Characterization of the materials used in Chinese ink sticks by pyrolysis-gas chromatography–mass spectrometry

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ABSTRACT

Chinese ink stick has a long history and a special importance in Chinese culture. Its main components are soot (normally pine wood soot and lamp soot) and animal glue; however, additives were added from time to time for different purposes. In order to see whether the two types of soot can be differentiated and the other constituents in Chinese ink sticks can be identified or not by Pyrolysis-Gas Chromatography–Mass Spectrometry (Py-GC–MS) and GC–MS techniques, an initial study has been carried out. The main polycyclic aromatic hydrocarbons (PAHs) in soot could be identified, which are anthracene, fluoranthene, triphenylene and benz[e]acephenanthrylene. The main difference between those two types of soot is that the detectable amount of PAHs in lamp soot is much lower than in pine wood soot. In addition to this, the relative concentration of the main polycyclic aromatic hydrocarbons including anthracene, fluoranthene, pyrene, triphenylene and its isomer, benzo[k]fluoranthene and its isomers are different in the two types of soot. The relative content of benzo[k]fluoranthene is higher in pine soot than in lamp soot, which could be used to as a criterion to differentiate the two types of soot. Py-GC–MS technique is a very effective method to identify the main components of Chinese ink sticks, including the PAHs of soot, binding media and the additives of camphor and borneol in one analysis.

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1. Introduction

Chinese ink has been used in East Asia for centuries as the sole black paint of choice. The solid form of ink, Chinese ink stick has a long history and a special importance in Chinese culture. The oldest ink fragments discovered at archaeological excavation sites date back to the third century B.C. to 220 A.D. [1]. The main ingredients of Chinese ink stick are soot and animal glue. Ink stick was originally based on pine wood soot, but lamp soot from oil lamps became dominant after about the 11th century. T'ien Gong [2] gives detailed descriptions of making both pinewood soot, and lamp soot from oil or lard. Miscellaneous materials were added from time to time [3] The most common additives are perfumes (e.g., camphor, cinnamon) to conceal the smell of animal glue and to promote sales. Other additives may help in ink dispersion or avoid cracking of the ink stick [4]. Manufacture of ink sticks consists of mixing soot with pre-dissolved glue and additives, followed by kneading, pounding, molding and drying [5].

The production of soot in a flame is a complex process consisting of several chemical reactions taking place in series. It is only in incomplete combustion that the soot is able to form and escape the flame [6]. Soot made from oils and wood burned in air, may have an elemental carbon content as low as 60% with variable amounts of organic carbon, such as polycyclic aromatic hydrocarbons (PAHs) [7]. Soot is composed of spherical primary carbon particles ranging in size from about 10 to 150 nm [8].

In order to understand the materials used in Chinese ink sticks, in the literature different techniques focus on characterization of the size and the morphology of the soot particles using photon correlation spectroscopy (PCS) size measurements and scanning electron microscopy (SEM) [9,10]. These techniques enable to measure individual carbon particles and some approximate particle size distributions. Lamp black inks seem to have a fairly narrow particle size distribution; pine soot inks give more variable distributions [10]. Surface chemistry of the particles was examined using laser Doppler electrophoresis (LDE) for the determination of the isoelectric point (IEP) [4].

Although the particles' size of soot can influence the quality of a typical dispersion system, the relative amount of PAHs may also play an important role. However, there are very few studies about the chemistry of the soot and the additives in the Chinese ink sticks. gas chromatography–mass spectrometry (GC–MS) [11–13] and Pyrolysis Gas Chromatography–Mass Spectrometry (Py-GC–MS) [14–16] have been applied for the identification of the binding media in artworks. It will be of great interest to use

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Samples (Code)	Comments
Jiangxi pine soot I (PS 1)	Factory in Jiangxi Province
Jiangxi pine soot II(PS 2)	Factory in Jiangxi Province
Jixi pine soot (PS 3)	Factory in Jixi of Huizhou
She county pine soot (PS 4)	Factory in She count of Huizhou
She county lamp soot (LS 1)	Factory in She count of Huizhou
Jixi lamp soot I (LS 2)	Factory in Jixi of Huizhou
Jixi lamp soot II (LS 3)	Factory in Jixi of Huizhou
Jixi Carbon black (CB)	Factory in Jixi of Huizhou
JiXi pine soot ink stick (PM)	Factory in Jixi of Huizhou
Dunxi lamp soot ink stick (LM)	Factory in Dunshi of Huizhou
Hukai wen ink stick (HK)	ISTA collection
Qing mo Ink stick (QM)	ISTA collection

those techniques for the characterization of Chinese ink sticks too. Although PAHs in soot were discussed in the environmental field [8,17], it is the first time to be studied in Chinese ink sticks. The purpose of this paper is to study the possibility of differentiating the two types of soot (lamp soot and pine wood soot) by Py-GC–MS and to develop a method for the characterization of Chinese ink sticks, including the binding media (animal glue) and other additives.

2. Experimental

2.1. The Samples

Two types of soot including pine soot and lamp soot, as well as carbon black samples of different origins were available for this study (Table 1). Nowadays, only a few factories in China produce soot for making Chinese ink sticks, where the samples are obtained. Animal glue and two other types of ink sticks are from the collection of the Institute of Natural Science and Technology in Art, Academy of Fine Arts in Vienna (ISTA). One ink stick is named as Hu Kaiwen (with Chinese characters 'long xiang feng wu'), labelled as HK; another ink stick is called Qing Mo, labelled as QM, which are from the 1970s.

2.2. Instruments and parameters

Both Pyrolysis Gas Chromatography–Mass Spectrometry (Py-GC–MS) and of Gas Chromatography–Mass Spectrometry (GC–MS)

measurements were carried out. A double shot pyrolyzer type PY-2010iD of Frontier Lab, Japan, and gas chromatograph mass spectrometer, GC-MS-QP2010 Plus of Shimadzu, Japan were employed. Shimadzu GC–MS real time analysis software was used for GC–MS control, peak integration and mass spectra evaluation. The pyrolysis was performed at 600 °C for 12 s. The pyrolyser interface was set at 320 °C and the injector was set at 250 °C, respectively. A capillary column SLB-5MS (5% diphenyl/95% dimethyl siloxane) 0.25 mm internal diameter, 0.25 μm film thickness, and 30 m length [Supelco] was used in order to provide an adequate separation of the components. The chromatographic conditions were as follows: the oven initial temperature was set at 40 °C for 5 min, then followed with a gradient of 6 °C/min up to 292 °C for 3 min. The carrier gas used was Helium (He, purity 99.999%). The electronic pressure control was set to constant flow at 0.6 ml/min, in split mode at 1:100 ratios. Ions were generated by electron ionisation (70 eV) in the ionisation chamber of the mass spectrometer. The mass spectrometer was set from m/z 50 to 750, with a cycle time of 0.5 s. EI mass spectra were acquired by total ion monitoring mode. The temperatures of the interface and the source were 280 °C and 200 °C, respectively. NIST 05 and NIST 05 s Library of Mass Spectra were used for the identification of the compounds.

For GC–MS analysis a capillary column SLB-5MS was used. The chromatographic conditions were as follows: The oven initial temperature was set at 50 °C, and then followed with a gradient of 8 °C/min up to 298 °C 19 min. The carrier gas used was Helium. The electronic pressure control was set to constant flow at 0.8 ml/min, in splitless mode. Injector temperature was set to 250 °C. The MS parameter was the same as for the Py-GC–MS analysis.

2.3. Sample preparation

For Py-GC–MS analysis, about 0.1 mg of sample was placed in a sample cup. The cup was placed on top of the pyrolyzer at near ambient temperature and then it was introduced into the furnace at 600 °C, afterwards the temperature program of the GC–MS was started.

For GC–MS analysis: about 0.5 mg sample was taken, 50 μl of chloroform was added and shaken thoroughly, then 25 μl trimethylsulfonium hydroxide (TMSH) reagent was added, ultra sonicated for 1 h and 1 μl of the solution was injected into the GC–MS. This procedure worked well for the characterization of

Table 2
The compounds identified in pine soot by Py-GC–MS analysis.

Peak no.	RT	Area (%)	Main Ions (m/z)	Name of the compounds	Molecular	MW
1	20.03	0.52	51, 102, (128)	Naphthalene	C10H8	128
2	26.35	0.94	76, (152)	Biphenylene	C12H8	152
3	29.14	1.24	82, 139, (166)	Fluorene	C13H10	166
4	33.02	13.82	76,152,(178)	Anthracene	C14H10	178
5	33.19	5.27	76, 152, (178)	Phenanthrene	C14H10	178
6	35.33	1.71	95, 163,(190)	Cyclopentaphenanthrene	C15H10	190
7	36.16	1.59	76, 101, (204)	2-Phenylnaphthalene	C16H12	204
8	37.77	11.33	88, 101, (202)	Fluoranthene (1)	C16H12	202
9	38.11	2.43	88, 101, (202)	Fluoranthene (2)	C16H10	202
10	38.66	12.37	88, 101, (202)	Pyrene	C16H10	202
11	39.97	0.89	108,163, (216)	11H-Benzo[b]fluorene (1)	C17H12	216
12	40.25	0.72	108,163, (216)	11H-Benzo[b]fluorene (2)	C17H12	216
13	42.59	1.88	113, 198, (226)	Benzo[ghi]fluoranthene	C18H10	226
14	43.41	7	101, 113, (228)	Triphenylene	C18H12	228
15	43.56	4.83	101, 113, (228)	Naphthacene	C18H12	228
16	43.84	1.3	101, 113, (228)	Benzo[c]phenanthrene	C18H12	228
17	44.01	0.8	101,202, (230)	7H-Benz[de]anthracen-7-one	C17H10O	230
18	45.23	7.09	138, 248, (276)	Indeno[1,2,3-cd]pyrene	C22H12	276
19	47.20	6.86	138, 248, (276)	Benzo[ghi]perylene	C22H12	276
20	47.45	7.25	113, 125, (252)	Benzo[e]pyrene (1)	C20H12	252
21	48.46	2.5	113, 125, (252)	Benzo[e]pyrene (2)	C20H12	252
22	48.68	6.23	113, 125, (252)	Benzo[k]fluoranthene	C20H12	252
23	48.98	1.43	113, 125, (252)	Perylene	C20H12	252