Forensic Science International 291 (2018) 230–233

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Changes in thallium distribution in the scalp hair after an intoxication incident

Takehisa Matsukawa[a,*], Momoko Chiba[a], Atsuko Shinohara[a,b], Yuki Matsumoto-Omori[a,c], Kazuhito Yokoyama[a]

[a] Juntendo University Faculty of Medicine, 2-1-1 Hongo, Bunkyo-ku, Tokyo 113-8421, Japan
[b] Seisen University, Research Institute for Cultural Studies, 3-16-21 Higashi Gotanda, Shinagawa-ku, Tokyo 141-8642, Japan
[c] Kitasato University School of Medicine, 1-15-1 Kitasato, Minami-ku, Sagamihara, Kanagawa 252-0373, Japan

ARTICLE INFO

Article history:
Received 25 April 2018
Received in revised form 18 August 2018
Accepted 20 August 2018
Available online 5 September 2018

Keywords:
Thallium
Scalp hair
Inductively coupled plasma mass spectrometry
Forensic science

ABSTRACT

In cases of criminal thallium poisoning, forensic investigation is required to identify the amount and time of thallium exposure. Usually, blood and urine thallium levels are respectively used as biomarkers. Additionally, hair has the unique potential to reveal retrospective information. Although several studies have attempted to clarify how thallium is distributed in hair after thallium poisoning, none have evaluated the time course of changing thallium distribution. We investigated changes in the distribution of thallium in hair at different time points after exposure in five criminal thallotoxicosis patients. Scalp hair samples were collected twice, at 2.6 and 4.2–4.5 months after an exposure incident by police. Results of our segmented analysis, a considerable amount of thallium was detected in almost all hair sample segments. The thallium exposure date estimated from both hair sample collections matched the actual exposure date. We found that determination of thallium amounts in hair samples divided into consecutive segments provides valuable information about exposure period even if a considerable time passes after exposure. Moreover, when estimating the amount of thallium exposure from a scalp hair sample, it is necessary to pay sufficient attention to individual differences in its decrease from hair.

1. Introduction

Thallium has been using as an industrial material in the manufacture of optical lenses, semiconductors, scintillation counters, low-temperature thermometers, green-colored fireworks and chemical catalysts [1]. Thallium intoxication typically shows symptoms of gastrointestinal disturbances, peripheral and central nervous system disorders, and hair loss [2–5]. Its presence in blood, urine or hair are essential for confirmation of exposure [6,7]. Industrial usage of thallium has decreased over recent decades because of its severe toxicity [2]. However, because of its colorless, odorless and tasteless nature, thallium is used for criminal purposes [8–10], which has attracted social attention in Japan [11]. For the assistance of prompt investigation of future thallium poisonings, it is, therefore, desirable to collect for much biological sample information about thallium exposure. In cases of criminal thallium poisoning, forensic investigation is required to identify the amount and time of thallium exposure [12]. Usually, blood and urine thallium levels are respectively used as biomarkers for identifying intoxication [13] and predicting the long-term outcome [1]. Because of variance among individuals and the long half-life of thallium (2–15 days) [14], blood or urine concentrations one month after exposure may be used to qualitatively confirm exposure, but do not correlate quantitatively with exposure amount. Moreover, it is difficult to estimate the exposure period using blood or urine.

Hair has the unique potential to reveal retrospective information. Thallium is incorporated into the growing hair from blood plasma, and incorporated thallium remains stable for long periods of time. Moreover, because human hair is known to grow at an average rate of approximately 1 cm/month [15], several studies suggest that thallium levels in hair segments which differ in proximity to the scalp can, under certain conditions, be used as a retrospective calendar of thallium intoxication during time periods preceding sample collection [16–18]. However, in criminal cases, it is possible that the hair cannot be sampled at an appropriate time for such retrospective analysis. Moreover, it is known that drug

* Corresponding author.
E-mail addresses: tmatsuka@juntendo.ac.jp (T. Matsukawa), mmchiba@juntendo.ac.jp (M. Chiba), atsukos@seisen-u.ac.jp (A. Shinohara), yomori@med.kitasato-u.ac.jp (Y. Matsumoto-Omori), kyokoya@juntendo.ac.jp (K. Yokoyama).

https://doi.org/10.1016/j.forsciint.2018.08.019
0379-0738/

distribution along a hair sample may vary from many causes [19], including hair growth rate and cycle, and incorporation from sweat or sebum. Although several studies have attempted to clarify how thallium is distributed in hair after thallium poisoning [6,7], none have evaluated the time course of changing thallium distribution.

In the study presented here, we investigated changes in the distribution of thallium in scalp hair at different time points after poisoning, to assess the utility of hair for retrospective analysis of poisoning.

2. Material and methods

2.1. Subject and sample collection

Four male and one female workers at a company in Kanagawa Prefecture, Japan, were poisoned with thallium. Table 1 shows characteristics of these five thallium intoxication cases. According to the police, thallium sulfate had been added to a bottle of tea that they consumed. The thallium concentration in the tea was estimated at approximately 400 mg/l; five victims drank one or two cups (300–700 ml) of the tea. All cases developed severe pain with paresthesia in the lower extremities, beginning 2 or 3 days after exposure. Two males (cases 3 and 4) and one female (case 5) showed characteristic loss of hair from 10 days after the exposure. The remaining two males (cases 1 and 2) did not show this symptom. Because one victim complained that they were poisoned by thallium, the employer considered that police investigation was necessary, which began on day 26. The police science laboratory found thallium in blood and spot urine samples collected on day 29.

For further forensic analyses, the police brought blood and urine samples to our department. They also gave us scalp hair samples collected from each case as evidential material. The hair samples were collected from the upper back of the head by cutting at exactly at the scalp surface, on day 79 or 80 (2.6 months after exposure, the first sample collection), and on day 125, 126, 127 or 134 (4.2–4.5 months after exposure, the second sample collection). Since the police collected hair at the time of interview about the incident, hair samples were in different lengths. Case 5 provided hair samples only once, refusing the later collection. The Ethical Committee of Juntendo University review board decided that this study did not require ethical approval as it was carried out by a commissioned service.

2.2. Measurement of thallium by inductively coupled plasma mass spectrometry (ICP-MS)

Thallium concentrations in scalp hair, blood and urine samples were determined by ICP-MS after microwave digestion, using a previously reported method [20–22]. For each case, 28 scalp hair samples from the first sample collection were segmented every 3 mm from the scalp surface to 30 mm, and the remaining portions were cut every 10 mm to –60 mm. Similarly, 28 scalp hair samples from the second sample collection were segmented every 10 mm from the scalp surface to the tip, until there was no hair residue. Each bundle of segmented hair was placed into a perfluoroalkoxy alkane–Teflon (PFA) vial (GL Sciences Inc., Tokyo, Japan). Samples of blood or urine (100 μl) were also placed in PFA vials.

The hair, blood and urine samples were then digested with 0.4 ml of concentrated nitric acid (Ultrapure Grade, Tama Chemicals Co., Kawasaki, Japan) and 0.2 ml hydrogen peroxide (Ultrapure Grade, Tama Chemicals Co.) in a microwave oven (MLS-1200 MEGA, Milestone S.R.L., Bergamo, Italy) in the following five steps: power was set at 250, 0, 250, 400 and 600 W for 5, 1, 5, 5 and 5 min, respectively. The volume of the digested sample was then adjusted to 1.0 ml with ultrapure water. The fixed-volume solution was diluted 100 times with 0.5% nitric acid and 20 ng/ml yttrium as an internal standard. Thallium concentrations in the diluted solution were determined using an inductively coupled plasma mass spectrometer (Elan DRC-II, PerkinElmer, Waltham, MA, USA) at a mass-to-charge ratio (m/z) of 205. The ICP-MS conditions were optimized using a 1 ng/ml tuning solution containing thallium in 0.5% nitric acid. Quantification was performed by the internal standard method using an m/z of 89 for yttrium. Thallium measurements about hair were repeated three times and blood and urine were repeated twice. The average value was used for subsequent analysis.

Whereas thallium concentrations were shown the result per weight in other studies [16,17], in the present study, the amount of thallium was expressed as the data per length of hair like Yoshinaga's study [18]. This was because of decrease in the hair density after thallium intoxication (Appendix A in Supplementary material), which might have led to the difficulty in an estimation of exposure period from the distribution of hair thallium concentration. For reference, the results using the data per weight of hair are given in Appendix B in Supplementary material.

2.3. Quality control and quality assurance

Suitable certified reference materials for the assessment of chemical analyses of thallium in scalp hair, blood and urine are not commercially available. For internal quality assurance of the thallium determination, we analyzed the quality control materials, Seronorm Trace Elements Whole Blood Control Level-2 and Level-3 (SERO, Billingstad, Norway) [21] with target thallium value of 5.2 and 10.2 ng/ml, respectively. Our mean concentrations from day-to-day (n = 20) for these control materials were 5.3 and 9.9 ng/ml, respectively, which is in good agreement with the target values.

Table 1
Characteristics of five thallium intoxication cases.

	Case				
	1	2	3	4	5
Sex	Male	Male	Male	Male	Female
Age group	50–59	50–59	30–39	20–29	30–39
Intake of tea containing thallium (cups)	1	1	1	2	2
Estimated thallium intake (mg)	120–140	120–140	120–140	240–280	240–280
Signs and symptoms					
Lower limb pain	+	+	+	+	+
Mee's line/deformed nail	+			+	+
Alopecia			+	+	+
Abdominal pain	+	+	+		
Chest tightness		+		+	+