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# Synthetic arsenic sulfides in Japanese prints of the Meiji period

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## Abstract

A multi-analytical investigation of Japanese woodblock prints ranging in date from 1864 to 1895 and covering essentially the time span between the very end of the Edo period and the middle of the Meiji period showed a widespread use of arsenic sulfides for yellow and green colored areas (the latter obtained by mixing Prussian blue to the yellow arsenic sulfides). Analysis by optical microscopy, X-ray fluorescence spectroscopy, Raman microscopy, and Scanning Electron Microscopy confirmed that the yellow pigment is usually a compound belonging to the solid solution series  $(As_8S_8)-(As_8S_9)$ . The poor crystallinity of the pigment as shown by Raman microscopy, the non-stoichiometric As/S ratio, as well as the presence of excess uncombined sulfur point to a synthetic origin for the pigment. Period literary sources suggest that synthetic arsenic sulfide pigments manufacture might have started in the Iwashiro province in 1846. This is to our knowledge the first conclusive evidence for the use of synthetic arsenic sulfides in woodblock prints in Japan.

**Keywords:** Japanese woodblock prints, Synthetic arsenic sulfides, Alacranite, Micro-Raman spectroscopy, Micro-XRF, SEM-EDS

## Background

Because of their vivid colors, ranging from yellow to red, arsenic sulfides were used as pigments since ancient times [1, 2]. Natural arsenic sulfide pigments differ for their As:S ratios, and include realgar ( $\alpha$ -AsS), pararealgar ( $\beta$ -AsS), and orpiment ( $As_2S_3$ ). Realgar, a widely used orange/red pigment, occurs in low-temperature hydrothermal deposits [3–5]. Pararealgar is the light-induced degradation yellow form of realgar and alacranite [6, 7]. Mixtures of pararealgar and/or realgar have been systematically observed in many studies [8–10]. Orpiment was widely used as a yellow colorant besides yellow ochre since ancient times [11]. Another arsenic sulfide, alacranite ( $As_8S_9$ ) [12] is a rather uncommon red mineral showing a complicated crystallographic structure where clusters of  $As_4S_4$  (realgar-type) and  $As_4S_5$  coexist in an ordered cagelike structure [3]. Although rare in nature, alacranite has been documented in works of art as a possible artificial product deriving from the arsenolite

smelting [13–15]. The production of artificial orpiment in Western Europe was first mentioned by Johannes Alcherius in his recipe collection (1380–1420) [16], but the very first description of this synthetic pigment was made by Cennino Cennini in his treatise [17]. According to these and later sources artificial orpiment was initially obtained by sublimation, using the dry-process method [15]. The wet-process method, which produces a yellow precipitate, was introduced at the end of the nineteenth century [2 and references therein, 18].

Characterizing arsenic sulfide pigments and accurately distinguishing between natural and synthetic origin is a challenging chemical and crystallographic problem which requires a multi-analytical approach. Techniques such as polarized light microscopy (PLM), micro-Raman spectroscopy (RM), X-Ray Fluorescence spectrometry, X-Ray Diffraction (XRD), Scanning Electron Microscopy with Energy Dispersive microanalysis (SEM-EDS) [15] are best suited to this task: some of them allow non-invasive analysis while others require microsampling. An in-depth study carried out on natural and artificial orpiment, the latter obtained through both wet- and dry-process, pointed out how only the results from the

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combination of several techniques allowed to identify the actual nature of the pigment [2, 14]. In particular, the presence of spherules of arsenic sulfide glass or alacranite solid solution series ( $\text{As}_8\text{S}_8$ )–( $\text{As}_8\text{S}_9$ ) was shown to be conclusive evidence for an artificial origin for orpiment [14].

In this work we investigated green and yellow pigments in Japanese woodblock prints dating to the late Edo (1615–1868) and early Meiji period (1868–1912). A collection of 30 dated prints ranging from 1864 to 1887 (Table 1) was assembled by one of the authors with the purpose of examining the chronology of the introduction of synthetic organic dyes in Japan (a paper on this topic is forthcoming). In the course of this study we initially surveyed the prints in all colored areas with X-ray Fluorescence Spectroscopy. The discovery of arsenic in the yellow and green areas, usually interpreted as a sign of the use of the pigment orpiment ( $\text{As}_2\text{S}_3$ ) was rather interesting. Yellow pigments traditionally used in Japan for painting include orpiment, yellow earth, gamboge, and berberin [19, 20]. A recent study by Yamato [21] on Japanese prints dating to 1811–29 and 1836–91 similarly noted a widespread use of arsenic containing pigments for yellow and green areas, with turmeric often present in the yellow area.

For woodblock prints, a commercial form of art, the use of cheaper pigments is generally expected, making the use of natural orpiment, usually an expensive pigment, quite unlikely. In her study, Yamato used the appearance of the pigment under optical microscopy observation to distinguish between synthetic and natural arsenic sulfides. In this study, we offer a fully multianalytical classification based on optical microscopy, Raman microscopy, and Scanning Electron microscopy with Energy Dispersive Spectrometry.

## Methods

### Samples

30 Japanese prints dated from 1864 to 1887 were selected for the analyses. A complete list of the prints alongside with their titles and authors is reported in Table 1.

A multi-technique approach, which includes micro-X-ray fluorescence, micro-Raman spectroscopy and Scanning Electron Microscopy equipped with Energy Dispersive Spectrometry, was followed in this study. The use of X-ray Diffraction was ruled out because of the small dimensions of the pigment particles and the low pigment coverage, which would have resulted in unacceptably large samples.

### Micro-XRF

Micro X-ray fluorescence (micro-XRF) measurements were acquired with a Bruker ARTAX 400 instrument

using unfiltered Rh radiation at 50 kV, 700  $\mu\text{A}$ . Spectra were acquired with a 1 mm collimator for 120 s live-time accumulations.

### Micro-Raman spectroscopy

Micro-Raman spectra were acquired with using a Bruker Senterra™ dispersive Raman microscope system, operating at 785 nm. Raman spectra were acquired directly from the prints using an Olympus LMPlanFL 50 $\times$  long working distance objective, at a spectral resolution of 3–5  $\text{cm}^{-1}$  and 30 s integration time. To avoid degradation or heat induced physical changes, the power at the laser injection port was limited to 1 mW. Integration times of 30 s were employed and three accumulations were averaged for each spectrum to obtain an adequate signal-to-noise ratio. Spectra were acquired and processed using the Opus 7.0 Raman software.

### SEM-EDS

Pigment coated paper fiber samples for SEM-EDS analysis were mounted on aluminum stubs using a carbon adhesive tab and coated with a 10 nm carbon layer. SEM analyses (backscattered electron images and point analyses) were performed with a FE-SEM Zeiss Sigma HD, equipped with an Oxford Instrument X-MaxN 80 SDD detector. EDS microanalyses were run at 20 kV acceleration voltage and a working distance of 8.5 mm. Data were acquired and processed using the AZtec software system, v. 2.2 SP2 (Oxford Instruments).

## Results and discussion

The majority of data was initially acquired by using non-destructive techniques, and for all the prints the same analytical approach was followed: XRF was systematically run on all the colored portions of each print, then, according to the elemental composition Raman measurements were acquired on selected areas. Finally, selective sampling was carried out to proceed with SEM-EDS analyses.

### XRF

XRF data for green and yellow areas show the presence of arsenic and sulfur with other minor elements, notably iron, due to the paper matrix. The iron concentration seems higher in the green areas, possibly reflecting the use of Prussian blue mixed with the yellow to obtain the green shade.

### Micro-Raman spectroscopy

Raman measurements were collected on both green (Fig. 1) and yellow (Fig. 2) areas from all the prints. Spectra resulting from the arsenic containing green- and yellow-colored areas display the same characteristic features

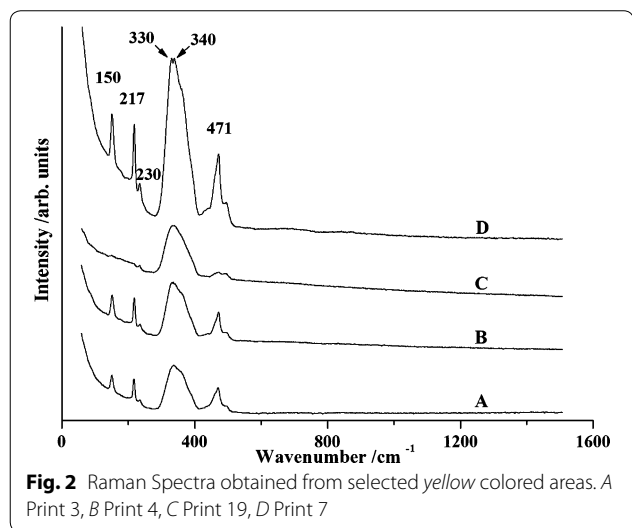
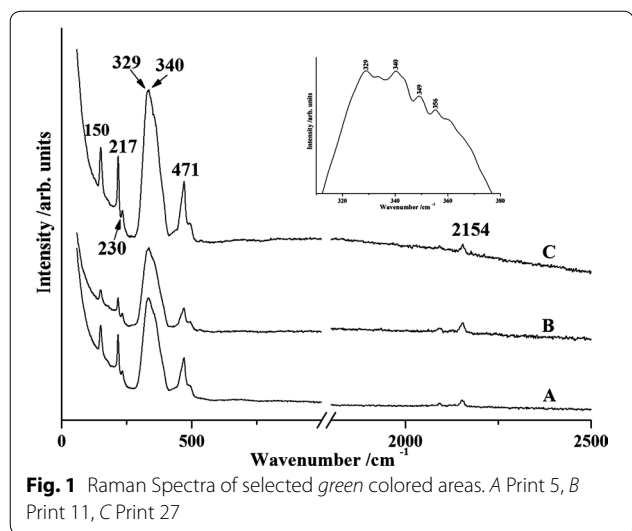
**Table 1 List of the prints analyzed in this research, complete of dates, authors, and titles**

No.	Date	Artist	Title
1	1864	Yoshitsuya	No. 35, Nakanuma Chûbei attacks Michihide in the Dark of Night (Nakanuma Chûbei an'ya ni Michihide o tsuku), from the series "Fifty-four Scenes from the Story of Hideyoshi" (Hisago gundan gojûyôjô)
2	1865/10	Kunichika	The actor Kawarazaki Gonjûrô, from the series "Shindô Suikoden"
3	1867/04	Kunichika	Death memorial portrait (shini-e) of the actor Kawarazaki Kunitarô, d. 1867-04-21, age 19
4	1868/11	Hiroshige III	Daimon Gate at Shiba Zôjôji Temple, from the series Famous Views of Tokyo (Tôkyô meishô zue)
5	1869/01	Kunichika	The Cleaning-up Job (Ato kara gakari), from the series, Thirty-two Fashionable Physiognomies (Tôsei sanjûnisô)
6	1870/05	Kunichika	Nakamura Chûzô as Konkara-bô and Sawamura Tosshô as Seikô-bô in the kabuki play "Oni mo jûshichi." Possibly one panel of triptych
7	1870/11	Kunichika	Kuruma-ôgi restaurant, Shinmei-mae, with geisha Matsutoku of Shinmei, from the series "Tôkyô sanjûroku kaiseki" (Thirty-six famous restaurants in Tokyo)
8	ca. 1872	Yoshitaki	The three brothers in the kabuki play Sugawara denju tenarai kagami" (Sugawara and the Secrets of Calligraphy): Arashi Rikan as Sakura-maru, Nakamura Fukusuke as Umeko-maru, and Ôtani Tomoemon as Matsu-o-maru. Chûban triptych, Osaka
9	1872	Shôsai Ikkei	Ikenohata Shinobazu Benten, from the series "Tôkyô meisho sanjûroku gesen" (Thirty-six Comic Views of Tokyo)
10	1872/10	Yoshitora	Hamamatsu, from the series "Shoga gojûsan eki" (Calligraphy and Pictures for the Fifty-three Stations of the Tôkaidô)
11	1873/09	Kunichika	Kawarazaki Gonnosuke as Nanbei (actually Abe no Munetô) in Adachigahara in Ôshû (Ôshû Adachigahara). Center panel of triptych
12	1874/10	Adachi Ginkô	Bandô Hikosaburô as Yakko in the kabuki play Kotobuki Utsubozaru. Right sheet of triptych
13	1875/04	Yoshitoshi	Police raid on unlicensed prostitutes, illustration of news story from No. 425 of Yûbin Hôchi Shinbun
14	1877/04	Chikanobu	Nos 5-8, in series Lineage of the emperors of Japan (Honchô Kôtôki)
15	1877/02	Shôzan	News from Kagoshima (Kagoshima Nippô)
16	1877/05	Yoshitora	The Two Generals Face off at the Battle of Kawanakajima in Shinshû (Shinshû Kawanakajima ryôshô jikisen no zu)
17	1878/01	Kunichika	Shinagawa-machi Manrin Restaurant from the series Thirty-six Restaurants of Enlightenment (Kaika sanjûroku kaiseki)
18	1878/10	Hôsai Baidô	Nakamura Sôjûrô as Chichibu Shigetô in kabuki play "Nichô no yumichigusa no Shigetô." Center panel of a triptych
19	ca 1878	Chikashige	Kyôbashi Brick Buildings (Kyôbashi rengaishi), from the series Beauties in the Famous Places of Tokyo (Tôkyô meisho bijin awase)
20	1879/03	Kunitoshi	The courtesan Ô-Yodo of Kinkanrô, from the series A Ranking of the Pleasure Quarters (Hana no kuruwa zensei kurabe)
21	1879/07	Chikanobu	Lively Poetry Gathering (Uta-awase no nigiwai), with Meiji empress in the center
22	1881	Kunitoshi	Panorama of the Precincts of Sensôji Temple in Asakusa (Asakusa-ku Kinryûzan Sensôji keidai ichiran), from the series Famous Places of Tokyo (Tôkyô meisho no uchi)
23	1881/01	Kunichika	Enjoying a comparison of the flowers of the four seasons
24	1881/03	Kunichika	Shin-Yoshiwara Hachimanrô, from the series Embellishments for Thirty-Six Flowers (Junshoku sanjûroku kasen)
25	1882/08	Hôsai Baidô	Onoe Taganojô as Takao, from the kabuki play Mukashi hinagata date no utsushi-e. Right sheet of a triptych
26	1884/02	Chikanobu	Counting Song for Enlightened Education (Kaika kyôiku kazoeuta)
27	1885/04	Kunichika	Ichikawa Danjûrô as Katô Toranosuke (L) and Hashiba Hisayoshi (C), and Ichikawa Sadanji as Hihôden (R), in the kabuki play Hanamidoki Hisago Taikôki
28	1887	Ikuhide	Cherry Blossoms at Asakusa Kannon Temple (Asakusa Kanzeon no sakura)
29	1893/04	Hôsai Baidô	From the Eighteen Great Kabuki Plays: Kanjinchô (Kabuki jûhachiban no uchi: Kanjincho). Nakamura Fukusuke as Minamoto Yoshitsune, Ichikawa Danjûrô as Musashibô Benkei, and Ichikawa Sadanji as Togashi Saemon
30	1894	Kawanabe Gyôsui	Women's Ceremonies: Poem Contests (Onna reishiki uta-awase)
31	1895	Chikanobu	Index sheets for the series The Inner Palace of Chiyoda (Chiyoda no Ôoku)

across the range of prints examined: a broad band at 329–340  $\text{cm}^{-1}$ , with a shoulder at 365  $\text{cm}^{-1}$  (Figs. 1, 2) as well as small bands at 230 and 471  $\text{cm}^{-1}$ . Only spectra collected from green areas exhibit an additional band at 2154  $\text{cm}^{-1}$  (Fig. 1), which is the diagnostic band of Prussian blue. The band at 471  $\text{cm}^{-1}$  was detected in all the prints, with variable intensity: this band and the

associated bands at 150 and 217  $\text{cm}^{-1}$  are characteristic of sulfur. The broad peak at 329–340  $\text{cm}^{-1}$  and that at 230  $\text{cm}^{-1}$  find a good match with alacranite [22]. No matches with natural orpiment were found [23, 24].

The strong characteristic peaks at 329 and 340  $\text{cm}^{-1}$  may be attributed to the monomer units in the alacranite structure, forming the shoulder at 360  $\text{cm}^{-1}$ . The insert



in Fig. 1 shows also the characteristic peaks at about 349 and 355  $\text{cm}^{-1}$ , which may be assigned to the deformation and cage breath of the monomer  $\text{As}_4\text{S}_4$  [22].

### SEM-EDS

Backscattered electron images of some fibers taken from the yellow colored areas, display variously shaped and sized particles, scattered on single fibers (Fig. 3). Some particles show an irregular, elongated shape with sharp edges and sizes up to 13  $\mu\text{m}$  (Fig. 3a). Rare particles are very small spheres (Fig. 3b), up to 8  $\mu\text{m}$  in size, perfectly round and smooth. Semi-quantitative EDS micro-analyses have been performed on both these particle typologies, and all showed similar compositions, with

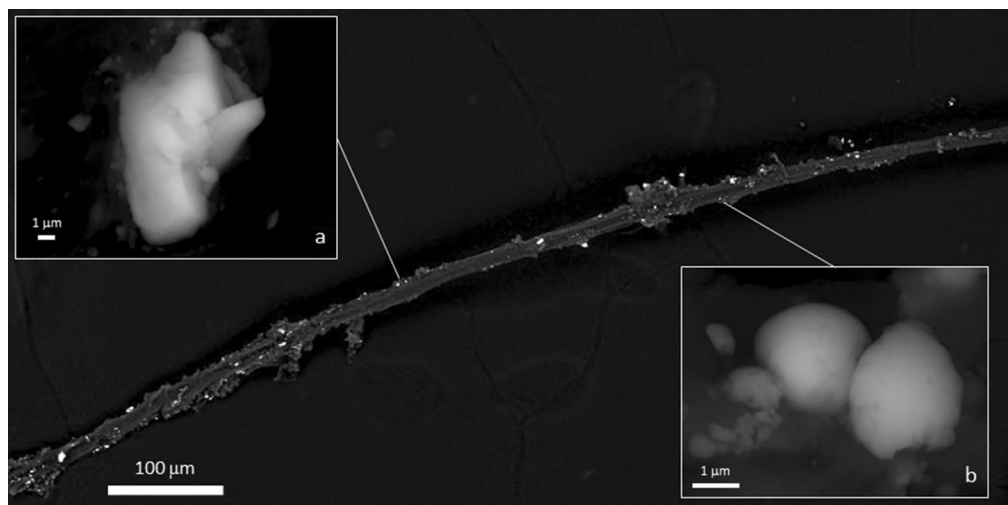
an average sulfur content of  $53.8 \pm 3.9$  wt% and arsenic of  $45.2 \pm 3.8$  wt%. This composition is consistent with that of arsenic sulfide pigments, with sulfur unusually exceeding the arsenic concentration. Similar compositions have been detected also in the arsenic sulfide pigments used to decorate the Japanese tower in Laeken, Belgium [13]. These results are not consistent with the use of a natural arsenic sulfide (e.g., orpiment), as none of the observed particles did exhibit the foliated structure of natural orpiment and the chemical compositions are non-stoichiometric. It is worth to note that every arsenic sulfide particle is characterized by the presence of copper as minor component. No  $\text{As}_2\text{O}_3$  particles have been observed on the selected fibers.

### Discussion

In all the prints from late Edo to Meiji period analyzed in this study, the systematic presence of arsenic and sulfur for the yellow and green colors indicates the use of arsenic sulfide-based pigments. This is consistent with results obtained by Yamato [21].

Micro-Raman spectroscopy showed the presence of alacranite and sulfur in the yellows, with additional Prussian blue added to obtain the green shades. The mixture of arsenic sulfide and Prussian blue explain the higher iron concentration detected by XRF in the green pigments. The broadening of the alacranite bands in the range between 329 and 340  $\text{cm}^{-1}$ , indicative of the presence of amorphous arsenic sulfide glass is consistent with the use of synthetic arsenic sulfides as shown by Vermeulen et al. [13]. Likewise, the presence of free sulfur has been interpreted by Vermeulen et al. [13] as due to the dry-process method used to synthesize the pigment. SEM-EDS analyses further strengthen this hypothesis, since the presence of alacranite spherules (Fig. 3b), with non-stoichiometric ratio between arsenic and sulfur, is indicated in literature as the evidence for synthetic arsenic sulfides produced by dry-process rather than a wet-process method [2, 14, 15]. Interestingly, the analyses of the Aizu synthetic arsenic sulfide pigment carried out by Takamatsu in 1878 also show excess free sulfur [25].

The production of arsenic sulfides by sublimation from burning arsenolite and sulfur, dates back to the fourteenth century in Western Europe, but no sources have been found about their production in East Asia. The only reference known, that of Takamatsu in 1878 [25], refers to a possible production of artificial orpiment in Japan in about 1846, by burning arsenical stones with sulfur, in Aizu (in the present Fukushima prefecture). The very low concentration of copper may be explained by the exploitation of arsenic ores related to copper mining, largely attested in Japan [26–28].



**Fig. 3** Back-scattered Electron image of a yellow colored fiber from Print 2, Kunichika, *The actor Kawarazaki Gonjūrō*, from the series *Shindō Suikoden*. **a** prismatic particle of arsenic sulfide; **b** spherical arsenic sulfides

## Conclusions

The evidence presented in this study demonstrates that synthetic arsenic sulfide pigments were most likely manufactured in Japan in the late Edo period and in the early Meiji period. We show conclusively that this pigment was commonly used in woodblock printing, probably due to its low cost and easy availability. Takamatsu [25] reports “large scale” manufacture of orpiment in the Aizu region in northern Japan, and mentions the use of the pigment for tinting varnishes and painting book covers. No mention is made however of its use for woodblock prints. Takamatsu reports also that manufacture of synthetic orpiment would have started after 1846: while it is tempting to correlate this report with the finding of realgar (likely available and mined in the prefecture of Gunma) in several Edo period prints in the collection of the Metropolitan Museum of Art (results unpublished), a full study of arsenic pigments in Edo period woodblock prints will need to be carried before giving excessive weight to this date.

Finally, Takamatsu’s article also allows us to compare the price of artificial orpiment with that of gamboge, an imported and expensive yellow pigment also traditionally used on woodblock prints. The price of synthetic orpiment is quoted as 42 *sen* per 1 *kin*, while that of gamboge is 1.35 *yen* per 1 *kin*. At 100 *sen* to the *yen*, synthetic orpiment is less than one third the price of gamboge, making it a very attractive pigment for the woodblock printing trade.

## Authors’ contributions

The prints selected for analyses were assembled and dated by HDS. II. XRF and Raman data was collected by YL. SEM-EDS analyses were carried out by EB. The manuscript was prepared by YL, EB, and ML. All authors read and approved the final manuscript.

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## Competing interests

The authors declare that they have no competing interests.

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