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DISTINCTION OF ORIGINAL AND FORGED LITHOGRAPHS BY MEANS OF THERMOGRAVIMETRY AND RAMAN SPECTROSCOPY

C. Marcolli[1] *and H. G. Wiedemann*[2]

[1]Solvias AG, Klybeckstrasse 191, 4000 Basel, Switzerland
[2]Mettler-Toledo GmbH, CH-8603 Schwerzenbach, Switzerland

Abstract

Thermal analysis has been used to study the composition of paper and paper-like materials for some decades. The application of these techniques permits to distinguish between the original paper which was used by the artists and possible forgeries. Quite often, however, the identification of the differences demands the simultaneous application of several other techniques. The present investigation includes Asiatic wood-prints from China and Japan, and lithographs of European artists, such as Pablo Picasso, Salvador Dali, and Marc Chagall. Utamaro (1753–1806) is one of the most celebrated artists in the history of the Japanese woodblock print. He became one of the famous painters of 'Ukiyo-e' (Ukiyo-e means transitory world). In China Utamaro's pictures were also produced. The differences are found in the kind of paper: The Japanese used Mitsumata paper, while the Chinese printed on Bamboo paper mixed with silk fibers. Hu-jü-zong (Nanking, 1619) and a group of famous Chinese painters created the book of the 'Ten Bamboo Studio' which contains woodblock prints as visual aids for young artists. A reprint of these woodblock prints appeared in 1717. Later, a bootleg of this book appeared in Japan (1817). The differentiation is possible by thermogravimetric investigation of the used papers. Statistic evaluations in Europe show that more than 1 000 000 bootleg copies of lithographs of Pablo Picasso, Salvador Dali, and Marc Chagall exist. Thermoanalytical measurements allow the distinction between the original artifacts and the bootlegs. Raman spectroscopy gives an additional possibility for the distinction between the applied color pigments.

Keywords: forgery, lithograph, paper, pigment, Raman spectrosccopy, thermogravimetry

Introduction

Paper is a material which played a major role in the development of cultures all over the world. Depending on the local vegetation, the discovery of papers is linked to different raw materials. The bark of certain trees and plants has been used as a writing and painting material in various periods and localities. Real paper was invented at about 105 A.D. in China where Ts'ai Lun produced the first usable writing material from tree bark and plant fibers, as well as from old rags and fishing nets. Since that time, paper has been in general use all over China.

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Later, thanks to the construction of the Silk Road, the use of paper traveled west, first to Turkestan and then to the Arabic countries. The manufacturing methods for the production of paper and silk were jealously guarded secrets which were not revealed to the Arabs until after the battle of Samarkand in 751 A.D. At this time, a Chinese prisoner of war divulged the secret. In Europe, it is virtually certain that techniques of paper manufacturing were not used until the time of the crusades, i.e., until the 12th and 13th century.

Advancing via Korea, the technology of paper manufacturing also arrived in Japan, where the first paper was produced in ca. 610 A.D. in Kyoto. Over the centuries the technology of paper manufacturing was constantly refined and modified with respect to the raw materials used in its production. In the 18th century, the Japanese produced paper from the bark of the mulberry tree. A mixture of rice starch and roots was added and served as a binder. This Japanese paper is called ‘kozo’. It is very dense and snow white, and is still produced today. Later-on, other suitable raw materials were discovered, such as the plants mitsumata and gampi. While kozo could be cultivated, mitsumata and gampi had to be produced from wild plants.

The purpose of the investigations reported here is to characterize and compare paper used for Japanese color woodcut prints, ‘ukiyo-e’, produced by certain Japanese artist schools from the 17th century on, as well as similar recent Japanese papers, using thermoanalytical and spectroscopic methods, such as Raman microscopy. These methods allow the determination of the kind and history of manufacture of the different papers [1, 2] and lead to an easy and definitive classification.

Experimental

Instruments

The Mettler Toledo Thermosystem TA8000 was used for thermogravimetric measurements (TGA850) in air. The samples were heated at a rate of 5 K min^{-1} in pans with platinum or alumina liners. The oxidation behavior of the different fibers in air was also measured by scanning calorimetry (TGA850) in platinum or alumina pans heated at rates between 0.5 and 5 K min^{-1}. The measured curves allow the recognition of the kind of paper and the determination of the composition of the lithographs.

Further, a Renishaw System 1000 Raman Microscope was used for the Raman measurements. This system comprises a Leika DM LM microscope equipped with a 50× objective, a spectrometer with a 1200 grooves/mm grating and a NIR enhanced, Peltier-cooled CCD camera.

For the blue and green pigments, an air-cooled argon ion laser served as the excitation source with a wavelength of 514 nm and an output of 20 mW. For the yellow and red pigments a stabilized diode laser (wavelength 785 nm, output 250 mW) was employed. When necessary, the laser power on the sample was reduced. The back-scattered laser radiation is prevented from entering the spectrograph by two holographic supernotch filters. Spectra were recorded in the frequency range 2000–100 cm^{-1} for the excitation at

785 nm, and 3500–50 cm^{-1} for the excitation at 514 nm. All spectra are baseline-corrected.

Materials

One of the paper samples was taken from an ukiyo-e print from 1820 by the artist Kunisada, showing an actor on stage, as illustrated in Fig. 1. For comparison, a recent Mitsumata paper, produced in 1952 and corresponding to the kind of paper used by Kunisada, was also investigated. Additional measurements were made on other papers of Japanese manufacture, which were put at our disposal by the company of E. Müller, Zürich. They are mulberry tree bark paper (kozo) and a plant paper (ohmi gampi shi), respectively, both dating from the 1950s. Other paper samples were taken from ukiyo-e prints from 1876 by the artist Utamaro and from an Utamaro print which was probably produced in China.

Fig. 1 Original Ukiyo-e print by Kunisada (1786–1864). It shows an actor on stage, 1846, (38×26 cm). Sign.: Toyokuni ga and toshidama seal

Results

The results of the thermogravimetric experiments (TG) on the two Mitsumata samples (Mitsumata, 1952 and Kunisada, 1847) are presented in Fig. 2, as DTG curves, omitting the simultaneously recorded TG curves. In this way the individual components of the papers can be differentiated best. The rates of the mass changes show the differences more clearly, i.e., the curves can be differentiated better. For a quantitative evaluation, it is necessary to represent both curves (TG and DTG) by projecting the distance between two minima onto the TG curve, which then corresponds to the respective mass change as given in Table 1.

Table 1 Results of TG analysis (%) of Mitsumata papers of different ages

Composition of paper	Mitsumata 1952	Kunisada 1846
Water	4.94	6.67
Monohydrate H_2O	0	0.50
Hemicellulose	0	25.66
Cellulose	70.45	42.71
Lignin 1	9.64	10.74
Lignin 2	8.50	5.06
Lignin 3	1.28	4.51
Ash	4.08	5.04

The first deflection of the curves indicates the loss of water (30–100 cm^3). The following small peaks at 140–160°C indicate whether the paper had been beaten during its production, which was the case for the Kunisada sample only. In this case the plant cells had been crushed and the oxalic acid which was set free had reacted with calcium to form calcium oxalate monohydrate. The slight mass loss corresponds to the dehydration of the monohydrate of calcium oxalate.

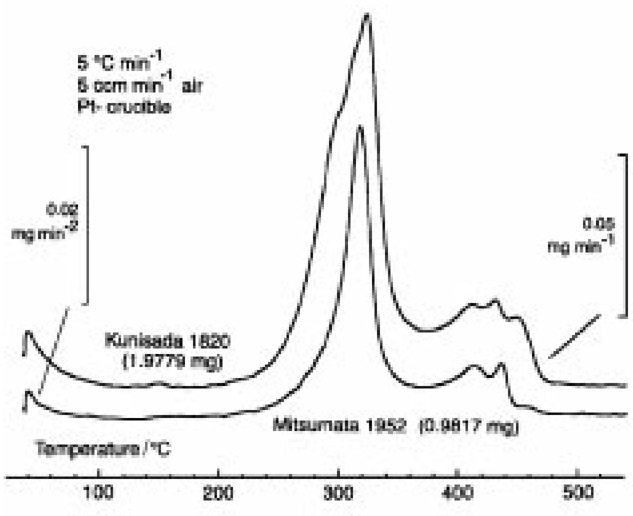

Fig. 2 DTG curves of Mitsumata prints of different ages

The most important mass loss is due to the burning of the cellulose of the papers. Both curves also show a group of three peaks, assignable to lignin. The values denoted as lignin 1–3 in Table 1 refer to mass changes due to the thermal decompositions of the different lignins. They reflect the different degrees of polycondensation of the substituted coniferyl alcohols [3] which exhibit different thermal stabilities. With progressing time and temperature, the polycondensation proceeds under evolu-

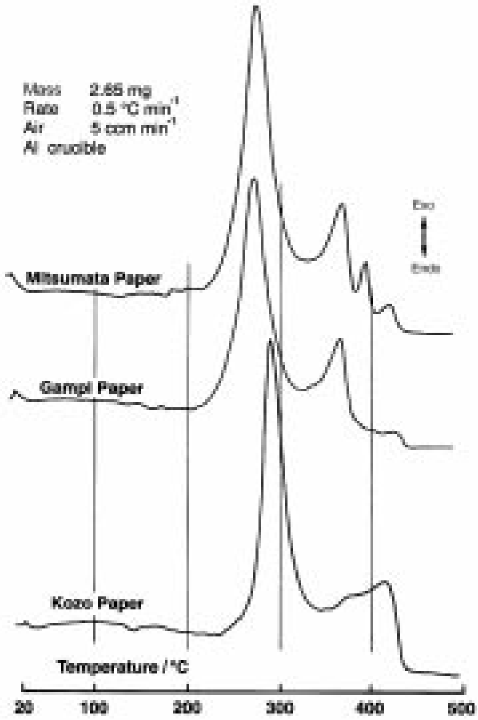

Fig. 3 Typical DSC curves of three different kinds of paper of Asia

tion of hydrogen. The decompositions of different lignins occur in discrete steps, from which the age of the papers can be estimated qualitatively. The Mitsumata paper used by Kunisada, which is more than 150 years old, shows different peak heights, which suggests that this print has been exposed to sunlight for extended periods of time. The relative values of the components of these two papers are listed in Table 1.

The DSC curves of the different papers used in Japan, both in earlier times and today, are compiled in Fig. 3. The shapes of these curves are so significantly different that it can rapidly be decided which fibers are present in a given paper.

Kitagawa Utamaro (1753–1806) is one of the most famous and well known masters for colored woodcuts before Kunisada. In Japan, the colored woodcut was mainly the creation of a certain school of painting in the 17th century. For this reason, the woodcut was given the name of 'Ukiyo-e' which, roughly translated has the meaning of 'images of the Fleeting World'. This type of painting deals with the smaller things of daily life rather than with the 'Eternal Truths' which were the subjects of the older schools.

In 1995 the British Museum organized an exhibition in London from more than 1000 pictures under the title: 'The Passionate Art of Kitagawa Utamaro' [4]. The picture reproduced as Fig. 4 is entitled 'Naniwaya Okita' and represents Okita, the pretty waitress of a famous Naniwaya teahouse. Another contemporary picture, shown as

Fig. 4 Reprint of a Ukiyo-e print by Kiagawa Utamaro (1753–1806) showing Naniwaya Okita, a waitress in a teahouse, 1793

Fig. 5 (p. 999), depicts 'Takashima Ohisa', the daughter of Takashima Chohei, the proprietor of a rice cake shop.

When such woodcuts were made, the contributions of not only the painter and the engraver, but also that of the paper maker, were considered essential. The excellent structure as well as the surface of the hand-made paper manufactured from Mitsumata has contributed to the soft, flower-like sheen of the color effect.

Raman spectroscopy was used to compare the red color of the Kunisada and the Utamaro woodcuts. In Fig. 6 the Raman spectrum of a red and of a neutral position in the Kunisada woodcut is given. Table 2 shows the peak lists of the spectra of the red

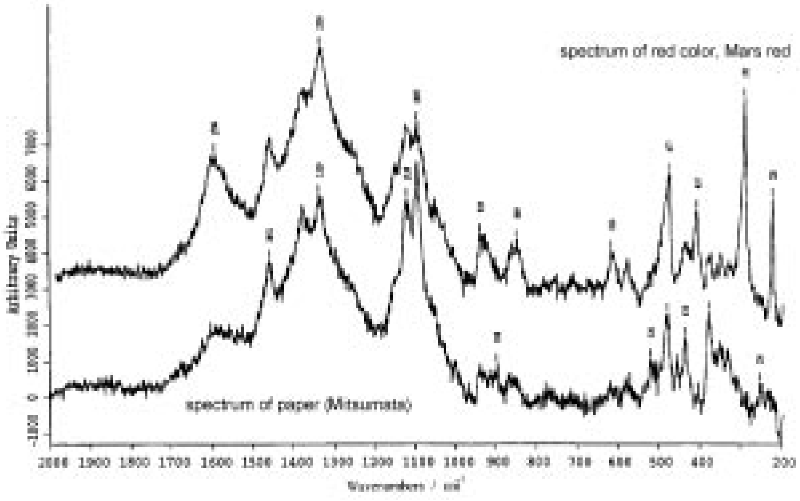

Fig. 6 Raman spectra of the Kunisada woodcut

pigments of the woodcuts together with reference spectra of mars red and vermilion [5]. The red pigment of the Kunisada (Fig. 1) is Mars red, Fe_2O_3. Both Utamaro's (Figs 4 and 5) contain Mars red, in Utamaro2 (Fig. 5) peaks of vermilion are also present. The black in these woodcuts is carbon black (peaks not listed here).

Table 2 Peak list of the spectra of the Kunisada and the Utamaros 1–3. As references, the peaks of Mars red and Vermilion are given [5]

Kunisada Japan	Utamaro1 Japan	Utamaro2 Japan	Utamaro3 China	Mars red	Vermilion
	1612 vw	1633 vw			
1596 m					
		1520 w			
1461 sh	1481 m	1481 m			
	1385 vw	1383 w			
1336 vs	1328 w	1328 m			
	1292 w	1294 m			
	1191 w	1191 w			
	1140 w	1121 m			
1095 s	1095 w	1095 m			
939 w					
849 w	823 vs	826 vs			
	650 w	658 w		660 w(sh)	
612 w		612 m		610 m	
576 w					
	486 w	486 m		494 w	
477 m					
		457 w			
		436 w			
410 m		411 m		407 m	
		378 m			
	357/340 m	341 m	343 m		343 m
292 s	292 w	293 s		291 vs	
			282 w		282 w(sh)
		255 m	252 vs		252 vs
226 m	226 w	227 s		224 vs	
Fig. 1	Fig. 4	Fig. 5	Fig. 7	[5]	[5]

The third Utamaro woodcut (Fig. 7) represents a couple sheaves of hair at the nape of the neck. The paper was investigated by TG-DTG and proved to be made of

Fig. 7 Bootleg of an Ukiyo-e print after Kitagawa Utamaro (1753–1806) showing a couple sheaves of hair at the nape of the neck, probably China, 18-19th century, (paper produced from bamboo fiber)

bamboo fibers which is typical of Chinese paper. Raman microscopy allowed to identify the red color as HgS (vermilion) [6] as shown in Table 2 and the black color as ivory black. From these results it must be concluded, that this picture was produced in China rather than in Japan.

Ten Bamboo Studio

Hu-jü-zong (Nanking, 1619) and a group of famous Chinese painters created the book of the ‘Ten Bamboo Studio’ which contains wood-block prints as visual aid for

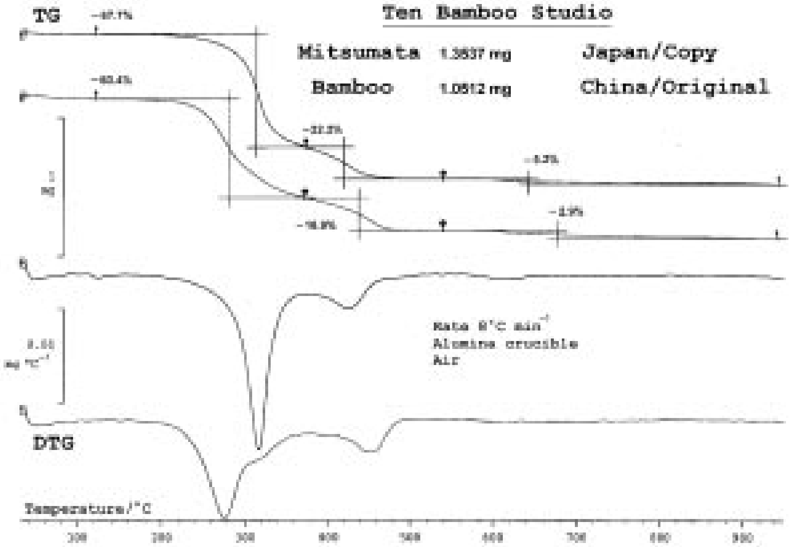

Fig. 8 TG-DTG curves of Japanese Mitsumata and of Chinese bamboo paper

Fig. 9 Bamboo, red robed, produced in Japan, 1817, Mitsumata paper; the red pigment is identified as Mars red (Fe_2O_3)

young artists. The reprint of the wood-prints appeared 1717 [7, 8]. Later a bootleg copy of this book emerged in Japan (1817). The original Chinese edition is printed on bamboo paper while the copy, the Japanese edition, is printed on Mitsumata paper [2, 9]. The differentiation is possible by thermogravimetric investigation. In Fig. 8 the difference of the two types of paper, Chinese bamboo fibers and Japanese Mitsumata fibers, is shown in the course of TG and DTG curves of their decomposition. In the Chinese wood-block print shown in Fig. 9 Vermilion/HgS was used for the red color, in the Japanese wood-block print shown in Fig. 10 (p. 999) Mars red/Fe_2O_3 was used as the red color.

Lithographs today

Statistic evaluations in Europe show more than 1 000 000 bootlegs of lithographs of Pablo Picasso, Salvador Dali, and Marc Chagall etc. Thermoanalytical measurements allow the distinction between original artifacts and bootlegs. Raman microscopy gives an additional possibility for the distinction between the applied color pigments [5].

Figure 11 shows a lithograph of Marc Chagall's 'Sacrifice of Time' [10] which appeared in the book from Jacques Lassaigne 'Chagall' edited Maeght, Paris. We compared the yellow and the red colors of this lithograph with the ones of another lithograph by M. Chagall, 'Cock in the Landscape', [11] (Fig. 12, p. 999) edited by Mourlot (1958). Figure 13 shows the Raman spectra taken at a red and at a yellow position. They show identical peaks which origin from the pigment chrome yellow ($PbCrO_4$). The red could be identified as permanent red (2,4,5-trichloranilin-2-hydroxy-3- naphtho-2-toluidin). The permanent red 112 and the chrome yellow were applied in both lithographs. The technique to use inorganic and organic pigments in one print has been abandoned since 1980. Today, only organic pigments and dyes are applied [12, 13].

Thermoanalytical investigations by TG and DTG were also applied to the papers of the Chagall prints. Figure 14 shows no considerable differences in the decomposi-

Fig. 11 Marc Chagall, Sacrifice of time (1957)

tion behavior of both papers, which indicates that the two prints are produced from paper with the same composition.

Last but not least the testing method was also applied to black and white lithographs. Two famous pieces by Pablo Picasso were examined by TG and DTG: a lithography of 'Les Déjeuneurs' [14] and a lithography of Picasso's Suite Vollard 'Sculptor and Model Watching Three Jugglers' (Figs 15 and 16). The measurements show no differences in the decomposition behaviour of both papers (Fig. 17). The black colour of the printings was confirmed to be carbon black by Raman microscopy.

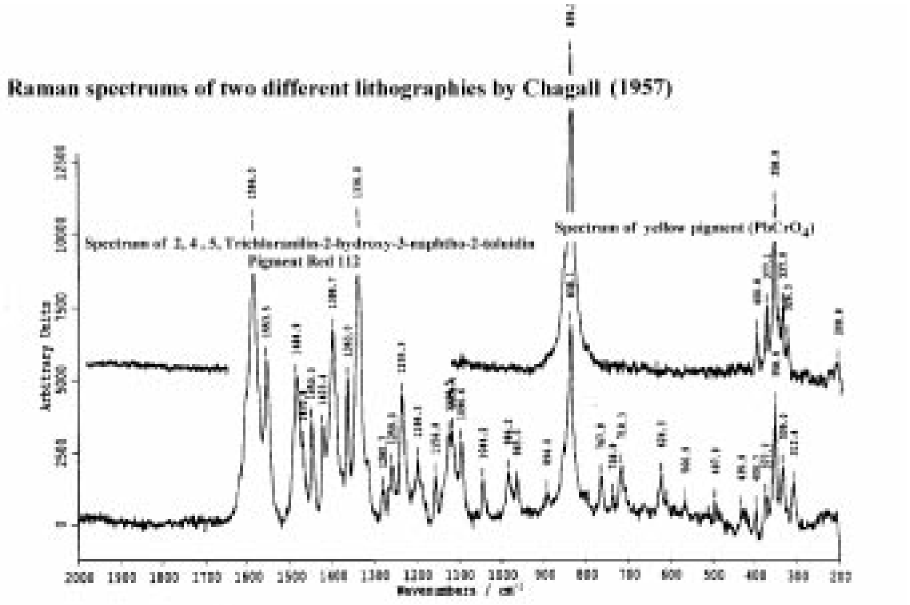

Fig. 13 Raman spectra of the lithographs by Chagall: yellow and red colors. (Permanent red=Pigment Red 112 [13] and yellow=Pb CrO$_4$ [5])

According to the current classification the Suite includes twenty seven separate sheets dealing with various themes, and seventy three sheets on five themes – Battle of Love (5 sheets), The Sculptor's Studio (46 sheets), Rembrandt (4 sheets), The Minotaur and The Blind Minotaur (15 sheets); and finally the three portraits of Ambroise Vollard [15].

The twenty seven detached sheets were done over seven years, from 1930 to 1936. The forty six sheets dealing with the Sculptor's Studio represent a unique creative eruption – forty of them were executed between March and May 5, 1933, and

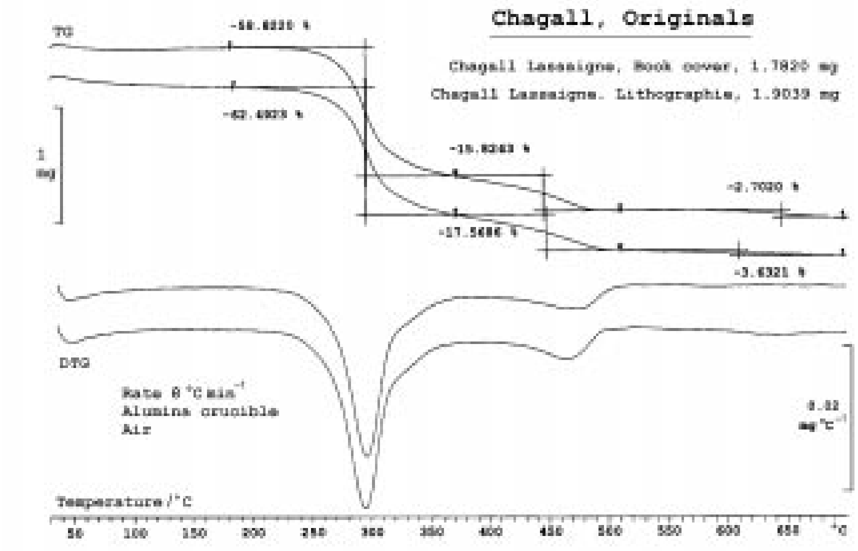

Fig. 14 TG-DTG curves, the used papers show the same decomposition rates

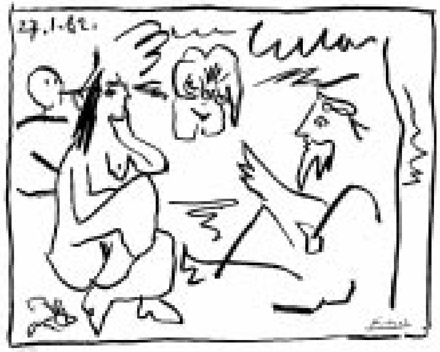

Fig. 15 Pablo Picasso 'Les Déjeuneurs', Lithography (27.1.62)

six between January and March of 1934. The eleven Minotaur sheets were completed between May 17 and June 18, 1933. The five sheets on the Battle of Love date from 1933. The Rembrandt sheets were done from January 7 to January 31, and the magnificent four sheets of the Blind Minotaur between September 22 and October 23, 1934. The series, which now comprised ninety seven sheets, was concluded in the course of 1937 with three magnificent portraits of Vollard.

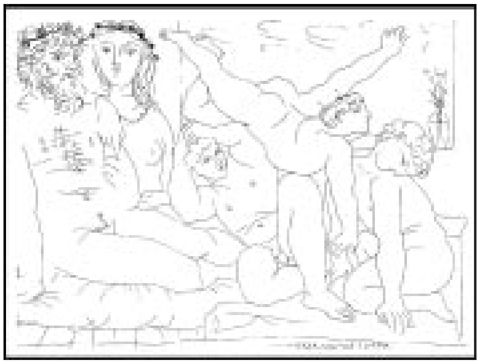

Fig. 16 Picasso's Vollard Suite, 'Sculptor and Model Watching Three Jugglers'. Etching. 1933 (7.62×10.5 inch)

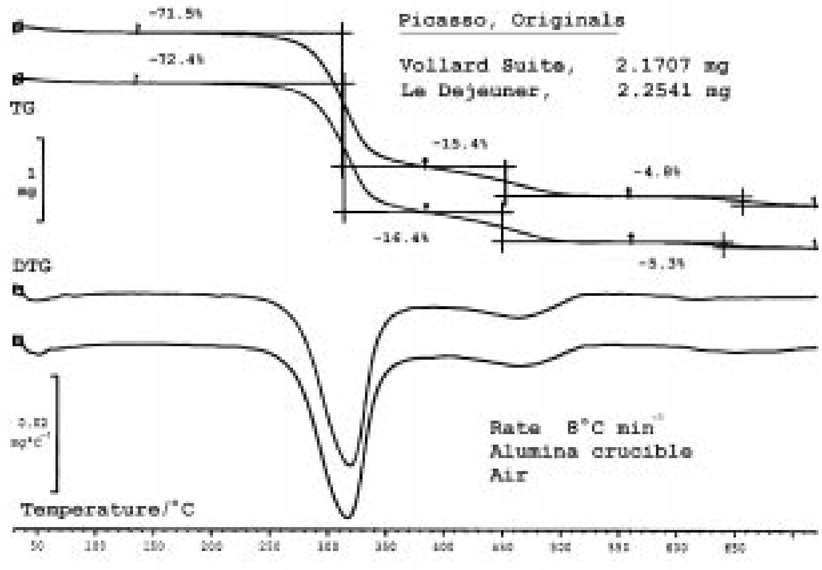

Fig. 17 TG-DTG curves of the used papers. They show a similarity of decomposition what indicates that both were produced from paper with the same composition

Fig. 5 Reprint of a Ukiyo-e print by Kiagawa Utamaro (1753–1806) showing Takashima Ohisa, daughter of a proprietor of a rice cake shop, 1793

Fig. 10 Bamboo, red robed, produced by Hu-jü-zong, Nanking, China, 1690. The paper is made of bamboo fiber, the red pigment is identified as Vermilion (HgS)

Fig. 12 Marc Chagall, Cock in the landscape (1958)

Conclusions

The combination of the methods employed in the described analyses makes it possible to distinguish the different kinds of paper. From the lignin values in the TG experiments, the age of the papers can be estimated qualitatively. Mechanical influences like beating of paper can be recognized by the loss of the crystal water of the calcium oxalate.

The simultaneous thermoanalytic and Raman spectrometric investigations give the possibility to differentiate with respect to the distinction between the applied color pigments. The change from inorganic to organic pigments has widened the range of applications, but made the identification more difficult.

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