.278
Mn	0.536	0.287	0.051	0.005
Mo	0.114	0.061	0.011	0.107
Na	8.494	4.546	0.803	4.041
Ni	2.477	1.326	0.234	0.252
Pb	0.227	0.122	0.021	0.001
Pd	0.039	0.021	0.020	0.020
Pt	0.001	0.001	0.001	0.001
Rb	0.077	0.041	0.007	0.001
Sb	12.801	6.850	1.210	0.174
Se	0.787	0.421	0.074	0.033
Sn	0.433	0.232	0.041	0.081
Sr	0.072	0.039	0.007	0.011
Te	0.047	0.025	0.004	0.002
Th	0.017	0.009	0.002	0.000
Ti	0.340	0.182	0.032	0.280
Tl	0.002	0.001	0.001	0.001
U	0.002	0.001	0.001	0.001
V	0.038	0.021	0.004	0.002
W	0.009	0.005	0.001	0.996
Zn	8.028	4.296	0.759	0.254
Zn	8.285	4.434	0.783	0.220
Zr	2.526	1.352	0.239	0.126

Table 7: LOD for liquid digestion analysis of hair samples

The following table gives the result of the BCR 397 material, which was investigated within the analytical run. It is evident that the values for Cr and Ni are not in agreement for low sample weights. This was to be expected since the concentration of these elements is very inhomogeneous in this material and above that by a factor of 100 higher compared to a normal expected range. Thus, this material is not suitable for Cr and Ni quantification at trace levels. Therefore, the TP-IAEA in house reference standard was furthermore applied for method validation. The values for TP-IAEA are in excellent agreement with the referenced values. Uncertainty calculations were performed according to GUM (guide for the uncertainty of measurements). The uncertainty of the quantification method is about 7 – 10 %. Nonetheless, sample heterogeneity increases estimated uncertainties up to 75 % for extremely low concentrations close to LOD accounting for 60 – 80 % of the total uncertainty.

		31.10.2007			04.11.2007		04.11.2007			05.11.07			05.11.07	
		PFA digestions			PFA digestions		PFA digestions			PFA digestions			MW digestion	
		1mg weight			2 mg weight		4 mg weight			4 mg weight			40 mg weight	
		Average	SDEV		Average		Average	SDEV		Average	SDEV		Average	SDEV
Element														
Ag		0.64	0.06		0.38		0.50	0.07		0.545	0.03		0.723	0.192
Al		70.04	2.98		nd		nd			65.537	5.09		171.910	95.284
As		0.23	0.04		0.31		0.25	0.02		0.150	0.01		0.403	0.105
Au		0.10	0.04		0.05		0.05	0.01		0.083	0.02		0.042	0.015
B		5.47	0.62		5.46		3.90	0.20		3.747	0.02		4.013	1.444
Ba		8.17	0.97		8.25		7.17	0.36		7.442	0.29		7.819	1.852
Be		<LOD			0.00		0.00	0.01		0.003	0.00		0.007	0.003
Bi		0.07	0.01		0.08		0.08	0.00		0.077	0.00		0.083	0.019
Ca		1466.94	98.37		1436.12		1523.72	57.89		1422.125	16.60		1658.750	374.502
Cd		0.58	0.08		0.58		0.58	0.02		0.479	0.03		0.495	0.035
Cd		0.66	0.03		0.71		0.69	0.02		0.579	0.02		0.628	0.103
Co		0.20	0.02		0.32		0.27	0.00		0.242	0.02		0.674	0.198
Cr	Standard	24.25	3.38		34.56		32.45	2.44		29.029	1.66		98.778	32.536
Cr	DRC mode						23.25	2.58		25.603	2.46		79.253	19.081
Cs		0.01	0.00		0.01		0.01	0.00		0.008	0.00		0.009	0.003
Cu		68.35	5.89		65.43		113.50	35.99		72.488	8.40		83.891	12.489
Fe		246.38	18.89		282.00		291.65	11.71		286.414	29.78		602.053	177.660
Ga		0.31	0.05		0.36		0.32	0.02		0.309	0.01		0.464	0.117
Hg		2.73	0.92		3.35		7.47	0.61		6.349	0.33		7.348	2.152
Li		0.16	0.03		0.18		0.20	0.03		0.140	0.04		0.108	0.028
Mg		149.23	8.71		137.53		143.63	2.26		140.215	2.42		182.034	43.961
Mn		4.13	0.13		4.64		4.80	0.07		4.323	0.35		11.806	4.128
Mo		0.82	0.13		0.97		0.99	0.15		0.869	0.13		5.721	2.305
Na		30.31	5.91		29.90		29.19	1.20		27.716	3.55		50.880	31.530
Ni		7.74	3.68		6.92		9.50	2.26		10.022	4.94		39.696	15.593
Pb		36.61	9.72		33.58		33.70	1.15		31.499	1.04		35.305	10.107
Pd		0.01	0.01		0.01		0.01	0.00		<LOD			0.008	0.000
Pt		0.00	0.00		0.00		0.00	0.00		0.001	0.00		0.000	0.000
Rb		0.13	0.01		0.14		0.16	0.01		0.160	0.03		0.344	0.163
Sb		17.04	7.03		-0.26		0.33	0.11		<LOD	0.25		0.438	0.315
Se		1.93	0.33		2.46		2.35	0.21		1.950	0.05		2.843	0.345
Sn		5.12	3.58		8.84		6.92	0.26		6.182	1.55		7.969	4.107
Sr		4.68	0.14		4.91		5.14	0.14		4.974	0.03		5.322	1.330
Te		<LOD			-0.81		-0.65	0.03		<LOD	0.01		<LOD	
Th		0.01	0.01		0.01		0.01	0.00		0.018	0.01		0.037	0.017
Ti		17.96	1.32		4.49		4.90	0.16		4.715	0.70		12.124	4.056
Tl		0.00	0.00		0.00		0.00	0.00		0.004	0.00		0.005	0.002
U		0.06	0.00		0.07		0.10	0.02		0.081	0.02		0.086	0.022
V		0.25	0.02		0.33		0.29	0.00		0.256	0.01		0.556	0.166
W		0.24	0.12		0.51		0.23	0.09		0.273	0.03		<LOD	0.117
Y		0.03	0.00		0.03		0.04	0.00		<LOD	0.02		0.079	0.030
Zn		233.63	57.96		216.60		207.77	20.36		176.104	3.70		231.445	31.712
Zr		0.14	0.09		0.07		0.11	0.07		<LOD	0.05		<LOD	0.063

Table 9: Analyzed values BCR 397

						31.10.2007		04.11.2007		04.11.2007		05.11.2007		
		certified				PFA digestions	1 mg weight	PFA digestions		PFA digestions		MW digestion	40 mg	
		TP_IAEA		Total		Average	SDEV	Average		average		Average	Stdev	RSD
Element	Isotope		SU	average	Stdev									
Ag	107	0.350	0.090	0.228	0.068	0.205	0.026			0.172		0.295	0.028	9.350
Al	27	7.800	2.100	9.260	2.374	7.497	1.022			nd		11.610	0.915	7.878
As	75	0.115	0.020	0.072	0.022	0.073	0.024	0.056		0.050		0.096	0.005	5.193
Au	197	0.035	0.010	0.039	0.043	0.081	0.048	0.016		0.011		0.016	0.011	67.405
B	11	3.000	0.500	3.394	0.747	4.027	0.690	3.617		2.381		3.074	0.080	2.617
Ba	138	0.150	0.070	0.122	0.028	0.149	0.029	0.105		0.108		0.107	0.015	14.058
Be	9	nd	nd	0.002	0.001	<LOD		<LOD		<LOD		0.002	0.001	72.048
Bi	209	0.020	0.050	0.016	0.004	0.015	0.006	0.012		0.016		0.019	0.002	8.815
Ca	44	180.000	50.000	192.857	30.092	172.327	25.178	184.400		183.856		231.870	5.410	2.333
Cd	112	0.100	0.050	0.049	0.011	0.063	0.003	0.049		0.035		0.045	0.003	6.590
Co	59	0.015	0.005	0.016	0.004	0.019	0.001	0.011		0.013		0.018	0.002	12.050
Cr	IDMS	0.099	0.037	0.086	0.125					0.078		0.120		
Cs	133	<LOD				<LOD		<LOD		<LOD		<LOD		
Cu	63	15.300	2.000	14.213	3.805	12.832	4.140	11.685		12.584		18.824	1.339	7.112
Fe	57	24.000	10.000	18.564	6.538	25.854	7.675	18.015		16.779		12.829	0.217	1.695
Ga	69	0.020	0.020	0.014	0.004	0.016	0.005	0.009		0.012		0.015	0.000	1.914
Hg	202			0.631	0.274	0.618	0.257	0.358		0.601		0.853	0.356	41.694
Li	7	0.040	0.020	0.026	0.015	0.043	0.003	0.020		0.014		<LOD	0.002	13.791
Mg	24	15.000	6.000	10.842	1.721	10.714	1.395	9.023		9.900		12.852	0.670	5.217
Mn	55	0.400	0.150	0.229	0.099	0.374	0.062	0.425		0.241		0.209	0.014	6.852
Mo	98	0.050	0.020	0.055	0.025	0.129	0.067	0.035		0.040		0.073	0.033	45.387
Na	23	51.000	16.000	46.683	11.931	43.972	11.651	34.755		42.666		60.928	0.753	1.236
Ni	61	0.246	0.080	0.440	0.259	0.607	0.282	<LOD		<LOD		0.273	0.063	22.969
Pb	208	1.750	0.200	1.304	0.267	1.045	0.049	1.120		1.488		1.564	0.057	3.621
Pd	106	nd	nd	<LOD		<LOD		<LOD		<LOD		<LOD		
Pt	194	nd	nd	<LOD		<LOD		<LOD		<LOD		<LOD		
Rb	85	0.112	0.080	0.064	0.021	0.076	0.025	0.038		0.054		0.070	0.003	3.590
Sb	121	nd	nd	0.104	0.007	nd		<LOD		<LOD		0.104	0.007	6.845
Se	82	0.912	0.240	0.688	0.283	0.733	0.407	0.483		0.492		0.895	0.021	2.365
Sn	120	0.843	0.281	0.750	0.235	0.935	0.316	0.614		0.651		0.660	0.126	19.019
Sr	88	0.270	0.070	0.191	0.047	0.226	0.057	0.145		0.164		0.193	0.027	13.949
Te	130	nd	nd	<LOD		<LOD		<LOD		<LOD		<LOD		
Th	232	<0.005		0.001	0.001	0.003	0.000	0.000		0.001		0.001	0.000	19.461
Tl	47	0.070	0.050	1.625	1.322	2.003	0.535	0.421		0.449		2.708	1.853	68.441
Tl	205	0.010	0.005	0.007	0.003	0.007	0.004	0.007		0.008		0.006	0.001	12.988
U	238	<0.005		0.006	0.001	0.006	0.002	0.005		0.006		0.008	0.000	3.966
V	51	0.050	0.020	0.037	0.023	0.053	0.032	0.041		0.016		0.029	0.002	6.398
W	183	<0.1		0.050	0.093	0.033	0.023	0.006		0.001		0.134	0.162	120.892
Y	89	<0.1		0.003	0.004	0.002	0.001	0.007		0.001		0.002	0.001	70.027
Zn	66	195.000	45.000	159.889	55.980	137.898	52.460	137.557		116.110		233.282	4.580	1.963
Zr	90	0.241	0.152	0.161	0.109	0.228	0.131	0.081		0.074		0.183	0.098	53.187

Table 10: Analyzed values TP-IAEA

2.6.3 Laser ablation analysis

Laser ablation LOD were calculated for Element/SO ratios according to 3 x STDEV of the blank signal. This LOD was compared to the LOD as calculated by the ablation of the glue in order to retrieve information whether the glue contributes significantly to the background or not. It is evident that the LOD for glue ablation is comparable to the pure gas blank except for In, Tl and Zr. Even for these elements, no significant contribution to the analysis can be observed since the values are <LOD within the analyzed hair samples.

		Ag107	Al27	As75	AsO91	Au197	B10	B11	Ba137	Ba138	Be9	Bi209
LOD(Kleber)		0.09	98.93	1.04	1.85	0.17	0.12	0.12	0.18	0.19	0.10	0.16
LOD (gas)		0.11	74.43	3.19	1.51	0.11	0.05	0.10	0.07	0.16	0.00	0.11
LOD(Kleber/gas)		0.8	1.3	0.3	1.2	1.5	2.4	1.2	2.7	1.2		1.5
		C13	Ca44	Cd112	Cd113	Cd111	Cd114	CeO156	Co59	Cr52	Cr53	Cs133
LOD(Kleber)		21.33	31485.15	1.17	0.36	0.09	1.16	0.10	18.60	10.39	23.26	0.29
LOD (gas)		10.80	33488.15	0.20	0.37	0.15	0.20	0.16	26.30	12.34	17.74	0.31
LOD(Kleber/gas)		2.0	0.9	6.0	1.0	0.6	5.9	0.6	0.7	0.8	1.3	0.9
		Cu63	Cu65	Fe57	Ga69	Hg201	Hg202	In115	Li7	Mg25	Mg24	Mn55
LOD(Kleber)		1.18	17.23	46.19	126.20	0.51	0.98	2.29	0.10	0.12	0.07	31.79
LOD (gas)		2.40	31.88	60.75	179.54	0.84	0.35	0.32	0.14	0.17	0.00	78.52
LOD(Kleber/gas)		0.5	0.5	0.8	0.7	0.6	2.8	7.2	0.7	0.7		0.4
		Mo98	Na23	Ni60	Pb208	Pb207	Pd105	Pd106	Pt194	Pt195	Rb85	Sb121
LOD(Kleber)		0.15	2.89	9.37	0.21	0.15	0.12	0.20	0.15	1.19	0.76	0.12
LOD (gas)		0.05	1.84	4.01	0.56	0.33	0.15	0.10	0.11	0.12	0.42	0.10
LOD(Kleber/gas)		3.0	1.6	2.3	0.4	0.4	0.8	2.0	1.4	10.1	1.8	1.2
		Se82	Sn118	SO48	Sr86	Sr88	Sr87	Te130	Te125	Th232	ThO248	Ti49
LOD(Kleber)		1.20	0.00	272.94	1.03	0.20	0.44	0.28	0.00	0.10	0.07	21.58
LOD (gas)		1.41	0.00	298.78	1.81	0.16	0.26	1.00	0.00	0.08	0.14	73.39
LOD(Kleber/gas)		0.9		0.9	0.6	1.2	1.7	0.3		1.3	0.5	0.3
		Tl205	U238	UO254	V51	W184	Y89	Zn64	Zn66	Zr90		
LOD(Kleber)		1.18	0.12	0.10	93.19	0.09	0.34	26.03	1.91	0.00		
LOD (gas)		0.11	0.11	0.12	482.04	0.10	0.31	40.99	2.82	0.27		
LOD(Kleber/gas)		11.0	1.1	0.9	0.2	0.9	1.1	0.6	0.7	0.0		

Table 11: LOD for gas blank and glue in LA-ICP-MS (N.B. Kleber = glue)

The following chart (figure 2) represents the comparison for washed and unwashed hair samples for all elements which are >LOD. It is evident that the washing procedure removes surface contaminants of ubiquitous elements, even though most elements are within the uncertainty range (green area). No contamination of an element could be observed, except for Ti, which is most probably an artifact since the analyzed values are close to LOD.

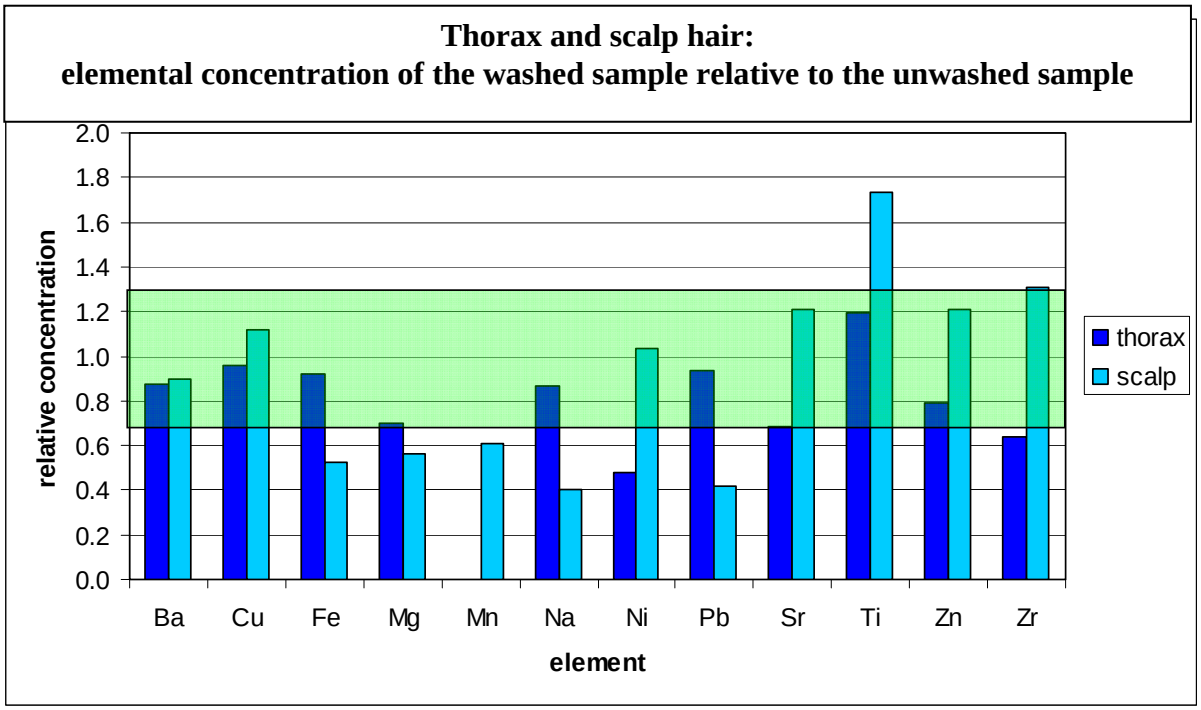

Figure 2: Relative elemental concentration of the washed hair relative to the unwashed hair for thorax and scalp hair of the person concerned.

Figure 3 shows a comparison of the elemental concentration of thorax hair relative to scalp hair after LA-ICP-MS analysis. It is evident that all elements except Pb show the same range of concentration. Even though Pb is elevated in thorax hair relative to scalp hair, it is in both hair pools (thorax and scalp) at the lower range of concentration found in healthy humans (see also Table 12). Since Sr shows a significant difference between washing and non-washing between thorax and scalp hair, but no difference in the elemental content after washing, it might be concluded that Sr is an exogenous contaminant rather than endogenous.

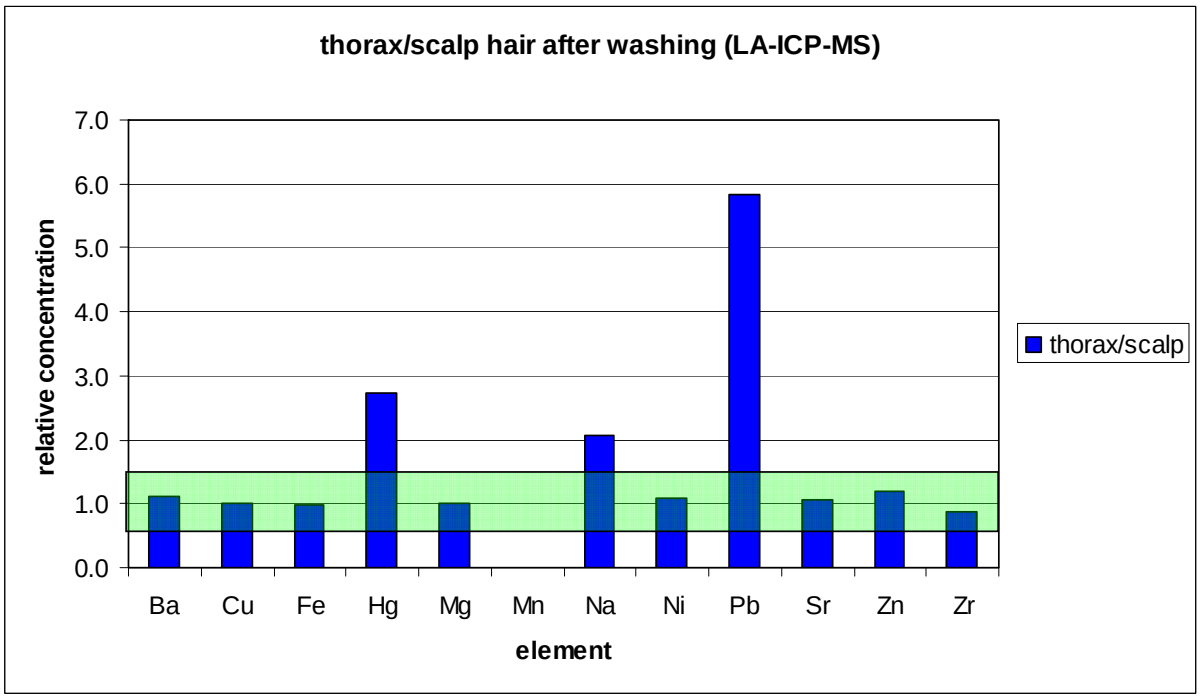

Figure 3: Comparison of thorax and scalp hair samples after washing (for elements >LOD in LA-ICP-MS)

3 Results and discussion

Liquid digestion experiments led to the following levels of trace elements in scalp and thorax hair.

The normal range referred to corresponds to the range published by Rodushkin et al. in 2000 on 114 individuals from a mixed population (42% men and 58% women, aged from 1 to 76 years) from residents of the medium-sized cities of Umea and Lulea in north-east Sweden. [8] Since this is one of the most complete studies with validated methodology (ICP-MS analysis), we refer to this range of samples in the following text as "normal range". Additionally, the complete set of "published ranges" are given in Table 12 according to Rodushkin[8] showing the complete range of results published in papers until 2000 without taking into account possible analytical artifacts in these papers.

Additionally, in Table 13 we give the elemental concentration ranges in hair of healthy French volunteers published by Goullé et al. in 2005 [9]. The reported ranges in these papers [8,9] are quite similar thus giving a good indication of an expectable "normal range".

	found ranges in human scalp hair [µg/g]					published ranges in human scalp hair [µg/g]				TP_IAEA	CaseO_Skalp	CaseO_Thorax	SU [%]	comment
target anal	mean [µg/g]	SD [µg/g]	median [µg/g]	lower limit [µg/g]	upper limit [µg/g]	lower limit [µg/g]	upper limit [µg/g]	published mean [µg/g]						
Ag	0.231	0.298	0.132	0.025	1.96	0.01	3.9	1.955		0.228	0.018	<LOD	45	
Al	8.2	4.8	6.4	2.7	25.6	0.1	191	95.55		9.26	7.4	<LOD	45	
As	0.085	0.054	0.067	0.034	0.319	0.015	26	13.0075		0.072	0.091	0.073	62	
Au	0.03	0.028	0.017	0.003	0.2	0.002	4.54	2.271		0.039	0.017	0.011	50	
B	0.67	0.62	0.46	0.13	3.3	0.88	8	4.44		3.4	1.3	1.1	25	
Ba	0.64	0.49	0.46	0.16	1.92	0.6	20	10.3		0.12	8.2	4.2	25	
Be	0.0013	0.0009	0.001	0.0004	0.0042	-	-	-		0.002	<LOD	<LOD	75	
Bi	0.019	0.025	0.009	0.002	0.255	0.03	-	-		0.016	0.001	0.001	75	
Cd	0.058	0.056	0.034	0.01	0.356	0.02	16	8.01		0.049	0.007	0.007	75	
Co	0.013	0.011	0.01	0.002	0.063	0.01	14.6	7.305		0.016	0.057	0.092	45	
Cr	0.167	0.118	0.131	0.046	0.527	0.03	33	16.515		0.086	0.083	0.092	62	ICP-DRC-M
Cs	0.00067	0.00046	0.00051	0.00017	0.0019	0.05	2.4	1.225		<LOD	<LOD	<LOD		
Cu	25	21	18	8.5	96	0.3	293	146.65		14.2	13.7	9.2	25	
Fe	9.6	4.4	8.4	4.9	23	3	900	451.5		18.6	15.8	16.5	25	
Hg	0.261	0.145	0.249	0.053	0.927	0.07	106	53.035		1.46	0.09	0.25	55	LA-ICP-MS
Mg	46	38	32	8.5	141	1.5	1040	520.75		11	370	244	25	
Mn	0.56	0.55	0.35	0.08	2.41	0.03	50	25.015		0.31	0.145	0.16	45	
Mo	0.042	0.02	0.037	0.021	0.165	0.01	3	1.505		0.08	0.062	0.026	75	
Na	147	149	94	17	670	0.04	2100	1050.02		47	40	100	45	
Ni	0.43	0.4	0.29	0.11	1.6	0.002	28	14.001		0.44	0.485	0.37	75	
Pb	0.96	0.85	0.66	0.22	7.26	0.004	95	47.502		1.3	0.16	0.33	25	
Pd	0.00032	0.00078	0.00006	0.00006	0.0021	-	0.02	0.02		<LOD	<LOD	<LOD		
Pt	0.00015	0.00017	0.00008	0.00002	0.00061	-	0.05	0.05		<LOD	<LOD	<LOD		
Rb	0.093	0.085	0.06	0.012	0.482	0.06	5.34	2.7		0.064	0.026	0.037	75	
Sb	0.022	0.017	0.017	0.07	0.122	0.016	38	19.008		0.104	0.07	<LOD	75	
Se	0.83	0.28	0.79	0.48	1.84	0.002	6.6	3.301		0.69	0.43	0.56	45	
Sn	0.32	0.39	0.195	0.06	1.41	0.02	90	45.01		0.752	<LOD	0.058	75	
Sr	1.2	1	0.97	0.014	5.54	0.2	860	430.1		0.19	17.9	9.5	25	
Te	0.00034	0.00033	0.00024	0.00007	0.001	-	-	-		<LOD	<LOD	<LOD		
Th	0.0013	0.001	0.001	0.0003	0.0044	0.005	2.7	1.3525		0.001	0.003	0.002	75	
Ti	830	0.68	0.58	0.12	2.71	0.04	35	17.52		1.62	0.62	0.45	45	
Tl	0.00061	0.00032	0.00053	0.0002	0.0016	-	-	-		0.007	<LOD	<LOD	75	
U	0.057	0.065	0.036	0.006	0.436	0.005	1.28	0.6425		0.006	0.014	0.027	75	
W	0.0053	0.0049	0.0035	0.001	0.021	0.0003	0.07	0.03515		0.05	0.02	0.003	75	MW results
V	0.027	0.024	0.018	0.005	0.134	0.005	160	80.0025		0.037	0.11	0.08	75	
Y	0.023	0.029	0.014	0.003	0.104	-	-	-		0.003	0.002	0.002	75	
Zn	142	29	144	68	198	40	327	183.5		156	207	163	25	
Zr	0.155	0.237	0.052	0.011	1.21	0.2	4.4	2.3		0.16	0.07	0.03	45	
S	47700	4100	48100	40700	55000	38000	82000	60000						

Table 12: Normal range according to Rodushkin et al [8] , published range and analyzed values for TP-IAEA, scalp hair (summary) and thorax hair (summary). Uncertainties are according to GUM. Major contributor to uncertainty is the homogeneity of the samples.

The results of our measurements are given in µg g^{-1}. Reported uncertainties are relative SU in % and are calculated according to GUM. A major contributor to the uncertainties is the inhomogeneity of the samples. Therefore, uncertainties range from 25 up to 75 % depending on the concentration level of the samples. These uncertainties are integrated in the following charts in order to give an overview of the overlap of the analyzed range and the published "normal range". If an overlap can be observed, a significant elevation compared to the "normal range" can be excluded. The values are taken as average values from all measurements.

	Goulle Forensic Sci. Int. 153, 2005, 39-44		
target analytes	median	5th percentile	95th percentile
Ag	0.08	0.02	1.31
Al	1.63	0.26	5.3
As	0.05	0.03	0.08
Au			
B	0.54	0.26	1.87
Ba	0.28	0.05	1.58
Be	0.007	0.003	0.012
Bi	0.009	0.0004	0.14
Cd		0.004	0.17
Co	0.023	0.004	0.14
Cr	0.2	0.11	0.52
Cs			
Cu	20.3	9	61.3
Fe			
Ga	0.011	0.002	0.068
Ge	0.004	0.001	0.039
Hg	0.66	0.31	1.66
Li	0.016	0.003	0.042
Mg			
Mn	0.067	0.016	0.57
Mo	0.021	0.01	0.028
Na			
Ni	0.23	0.08	0.9
Pb	0.41	0.13	4.57
Pd	0.01	0.004	0.049
Pt	0.00035	0.0004	0.0008
Rb	0.006	0.003	0.03
Sb	0.008	0.003	0.13
Se	0.54	0.37	1.37
Sn	0.046	0.007	0.34
Sr	0.89	0.17	4.63
Te	0.0003	0.0003	0.001
Th			
Ti			
Tl	0.0002	0.0001	0.0004
U	0.009	0.002	0.03
W	0.0013	0.00001	0.007
V	0.016	0.001	0.051
Y			
Zn	162	129	209

Table 13: Elemental concentration range in human hair of 45 healthy French volunteers reported by Goullé et al. [9]

The following chart gives the comparison of the elemental concentration range in thorax hair (red) to the “normal range” (turquoise).

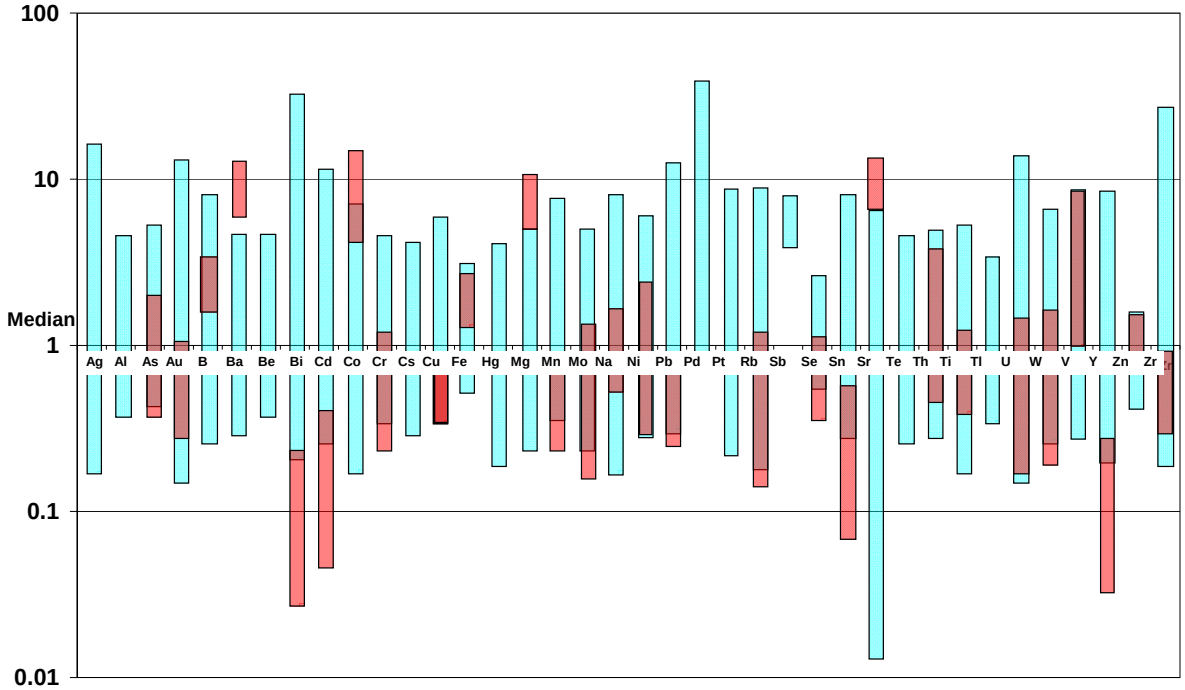

Figure 4: Comparison of the thorax hair (red) range (given by the average +/ SU) and the “normal range” published in literature. [8] The values are set relative to the median of the “normal range”.

The following chart gives the comparison of the elemental concentration range in scalp hair (red) to the “normal range” (turquoise).

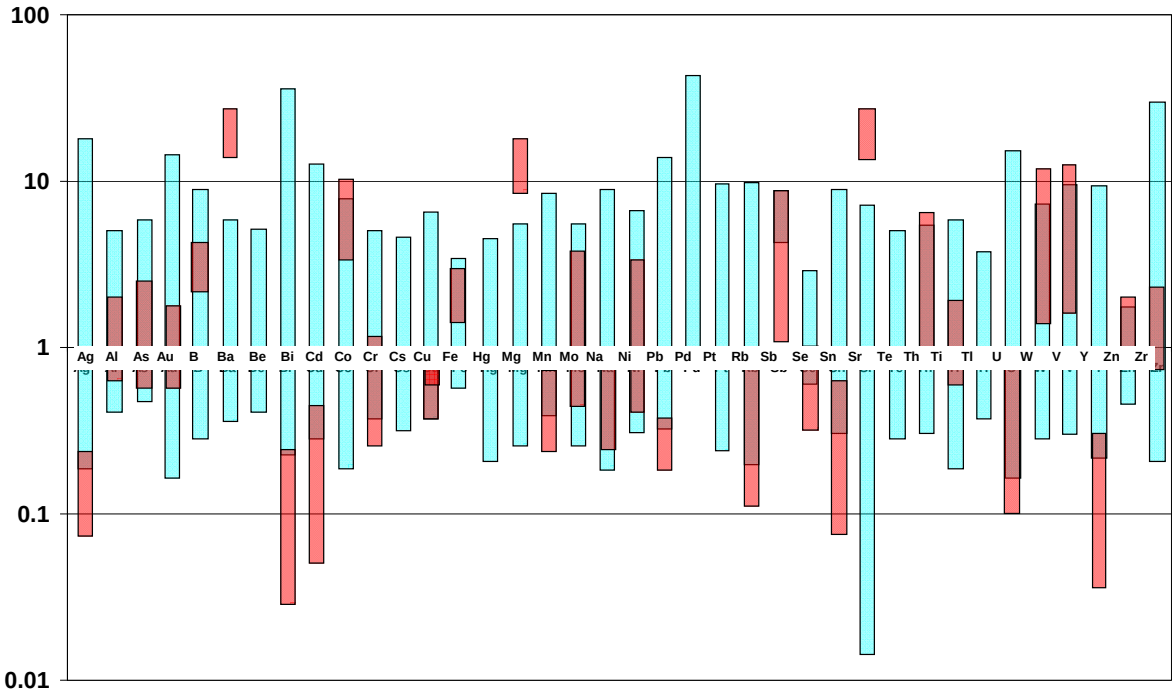

Figure 5: Comparison of the scalp hair (red) range (given by the average +/ SU) and the “normal range” published in literature.[8] The values are set relative to the median of the “normal range”.

All elemental concentration ranges are overlapping with the “normal range” (except Ba, Mg and Sr) and therefore no significant elevation compared to normal values can be interpreted except for Ba, Mg and Sr.

The elements Ba, Mg and Sr are elevated compared to the upper limit of the “normal range”. Ba is elevated by a factor of 4.3 and 2.1 for scalp and thorax hair respectively relative to an upper limit of 1.92 µg g^{-1}. Mg is elevated by a factor of 2.6 and 1.7 for scalp and thorax hair respectively relative to an upper limit of 141 µg g^{-1}. Sr is elevated by a factor of 3.2 and 1.7 for scalp and thorax hair respectively relative to an upper limit of 5.54 µg g^{-1}.

The results of the analysis of scalp hair were further compared to the level found in the TP-IAEA standard. In this comparison it is evident that all samples show a similar elevation. Ba, Mg and Sr results indicate that the surface concentration is relatively elevated compared to the core concentration. This can be an indication for exogenous long term contamination by solutions with elevated Ba, Sr and Mg levels leading to diffusion into the inner core of the hair. In the context of further interpretation of exogenous diffusion processes, further investigations would be desirable.

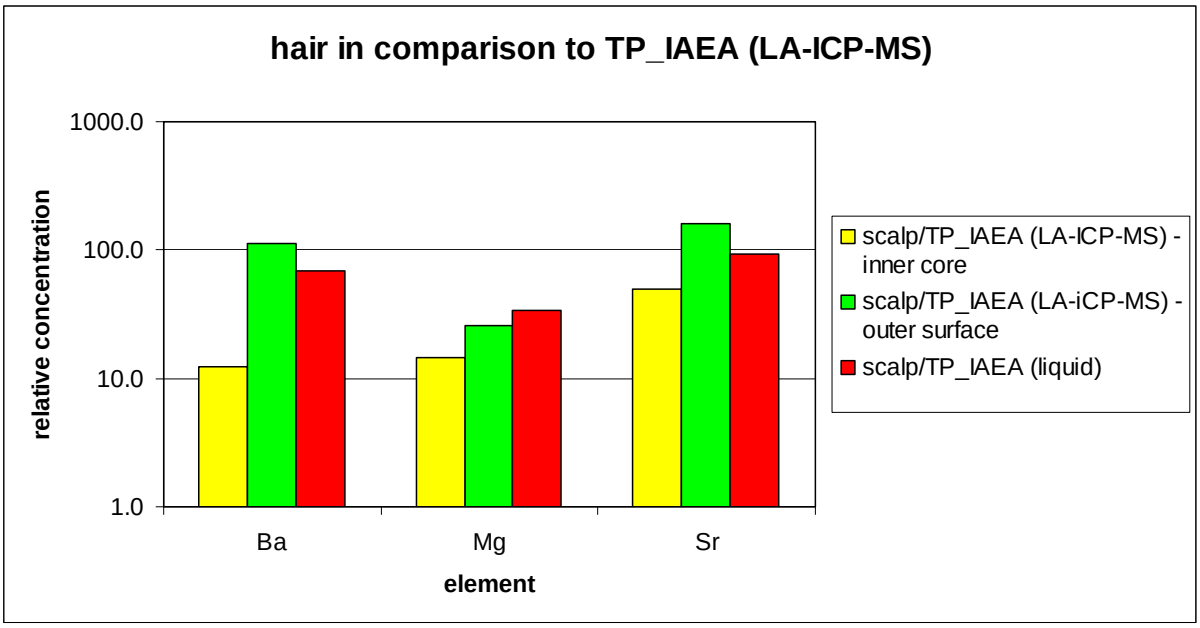

Figure 6: Comparison of the scalp hair of the person concerned to the results of the TP-IAEA hair in the hair surface (LA-ICP-MS), the inner core (LA-ICP-MS) and the liquid digestion.

Other elements like Cu, Fe, Hg and Pb are clearly endogenously incorporated elements. These elements are not found in elevated levels in the hair material.

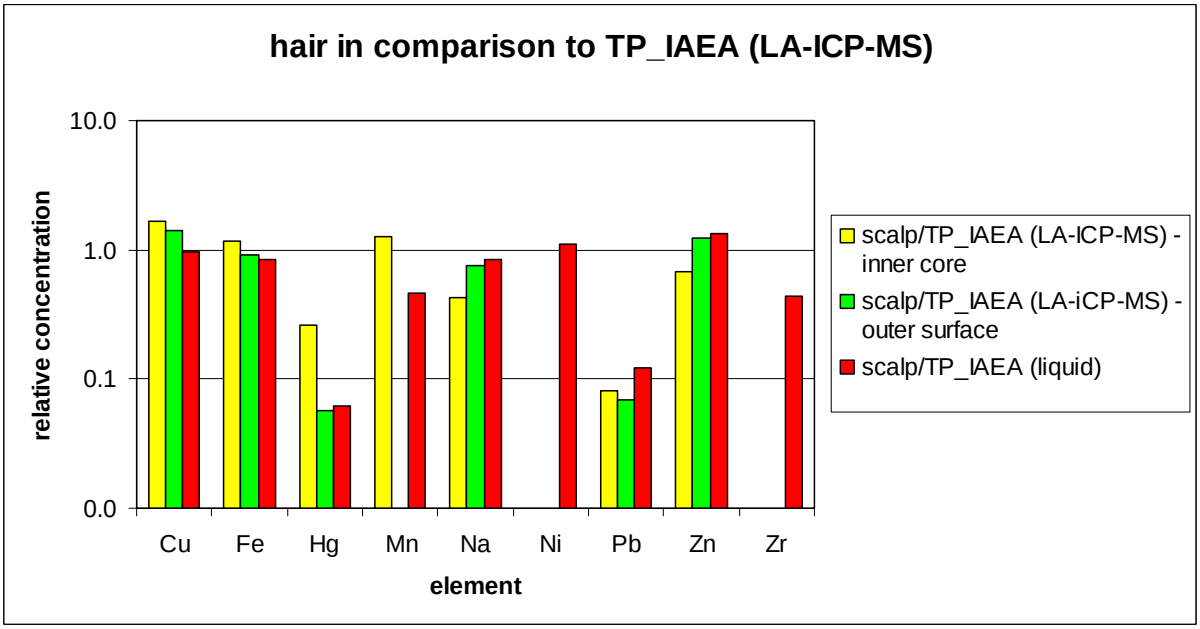

Figure 7: Comparison of the scalp hair of the person concerned to the results of the TP-IAEA hair in the hair surface (LA-ICP-MS), the inner core (LA-ICP-MS) and the liquid digestion.

In the following section, the analysis of Sr, Mg and Ba are monitored along single hair strands and reported accordingly:

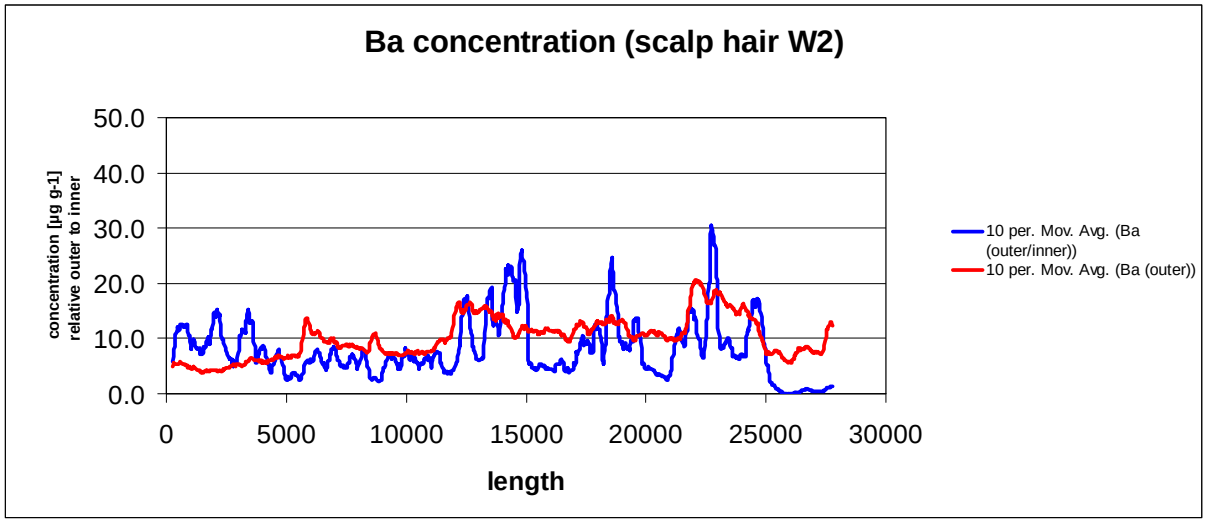

Figure 8: Ba concentration along scalp hair W2 and ratio between Ba concentration in the outer and inner part of the hair.

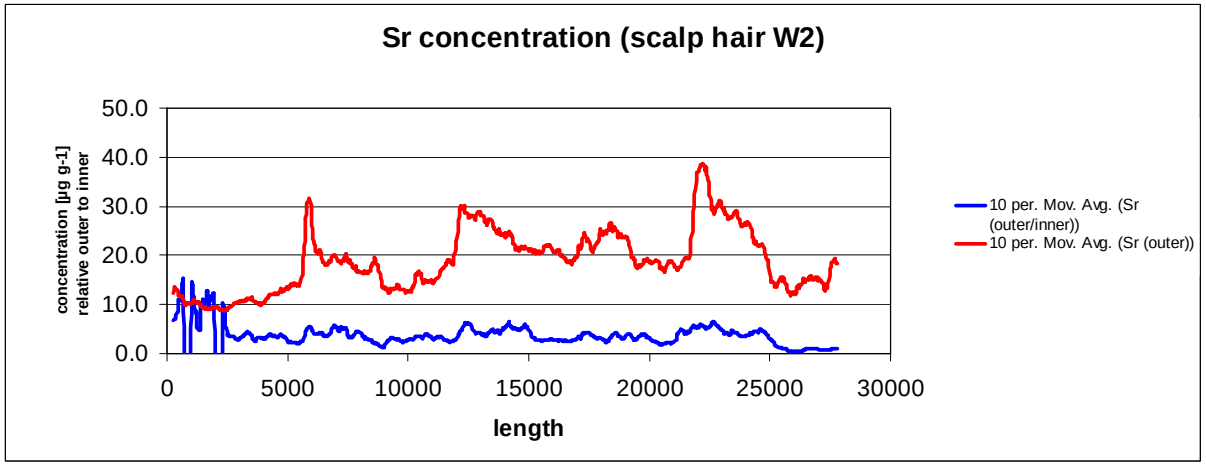

Figure 9: Sr concentration along scalp hair W2 and ratio between Sr concentration in the outer and inner part of the hair.

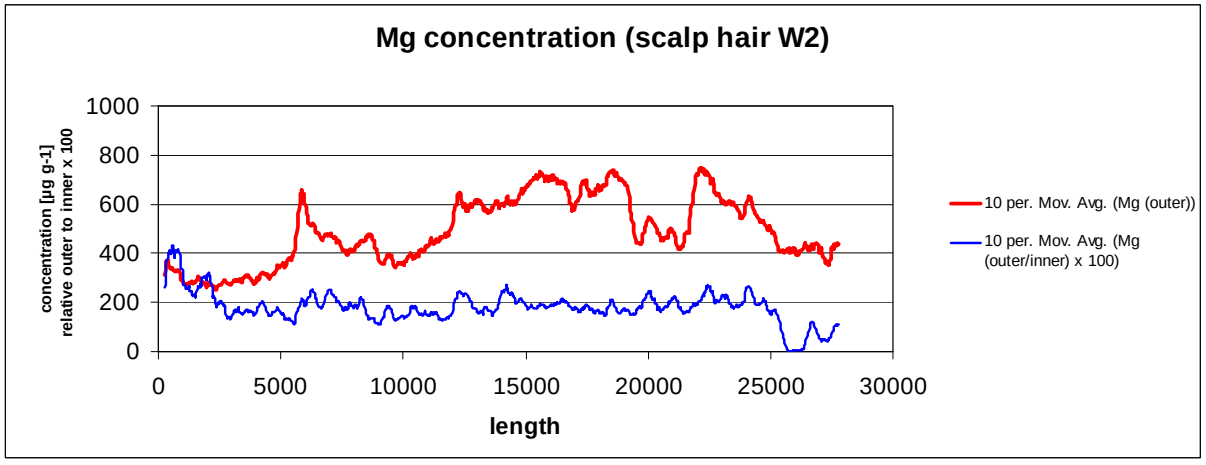

Figure 10: Mg concentration along scalp hair W2 and ratio between Mg concentration in the outer and inner part of the hair. The latter is multiplied by a factor of 100 for better visualization.

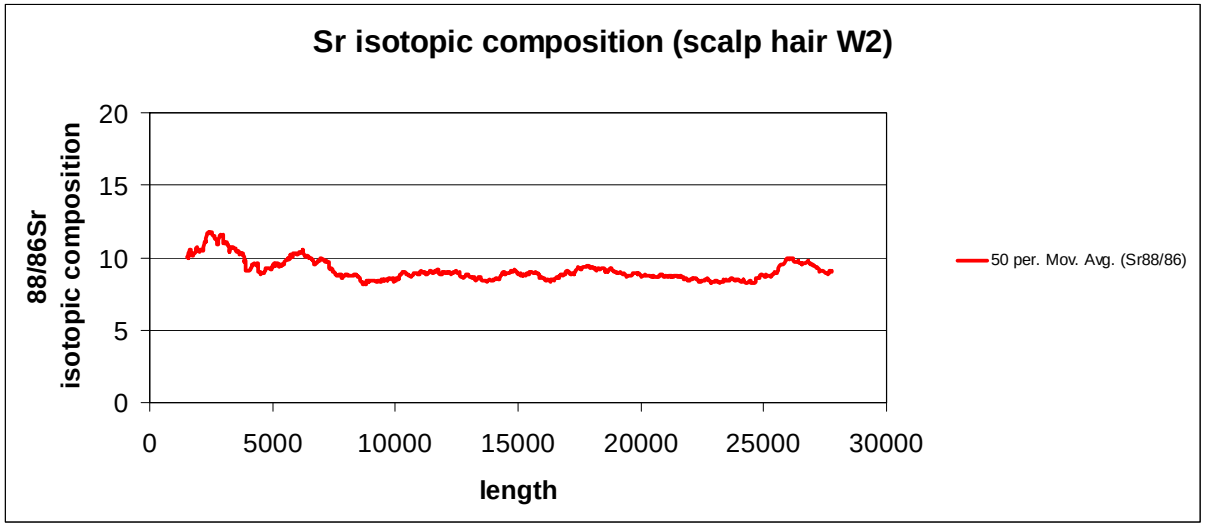

Figure 11: $^{88/86}$Sr isotopic ratio along scalp hair W2. (The ratio is a raw estimate and not analyzed in isotope ratio mode)

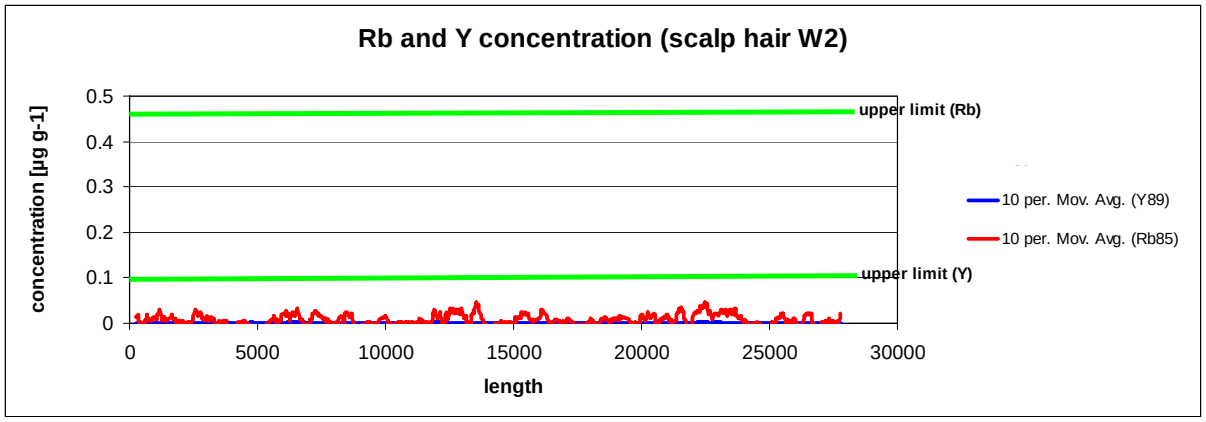

Figure 12: Rb and Y concentration along scalp hair W2.

The investigated scalp hair shows elevated levels of Ba, Sr and Mg along the whole investigated hair with variations which are parallel for all elements. This leads to the conclusion that Ba, Mg and Sr originate from the same source. The Sr isotopic composition shows no significant deviation from natural composition throughout the whole hair. There were no detectable levels of decay products of radiogenic ^{85}Sr or ^{89}Sr. The latter results are reproducible within all investigated hair samples and are summarized in the following charts exemplarily. (N.B.: the Mg concentrations are divided by 10 in the following charts in order to fit them into one graph).

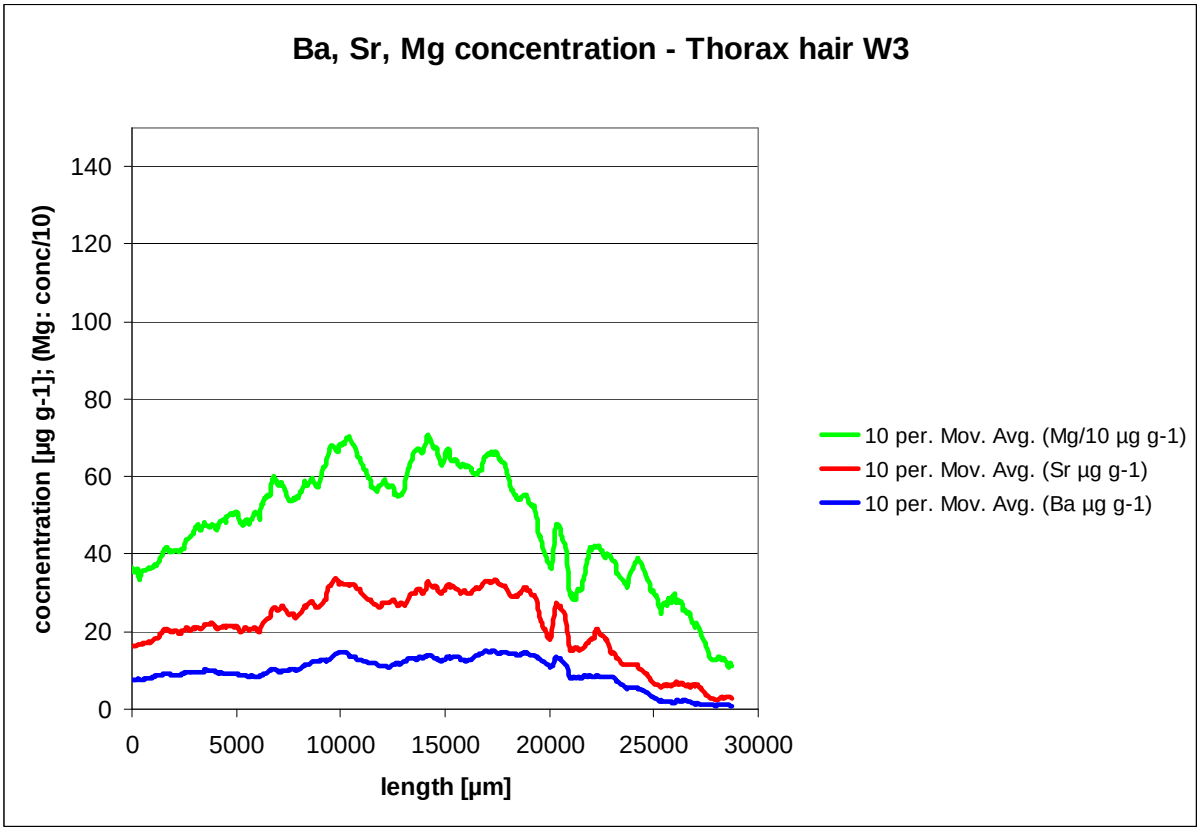

Figure 13: Ba, Sr and Mg concentration along thorax hair W3 (Mg is divided by 10 for better visualization).

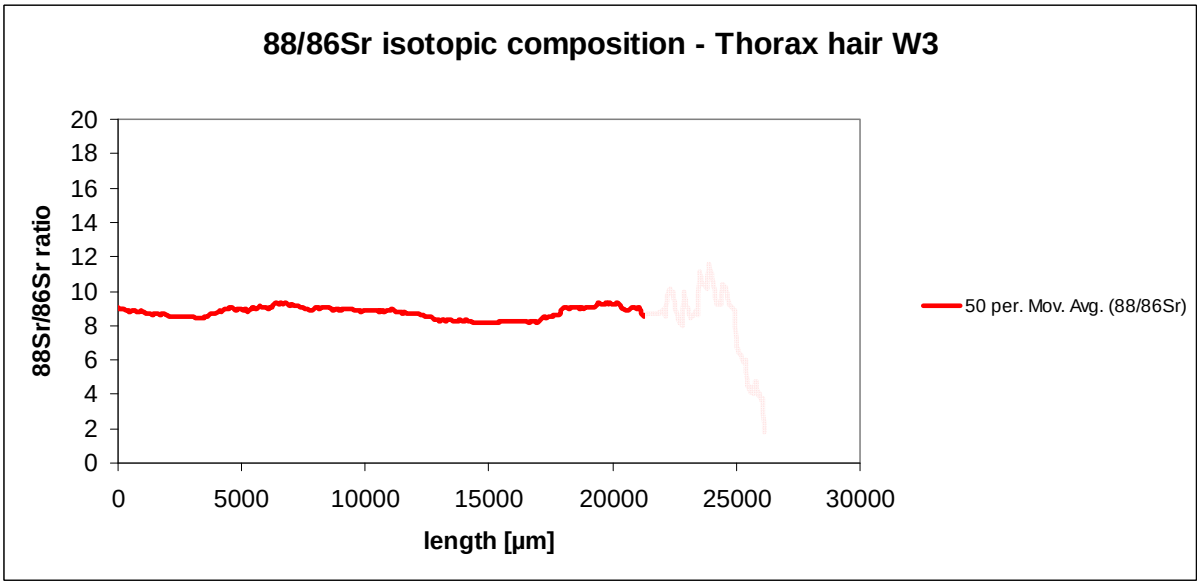

Figure 14: $^{88/86}$Sr isotopic ratio along thorax hair W3. (The ratio is a raw estimate and not analyzed in isotope ratio mode).

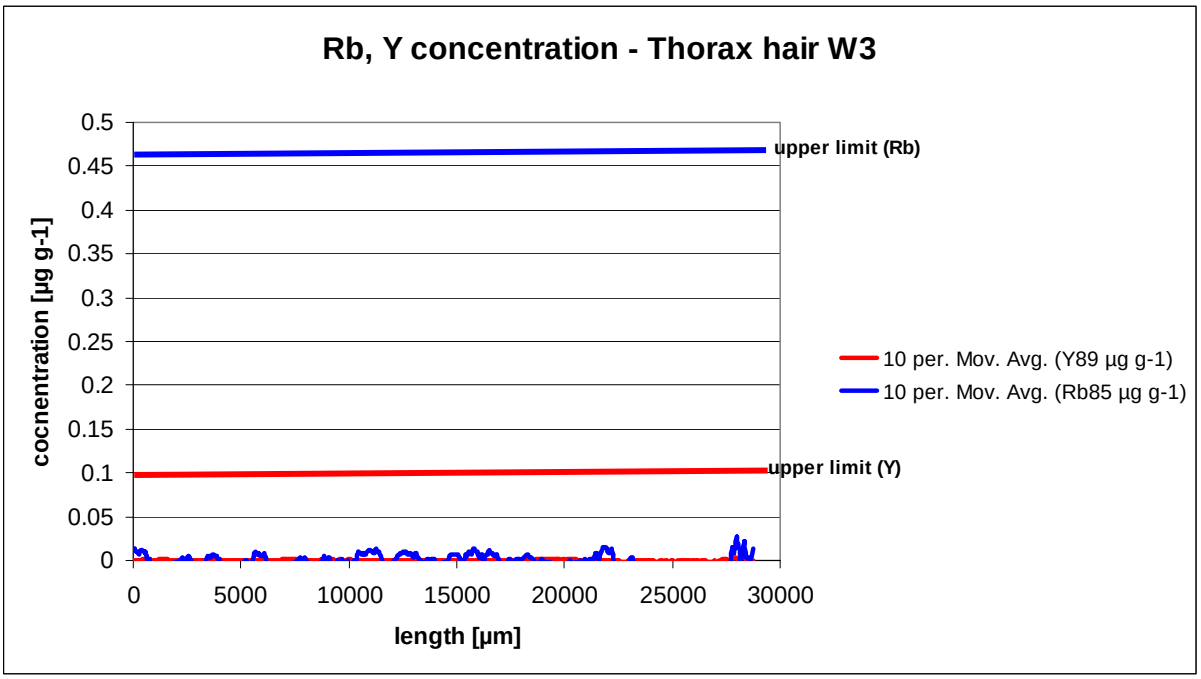

Figure 15: Rb and Y concentration along thorax hair W3. (Upper limits correspond to published elemental ranges)

The thorax hair shows the same features as the scalp hair: Ba, Mg and Sr are elevated and follow the same pattern. The Sr isotopic composition is natural. The decrease at the end of the line is an analytical artifact solely caused by the fact that the Sr concentration decreases at the end of the hair, where the hair gets thinner and more difficult to be analyzed by LA-ICP-MS. There were no detectable levels of decay products of radiogenic short lived Sr radio nuclides.

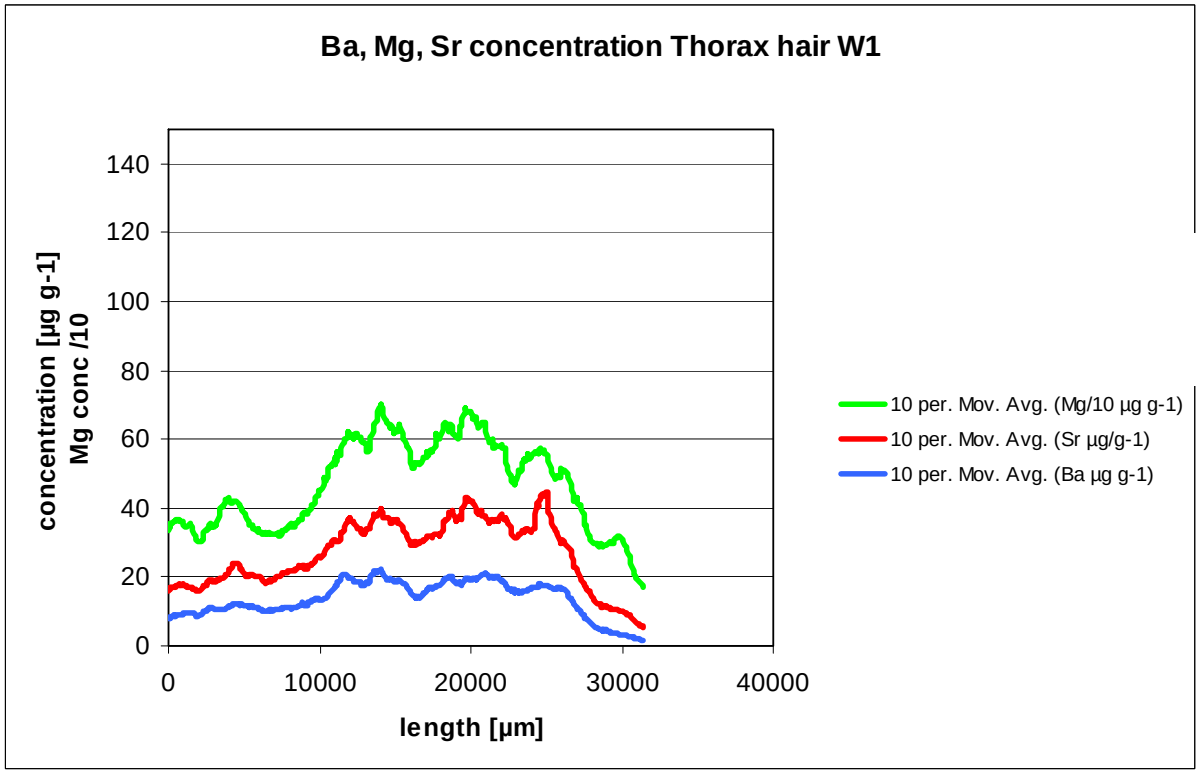

Figure 16: Ba, Mg and Sr concentration along thorax hair W1 (Mg is divided by 10 for better visualization).

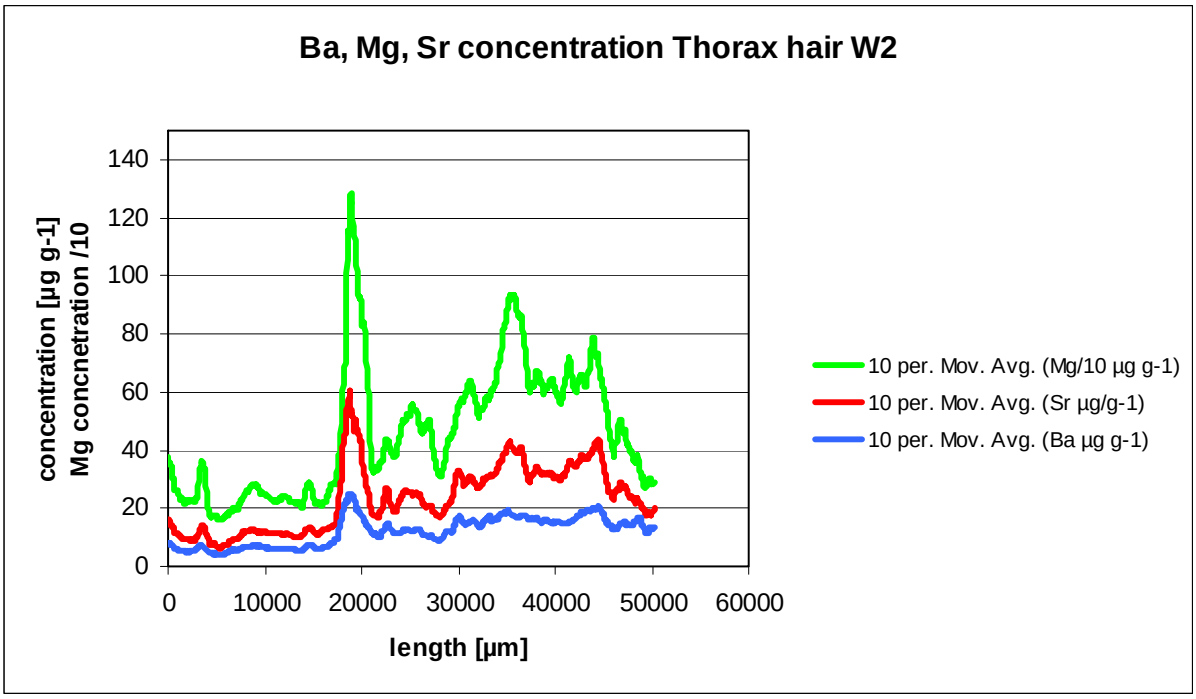

Figure 17: Ba, Mg and Sr concentration along thorax hair W2 (Mg is divided by 10 for better visualization).

Thorax hair W1 and W2 show the same pattern for Ba, Mg and Sr. Since the hair sample W2 is significantly longer, the pattern looks at the first sight different to W1 and W3. Nonetheless, the last 30 000 µm (towards the tip) show the same pattern for all hair samples and elements.

4 Summary

It can be summarized that compared to the “normal range” found in humans[8,9] no element shows a level in thorax or scalp hair of the person concerned that can be considered as toxic.

The elements Ba, Mg and Sr are nevertheless significantly elevated in both thorax and scalp hair. Since elevated levels are found in both the outer and inner layer of the hair, the elements are originating either from an endogenous source or from an exogenous source, which shows high concentration of these elements and has been in extended contact with the hair. In the latter case, diffusion of an exogenous source into the inner part of the hair is possible. The latter assumption requires further investigation on diffusion processes of Ba, Mg and Sr into hair.
Possible sources which have an elevated concentration of these elements are e.g. sea water or tap water originating from sea water sources. The following chart (Figure 18) gives an indication of the relative elemental concentration of Ba, Mg and Sr in sea water of the region[10] compared to thorax and scalp hair of the individual concerned. It is evident that similar elemental ratios of Ba, Sr and Mg in sea water are reflected in the investigated hair samples. Further investigations have to be conducted in order to prove these assumptions.

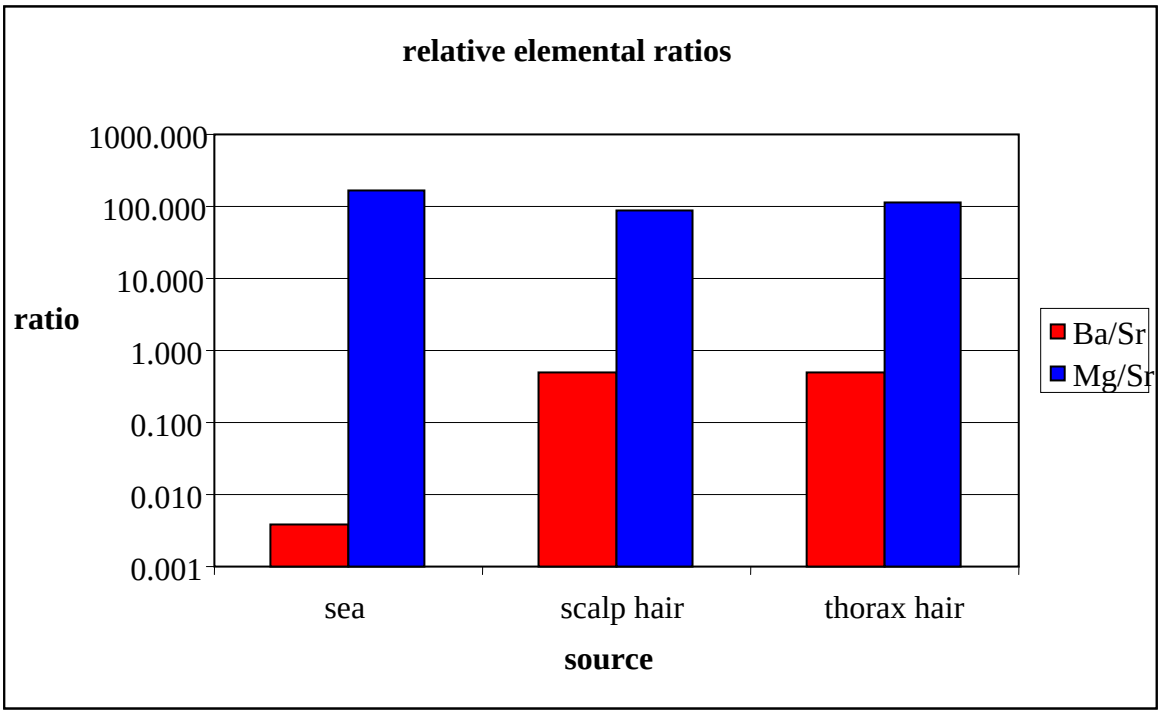

Figure 18: Comparison of Ba/Sr and Mg/Sr ratios in sea water and thorax and scalp hair of the person concerned.

All investigated hair samples show elevated levels of the elements Ba, Mg and Sr both in liquid digestion and LA experiments. The LA-ICP-MS results show that the Ba, Mg and Sr levels are elevated throughout the whole lengths of the single hair samples which were investigated leading to the conclusion that a continuous exposure of the hair to these elements had occurred (either endogenously or exogenously – see above).
Preliminary studies of the Sr isotopic composition lead to the conclusion that Sr originates from a natural non radiogenic source which is confirmed by the fact that no detectable levels of decay products of radiogenic ^{85}Sr or ^{89}Sr were found in any of the investigated hair samples.

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[10] G.E. Gordon, Chem 678 Environmental Chemistry (1984).

APPENDIX 2

Conclusions

1. Les concentrations en strontium, magnésium et barium mesurées dans les cheveux et les poils thoraciques du prisonnier Abdullah ÖCALAN par le Professeur PROHASKA ne sont pas de nature à être interprétées comme dangereuses pour la santé de l'intéressé. Ces concentrations certes apparemment élevées, sont à relativiser eu égard aux fourchettes de normalité des populations de référence de la littérature scientifique et à la grande variabilité des résultats analytiques d'un laboratoire à l'autre pour un même échantillon analysé. Les plaintes actuellement formulées par le prisonnier concernent pour l'essentiel la sphère ORL et sont à mettre en compte sur une pathologie locale d'ailleurs dûment objectivée.

2. Les teneurs en strontium, magnésium et barium des cheveux et des poils thoraciques du prisonnier Abdullah ÖCALAN sont probablement liées aux conditions environnementales de l'intéressé et notamment à l'environnement marin dont on sait qu'il est particulièrement riche en strontium notamment. Les habitudes alimentaires (alimentation riche en produits de la mer) et l'usage d'une eau du robinet elle-même particulièrement riche en strontium du fait de la proximité de la mer, pourraient constituer une explication.

3. Dans un but de prévention mais aussi pour confirmer l'hypothèse précédente, il y aurait lieu de prévoir un contrôle périodique, une fois par trimestre de la concentration en strontium, magnésium et barium d'un échantillon de sang et d'urine de l'intéressé. Dans la mesure où les résultats ne montreraient pas de modifications significatives, notamment dans le sens d'une augmentation, nous estimons qu'il n'y aurait pas lieu de renouveler ces analyses.

Fait à Lausanne, le 31 janvier 2008

Dr Franck SPORKERT Prof. Patrice MANGIN

APPENDIX 2
(translation)

Conclusions

1. The strontium, magnesium and barium concentrations found by Professor PROHASKA in the hair of the scalp and of the thorax of the prisoner Abdullah ÖCALAN are not such as to be interpreted as dangerous to the health of the person concerned. While these concentrations do appear to be high, they need to be placed in perspective in view of the normal ranges in reference populations reported in scientific literature and the great variability of the test results from different laboratories which have analysed the same sample. The complaints now made by the prisoner relate essentially to the ENT sphere and are to be attributed to a local pathology for which there is objective evidence.

2. The levels of strontium, magnesium and barium in the hair of the scalp and of the thorax of the prisoner Abdullah ÖCALAN are probably related to the environmental conditions of the person concerned, and especially the marine environment, which is known to be particularly rich in strontium, among other elements. Dietary habits (diet rich in seafood) and the use of tap water that is itself particularly rich in strontium because of proximity to the sea might provide an explanation.

3. With a view to preventive action, but also in order to confirm the above hypothesis, there would be good reason to schedule periodic monitoring, on a three-monthly basis, of the strontium, magnesium and barium concentrations in a blood and urine sample from the person concerned. Were the results to show no significant changes, particularly in terms of an increase, we consider that there would be no need to repeat these tests.

Lausanne, 31 January 2008

Dr Franck SPORKERT Prof. Patrice MANGIN