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Forensic Analysis of the Wakayama Arsenic Murder Case

Jun Kawai

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Abstract

This is a review paper of forensic analysis of a murder case of Wakayama arsenic poisoning incident. The influence of this case on scientific research was not small in such a way that papers related to PTSD, disaster medical, copycats, chemical analysis, unwanted chemicals in food, terrorism, and so on were published. The forensic analyses on Wakayama arsenic poisoning incidence have characteristic that SPring-8, a largest synchrotron radiation facility, was used, as well as many other analytical techniques, but now most of the forensic analyses submitted from the prosecutor have been revealed to be fabrication, hiding the truth by logarithmic calculations, and therefore not scientific. Most of the testimonies at the court by the analysts were also lies. Examples of such false analyses are explained.

Keywords: X-ray fluorescence (XRF), inductively coupled plasma (ICP), synchrotron radiation (SR), atomic absorption spectrometry (AAS), Wakayama arsenic poisoning case

1. Outline of the Wakayama arsenic murder case

Four people were killed by arsenic poisoned curry at a summer festival on July 25, 1998, and other 63 participants were heavily injured but survived though they ate the poisoned curry. It is still not well known whether some embryos or fetuses were included within 63 or not, because the personal data is not open. The arsenic intake was authorized by the arsenic analysis of urine. One of the two curry pots was poisoned during the cooking for the preparation of the festival in a small town in Wakayama city. Wakayama is a city near the Osaka Kansai International Airport. Although the outline was reported by Kimura [1], a brief chronologically ordered outline should be described here.
The curry was cooked in two pots in a garage of a festival organizer’s house. The curry was cooked from noon till 3 pm there, and then moved to the festival venue. During the noon and 3 pm, the curry pots were kept boiling by housewives of the organizers in turn. One of the housewives there, Mrs. H, was arrested on October 4 and prosecuted as the murder on December 29. She was sentenced to death on December 11, 2001, at the Local Court of Wakayama. Then again she was sentenced to death at Osaka Court of Appeal. Finally, May 18, 2009, the death penalty has been fixed at the Supreme Court of Japan. She has denied from the first until now, but she is now in the death row.

The only evidence was a paper cup found near the cooking site. This paper cup might have been used to poison the curry pot bringing arsenic. Powder of about 35 mg arsenic oxide, \( \text{As}_2\text{O}_3 \), was left inside of the paper cup. Her husband had arsenic oxide powders as white ant pesticide, as his job was white ant exterminator. Therefore the key forensic analysis was the identification of arsenic oxide powders between her husband’s and the powder adsorbed on the inner surface of the paper cup. “High concentration arsenic” was found on one of her hairs, which was one of the several hundreds of hairs cut on December 9, 1998, by the police. These two evidences are the main reasons of her death penalty. The hair was analyzed by synchrotron radiation X-ray fluorescence (SR-XRF) and also by atomic absorption spectrometry (AAS). Several impurity elements in the arsenic oxide powders were analyzed by the SR-XRF and inductively-coupled plasma atomic emission spectrometry (ICP-AES), as was reviewed by Kawai [2]. Infrared (IR), ion chromatography/inductively-coupled plasma mass spectrometry (IC/ICP-MS), X-ray diffraction (XRD), scanning electron microscope-energy dispersive X-ray analysis (SEM–EDX), and many other chemical analysis techniques were used.

Because the chemical poison was used by the Tokyo subway sarin attack in 1995, the Wakayama arsenic case attracted large attention by mass media, such as television, newspapers, and gossip magazines, at that time for about 1 year duration. The forensic analyses were performed mainly by the National Research Institute of Police Science, Tokyo University of Science, St. Marianna University School of Medicine, Osaka Electro-Communication University, and Hiroshima University. It was well known to the public at that time that SPring-8, one of the third generation synchrotron radiation facility, a 1.5 km circumference accelerator ring of 8 GeV, was used for the forensic analysis. The forensic analysis of SPring-8 was just 1 year after it became in use. Since 2012, Kawai, the author of the present paper, found many faults in the forensic analyses in this case, of which documents were submitted to the court from the prosecutor, and again this murder case becomes discussed in Japan.

2. Influence on the academic researches of Wakayama arsenic murder case

The sarin attack at Tokyo subway was just a few years before this arsenic murder case. Therefore, many academic research papers on Wakayama murder case were published, which discussed the relation of the subway sarin attack. Some examples of papers related to the Wakayama case are as follows.
From the point of view of medical treatment at disasters, such as Matsumoto sarin attack in 1994, Tokyo subway sarin attack in 1995, Wakayama arsenic murder case in 1998, and other bombing terrorism in Japan from 1990 to 2002, were compared and discussed a future risk of terrorism and emergency management [3]. However this kind of lessons were not used at the earthquake, tsunami, and nuclear disaster at March 11, 2011, Japan. Intoxication with arsenic curry was reported in the same journal [4]. Bioterrorism threats to food were discussed [5]. Related to the subway sarin attack, importance of information sharing systems among hospitals was discussed [6], because the victims were distributed to many hospitals in Wakayama city. The patients were first treated as taking rotten food, then organophosphorus pesticide or cyanide. Therefore the information sharing was important. “FACT-Graph”, a data analysis method, was used to analyze keywords “cyanide” and “arsenic” as nodes of the graph analysis [7]. PTSD (posttraumatic stress disorder) was discussed [8]. Copycat poisoning cases, such as sodium azide (Na₃N) and cyanide incidents in 1998, were discussed from the view point of chemical disaster response system [9]. A vast number of copycats appeared just after the Wakayama incidence. The importance of quality assurance against incidents of unwanted chemicals in food such as arsenic, cadmium, mercury, and lead, including Wakayama case, were systematically discussed [10]. Case seen in clinical practice at intentional acts such as nicotine, arsenic (Wakayama), rat poison, and methamidophos were discussed [11]. Economic impact of arsenic contamination in Bangladesh was studied referring to the Wakayama incidence [12].

Concerning medical treatment, dermatology [13–16], neurology [17], and many other papers were published.

Between the Wakayama incident on July 25, 1998, and the accusation of the suspect on December 29, 1998, many copycats were appeared mimicking poisoning [18], as mentioned above, using different chemicals, such as sodium azide, pesticides, and cyanide. At the first stage of Wakayama case, cyanide was erroneously detected, and this point was studied from the view point of chemical analysis [19–21].

Related to analytical chemistry, ICP-AES analysis of impurity elements of arsenous oxide in order to identify the As₂O₃ in paper cup and that of Mrs. H’s husband were reported by researchers of National Research Institute of Police Science, Japan [22–24]. Forensic analysis using SR-XRF analysis was reported [25–29]. The importance of SR-XRF for forensic analysis was also reported in an encyclopedia [30]. LC/MS [31] and HPLC/ICP-MS [32] were reported as arsenic chemical state analysis methods related to Wakayama case. A screening method of inorganic arsenic in urine was developed [33]. A large number of other papers can be found at Google Scholar by the key words, “Wakayama arsenic”.

3. Identification of arsenic oxide powders

There were eight kinds of arsenic oxide evidences. Mr. M, who was a brother of Mrs. H, kept arsenic oxide powders, which were originally used as the white ant pesticide by H’s husband, long before the incidence. The evidences were as follows: (1) Paper cup, (2) M’s green 50-kg
can, (3) M’s milk can, (4) M’s white can marked “Heavy”, (5) M’s brown Tupperware, (6) A milk can found at H’s old house (This house was at that time Mr. T’s house, and we call this “T’s milk can”), (7) A plastic container found at H’s kitchen, but a few particles of arsenic powders were attached on the inner surface of the container, and (8) arsenic oxide crystals found in curry pot. These are tabulated in Tables 1 and 2.

<table>
<thead>
<tr>
<th>No.</th>
<th>Evidence meaning</th>
<th>As wt% [34, 35]</th>
<th>As₂O₃ wt% [36]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Paper cup</td>
<td>74.80</td>
<td>98.7</td>
</tr>
<tr>
<td>(2)</td>
<td>M’s green 50-kg can</td>
<td>77.0±3.4</td>
<td>101.6</td>
</tr>
<tr>
<td>(3)</td>
<td>M’s milk can</td>
<td>77.6±4.0</td>
<td>102.4</td>
</tr>
<tr>
<td>(4)</td>
<td>M’s white can, “Heavy”</td>
<td>68.6±2.2</td>
<td>90.6</td>
</tr>
<tr>
<td>(5)</td>
<td>M’s brown tupper</td>
<td>65.7±1.6</td>
<td>86.7</td>
</tr>
<tr>
<td>(6)</td>
<td>T’s milk can</td>
<td>48.7±0.8</td>
<td>64.3</td>
</tr>
<tr>
<td>(7)</td>
<td>H’s kitchen container</td>
<td>Not available</td>
<td>Not available</td>
</tr>
<tr>
<td>(8)</td>
<td>Curry pot crystal</td>
<td>Not available</td>
<td>Not available</td>
</tr>
</tbody>
</table>

Table 1. Arsenic oxide powder evidences.

<table>
<thead>
<tr>
<th>No.</th>
<th>Evidence meaning</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>P</th>
<th>Ca</th>
<th>Fe</th>
<th>Zn</th>
<th>Ba</th>
<th>Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Paper cup</td>
<td>393</td>
<td>16</td>
<td>138</td>
<td>7</td>
<td>79</td>
<td>146</td>
<td>297</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>(2)</td>
<td>M’s green 50-kg can</td>
<td>35</td>
<td>6</td>
<td>0</td>
<td>5</td>
<td>3</td>
<td>36</td>
<td>203</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(3)</td>
<td>M’s milk can</td>
<td>32</td>
<td>5</td>
<td>0</td>
<td>5</td>
<td>6</td>
<td>28</td>
<td>201</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(4)</td>
<td>M’s “Heavy”</td>
<td>59</td>
<td>105</td>
<td>308</td>
<td>85</td>
<td>3965</td>
<td>303</td>
<td>178</td>
<td>2</td>
<td>+</td>
</tr>
<tr>
<td>(5)</td>
<td>M’s brown tupper</td>
<td>70</td>
<td>49</td>
<td>170</td>
<td>86</td>
<td>147</td>
<td>861</td>
<td>205</td>
<td>21</td>
<td>0(+)*</td>
</tr>
<tr>
<td>(6)</td>
<td>T’s milk can</td>
<td>87</td>
<td>203</td>
<td>2266</td>
<td>234</td>
<td>&gt;1%</td>
<td>153</td>
<td>124</td>
<td>7</td>
<td>+(0)</td>
</tr>
<tr>
<td>(7)</td>
<td>H’s kitchen container</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>24–36</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>(8)</td>
<td>Curry pot crystal</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>23</td>
<td>NA</td>
<td></td>
</tr>
</tbody>
</table>

NA: Not available.  
*: Positive.  
0(+): Three tests not detected, one test detected, out of 4-time tests.  
+(0): Three tests detected, one test not detected.

Table 2. Light element concentrations of arsenic oxide powder evidences (ppm).

The elemental concentrations analyzed using ICP-AES by the National Research Institute of Police Science are shown in Table 1. The judge wrote the death sentence by describing that one of the arsenics powders from evidences (2)–(7) was brought by H using the paper cup and put into the curry pot. However it is strange that the arsenic oxide powder concentration of the paper cup was 98.7 wt%, but evidences (4)–(6) were significantly lower than the paper cup. Finger prints were not found on the paper cup. It was known from testimony that the H’s
husband bought the 50-kg green can (2) more than 10 years before, and distributed into several small cans, (3)–(6). The prosecutor guessed that H brought the arsenic powder from her old house (6) using the container (7) to her new house kitchen at house-moving. Then she brought the arsenic powder using the paper cup (1) to the curry pot.

The National Research Institute of Police Science also analyzed five impurity elements, Se, Sn, Sb, Pb, and Bi, in (1)–(6). The chemical properties of these elements were quite similar to that of As, that is to say, Se is neighbor to As in the periodic table, Sb and Bi are in the same column, Sn and Pb are neighbors of Sb and Bi respectively, and thus they co-existed from earth crust. The concentrations of these elements were plotted as “radar chart” as shown in Figure 1, by the National Research Institute of Police Science (NRIPS). Similar radar charts of arsenic oxide powders from different industries are shown in Refs. [22] and [23]. However I found that the concentration ratios of Se/As, Sn/As, Sb/As, Pb/As, and Bi/As were multiplied by 1,000,000, then the logarithms were calculated and the radar chart was plotted by NRIPS. The pentagon radar charts of six evidences well overlap each other and looks like the arsenic oxide powders were identical as shown in Figure 1. However, both the 1,000,000 times and the logarithm are unfolded, and the radar chart is replotted including As concentration [37], then the hexagon of the paper cup (1) is significantly different from those of H’s arsenic powders (2)–(6), as is shown in Figure 2.

Figure 1. Radar chart of six evidences (1)–(6) taken from a document of the National Research Institute of Police Science, Japan. The document is a public document, not a copyrighted matter.

The hexagon radar chart is interpreted as follows.

1. The regular hexagons mean the same root as M’s green 50-kg can (2).
2. Large regular hexagon means that the arsenic powder was more diluted. H’s husband used diluted arsenic oxide powders for white ant pesticide.

3. A slight distortion from the regular hexagon means the error of quantitative analysis as well as inhomogeneity of arsenic oxide in a can. Evidences (2)–(6) were sampled five times and then analyzed five times. The As concentrations of evidences (2)–(6) in Table 1 are displayed as averages ± standard deviations of five time analyses.

4. Significantly distorted hexagon means different roots, such as the paper cup (1). Once, one of the Bi concentration data of M’s “Heavy” (4) had a small analytical error in its concentration out of five data of NRIPS, and the hexagon was distorted. Such one-time error in five measurements can be detected by the distortion: very sensitive to different root.

The root or origin of the paper cup (1) is significantly different from M’s green can (2). The multiplication of 1,000,000 and logarithmic calculation was in order to hide this truth.

The legal document of the National Research Institute of Police Science concluded that the arsenic oxide in the paper cup (1) and H’s arsenic oxide powders were less than 50% identical [38]. The small difference between paper cup (1) and H’s arsenic shown in Figure 2 could not be recognized by the XRF spectra of SPring-8. Two representative SPring-8 XRF spectra measured by the Tokyo University of Science are shown in Figures 3 and 4 [39], from which one cannot recognize the difference of the root. Though it has been revealed that spectra were measured only once for most of the evidences [40], the Tokyo University of Science concluded [39] that paper cup (1) was 100% identical to the H’s arsenic oxide powders (2)–(7) in
Table 1. The details of the SR-XRF method at SPring-8 was reported in Refs. [27, 28], and it is found from these papers that the precision of the SR-XRF quantitative analysis was not high enough for the present forensic analysis, and thus the discrimination was not possible. The SR-XRF analysis conclusion was a false conclusion forced by the prosecutor [37].

Figure 3. SR-XRF spectrum of paper cup (1), taken from the legal document of the Tokyo University of Science [39]. The document is a public document, not a copyrighted matter.

Figure 4. SR-XRF spectrum of M’s green 50-kg can (2), taken from the legal document of the Tokyo University of Science [39]. The document is a public document, not a copyrighted matter.
4. Hair analysis

H’s hair was analyzed by St. Marianna University School of Medicine, using AAS (atomic absorption spectrometry) after NaOH digestion and hydride generation technique. They found 90 ppb As\(^{3+}\) in her hair. The method was the same as reported in Ref. [41]. St. Marianna University knew that As\(^{3+}\) was not appropriately analyzed when using the method of Ref. [41], and thus they had not analyzed As\(^{3+}\) from 1984 to 1997 [42]. However they analyzed As\(^{3+}\) in 1998 in the forensic analysis of H’s hairs and concluded that 90 ppb As\(^{3+}\) was exogenously attached to her hair. They used an old atomic absorption spectrometer, which was made in 1970s, i.e. too old, using paper and a pen-recorder, and measured the peak height with a rule. In early 1990s, the chemical state analysis of arsenic had been performed by an ion chromatography (IC)/ICP-MS or an HPLC/MS [43] and the analytical instruments had been computerized. The advancements of these analytical instruments were due to the zenith of the semiconductor industry [44]. Therefore St. Marianna University obtained As\(^{3+}\) concentration using an old non-computerized AAS machine, where chemical state of arsenic compounds changed depending on pH. Therefore the forensic analysis results on the chemical state of arsenic of H’s hairs were quite doubtful.

Many of H’s hairs were also measured at BL-4A of KEK-PF (Photon Factory at High Energy Accelerator Research Organization, a synchrotron radiation facility in Tsukuba), and found an arsenic particle on a hair. The synchrotron radiation beam size was 4 or 1 mm width along with the hair shaft. It is still not clear how many hair shafts were measured and how many particles were found. It is said that arsenic particle was found on only one or two hair shaft(s), using 100 h of the KEK-PF beam time for hundreds of hair shafts.

At SPring-8, the same hair was measured but arsenic signal was not detected and testified that the spectral data was deleted [44].

![Figure 5. Photo of measuring the paper cup (1) at the beamline BL-4A of KEK-PF, taken from the legal document of the Tokyo University of Science [39]. The document is a public document, not a copyrighted matter.](image)
At KEK-PF, the paper cup (1) was measured, where arsenic powder was adsorbed on the surface of the cup (Figure 5). The hair shafts were measured at the same measurement chamber at the same beam time using a holder shown in Figure 6 [45]. The hair and the paper cup were handled carelessly and cross-contamination might have been happened. The detection limit of arsenic at KEK-PF was worse than 90 ppb, and thus the SR-XRF analysis results contradicted with the AAS results.

Figure 6. Photo of hair shaft holder used at BL-4A of KEK-PF, taken from the grant report document of the Tokyo University of Science [45]. The document is a public document, not a copyrighted matter.

It should be pointed out that scanning electron microscope energy dispersive X-ray analysis (SEM–EDX) was not used for the hair analysis. SEM–EDX was much easier and direct observation method compared with the SR-XRF line scan. Uranium particle attached to a hair shaft was clearly observed using an SEM–EDX rather than SR-XRF, which was reported in 2015 [46], but this type of SEM–EDX analysis was possible even in 1998. It is quite strange why such a direct observation using an SEM–EDX had not been performed in 1998.

5. Light elements analysis

The results of light elements analysis are summarized in Table 2. This table is the results of the National Research Institute of Police Science. M’s green can (2) was pure arsenic oxide imported from China. M’s milk can (3) was directly taken from the green can (2). If Table 2 is compared with Table 1, the concentrations of the impurity light elements are mostly inversely related to the arsenic concentration. That is to say, when As wt% was less, then Al and/or Ca concentrations were higher, for e.g., M’s “Heavy” (4), M’s brown tupper (5), and T’s milk can (6). However, paper cup (1) was different. Sodium and iron concentrations were higher, but
arsenic concentration was also high. If saline water like the sea water about one litter was poured into another green 50-kg can, and then dried, sodium concentration could be explained, but the sea water should take the mass ratio Na:Mg:Ca=100:12:4, which was significantly different from the ratio in Table 2. Based on the discussion at Section 3 and the present section, the paper cup arsenic oxide powder (1) was taken out from another green can imported from the same industry, but this green can was once exposed to saline water containing Na, Mg, and Ca, when mining, smelted, shipping, or in use.

It is known that arsenic green 50-kg cans were imported from China twice in a year for total 10 years. The M’s green can was one of the 60 cans imported at the same time by a ship, known by the shipping mark on the can. At the top, 10 or 15 cans were sold in Wakayama city in a month, and consequently at least more than one hundred cans were sold in Wakayama city before the arsenic curry incidence.

Starch was found for several arsenic oxide powder evidences using infrared (IR) analyses twice and iodine-starch tests twice. M’s brown tupper (5) and T’s milk can (6) results were contradicted as shown in Table 2. The paper cup (1) did not contain starch, and if the sentence was correct, starch powder mixed in the arsenic disappeared when taken by the paper cup.

Barium is not a light element but was found in several arsenic oxide evidences. Barium was an impurity element in SiO$_2$ for M’s brown tupper (5), because barium was not water soluble. Barium was an impurity element of Ca for T’s milk can (6), because it was water soluble; calcium was due to the cement. However, the barium in paper cup (1) has not been analyzed whether water soluble or not. Based on these fact, Osaka Electro-Communication University and Hiroshima University, who performed forensic analysis according to the order of judge in 2001, concluded that paper cup arsenic oxide (1) was identical to either M’s brown tupper (5) or T’s milk can with the probability of 80% [47]. But this was wrong, because the concentration of arsenic was higher for paper cup than those of (5) or (6); also because of the discussion related to the hexagon radar chart in Section 3.

6. Summary

I have published comments on the forensic analyses on Wakayama arsenic poisoned curry [2, 34, 35, 38, 40, 42, 44, 47–55], and revealed many false and truth-hiding reports step by step. Nakai of the Tokyo University of Science published papers in order to refute the above comments, but the refutations were not successful, and recently he has kept silence. The prosecutor sought some authoritative professors who could write documents against Kawai, but failed to find. The earlier discussion in the literature was cited by Chemistry Views [56], Spectroscopy Now [57], and Russian review paper [58].

The false forensic analyses were documents of National Research Institute of Police Science, of the Tokyo University of Science, of both Osaka Electro-Communication and Hiroshima Universities, and of the hair analysis of St. Marianna University School of Medicine. These four forensic reports had main role in the death penalty of Mrs. H. Forensic analysis reports of other
cases have been checked by me, and it was found that many of them were also false [44, 55]. Neufeld and Scheck [59] launched “Innocence Project” early 1990’s and many death row prisoners were released from jail. The innocence project in US was based on DNA analysis, but many other forensic analysis methods have been improved [60] due to the innocence project. Compared Japanese situation with US, the quality of forensic analysis is poor as discussed above. The National Research Institute for Police Science is not an independent research institute and they use forensic analysis in order to arrest a suspected person, but not for the proof of innocence. This is a big problem for the administration of justice in Japan.

False of four main forensic reports in Wakayama arsenic case means that all the important forensic reports submitted from prosecutor are false in Japan.

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