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Mass Spectrometric Analysis of Water-insoluble Yellow Monoazo Pigments

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Water-insoluble Yellow Monoazo Pigments were examined in order to establish a new analytical system using mass spectrometry. The characteristic ions observed were as follows: molecular ions, amine-component ions which are formed by the scission of the amide bond with hydrogen transfer and which are the most intense ones, ions at *m/e*: 43, and, in some cases, further-decomposed ions from the amine-component ions. A new analytical system was established on the basis of the analysis of the mass fragmentations of 27 samples, and applied to three unknown samples. The structure of these pigments can be deduced from the low-resolution mass spectra for those derived from substituted anilines, and from the high-resolution spectra for those derived from other amines.

Organic pigments have been widely used in many fields, such as printing inks, paints, plastics, and coatings. There have been many reports on the syntheses and physical properties of these pigments, but only a few on their analysis.[1] They are usually analysed by chemical methods, by infrared spectrometry, or by the X-ray diffraction method. The chemical analysis does not always give successful results in spite of its difficulty and its slowness. The latter two instrumental methods give information which can be compared with the known data, but not enough to elucidate their chemical structure.

On the other hand, mass spectrometry, developed recently in the field of organic chemistry, can be expected to give some information about the structure of organic pigments, because the pigments give molecular ions (as they have a long conjugated system in their structure) and because their chemical compositions can be practically determined by the high-resolution measurements. The final object of our research is to establish software for typing out the chemical structure of organic pigments after feeding the mass-spectrometric data into a computer. Some examples of such autoanalysis have already been reported in the cases of ketones[2] and fatty acid esters.[3] As the first step of our series of studies, we examined the mass-spectrometric analysis of Water-insoluble Yellow Monoazo Pigments (YMP) in order to find some characteristic peaks which differentiate them from other types of organic pigments, such as Water-insoluble Red Monoazo Pigments, and to determine the kind and location of the substituents.

Experimental

Apparatus and Measurement. The spectra were obtained using a JMS-O1SG double-focussing mass spectrometer (Japan Electron Optics Laboratory Co., Ltd.). Using 75 eV electrons at a regulated emission current of 200 μA, all the experiments were made by the electrical detection method under low-resolution conditions (*ca.* 1600); some results were also examined by the photo-plate detection method, using perfluoro kerosene under high-resolution conditions (*ca.* 20000), in order to confirm the elemental composition of the ions. Samples were introduced through a direct sample

1) A. McClure, J. Thomson, and J. Tannahill, *J. Oil Col. Chem. Assoc.*, **51**, 580 (1968).

2) A. M. Duffield, A. V. Robertson, C. Djerassi, B. G. Buchanan, G. L. Sutherland, E. A. Feigenbaum, and J. Lederberg, *J. Amer. Chem. Soc.*, **91**, 2977 (1969).

3) G. Schroll, A. M. Duffield, C. Djerassi, B. G. Buchanan, G. L. Sutherland, E. A. Feigenbaum, and J. Lederberg, *ibid.*, **91**, 7440 (1969).

inlet system at an ion-source temperature of 200—240°C and a sample-vaporizing temperature of 120—240°C.

Samples. The samples were all furnished by Dai-Nippon Ink and Chemicals, Inc., and were purified by recrystallization from nitrobenzene. The samples, with their various substituents, are shown in Table 1. The fundamental structure of YMP is shown by the following general formula:

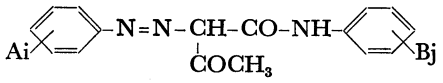


Table 1. Samples and their substituents

Samples	Substituents as Ai	Substituents as Bj
YMP-1	nothing	nothing
2	2-NO_2, 4-CH_3	nothing
3	2-NO_2, 4-Cl	2-Cl
4	2-NO_2, 4-Cl	4-OCH_3
5	2-NO_2, 4-Cl	2-OCH_3
6	2-NO_2, 4-Cl	2-$COOCH_3$
7	2-OCH_3, 4-NO_2	2-$COOCH_3$
8	2-NO_2, 4-OCH_3	2-$COOCH_3$
9	2-NO_2, 4-Cl	2,4-di-Cl
10	2-NO_2, 4-CH_3	2,4-di-Cl
11	2-NO_2, 4-OCH_3	2,4-di-Cl
12	2-NO_2, 4-Cl	2-CH_3, 5-Cl
13	2-NO_2, 4-OCH_3	2-CH_3, 5-Cl
14	2-NO_2, 4-CH_3	2-CH_3, 5-Cl
15	2-CH_3, 4-NO_2	2-OCH_3, 5-CH_3
16	2-NO_2, 4-OCH_3	2-OCH_3, 5-CH_3
17	2-NO_2, 4-Cl	2-OCH_3, 5-CH_3
18	2-NO_2, 4-CH_3	2-OCH_3, 5-CH_2
19	2-OCH_3, 4-NO_2	2-OCH_3, 5-CH_3
20	2-NO_2	2-OCH_3, 5-CH_3
21	4-NO_2	2-OCH_3, 5-CH_3
22	2-NO_2, 4-Cl	2-OCH_3, 5-Cl
23	2-NO_2, 4-CH_3	2,4-di-OCH_3
24	4-NO_2	2,5-di-OCH_3, 4-Cl
25	2-NO_2, 4-CH_3	2,5-di-OCH_3, 4-Cl
26	2,4-di-OCH_3, 5-$SO_2NHC_6H_5$	2-OCH_3, 5-$CONH_2$
27	2-NO_2, 4-OCH_3	2-OCH_3, 5-$CONH_2$

Results and Discussion

Fragmentation Process. Some examples of the mass spectra of YMP are shown in Fig. 1. In all cases except YMP-12, the most intense peak was the amine-component ion (Am^+) formed by the scission of the amide bond with hydrogen transfer. Furthermore, the molecular ion (M^+) and the ion at *m/e*: 43 ($Ac^+=CH_3CO^+$) were observed in every sample. When Am^+ has a methoxy or carbomethoxy group, a further-decomposed ion (Ad^+) was also observed at an appreciable intensity. The pattern coefficient, based on Am^+, and the sample-vaporizing temperature of each sample are shown in Table 2. The intensities of M^+, Ad^+, and Ac^+ were 10—50%, 10—40%, and 10—60%, respectively, based upon that of the base peak with some exceptions.

The fact that the scission of the amide bond with hydrogen transfer gives the most intense peak was also observed in *N,N*-diphenyl phenylacetamide.[4] In diphenyl acetanilide, an ion which arises from the scission of the amide bond with reverse hydrogen transfer was observed.[4] The cleavage of both sides of the carbonyl

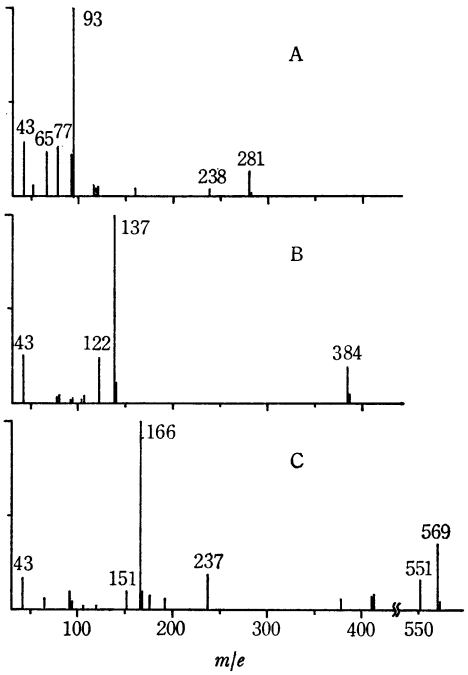


Fig. 1. Mass spectra of YMP.
A: YMP-1, B: YMP-15, C: YMP-26

Table 2. Relative intensities of M^+, Am^+, Ad^+, and Ac^+

Sample No.	Measured temp.	M^+		Am^+		Ad^+		Ac^+
		m/e	*R.I.*	*m/e*	*R.I.*	*m/e*	*R.I.*	*R.I.*
YMP-1	130°C	281	11	93	100	—	—	31
2	140	340	28	93	100	—	—	40
3	140	394	28	127	100	—	—	47
4	180	390	49	123	100	108	11	40
5	170	390	28	123	100	108	23	53
6	135	418	9	151	100	119	27	40
7	160	414	14	151	100	119	28	53
8	175	414	11	151	100	119	24	42
9	185	428	18	161	100	—	—	95
10	170	408	26	161	100	—	—	29
11	210	424	34	161	100	—	—	76
12	160	408	17	141	100	—	—	150
13	170	404	24	141	100	—	—	51
14	165	388	26	141	100	—	—	67
15	175	384	19	137	100	122	24	25
16	160	400	23	137	100	122	19	8
17	165	404	27	137	100	122	26	37
18	150	384	21	137	100	122	26	28
19	140	400	30	137	100	122	25	19
20	160	370	23	137	100	122	28	38
21	165	370	59	137	100	122	35	25
22	190	424	21	157	100	142	18	47
23	150	400	35	153	100	138	10	7
24	175	420	62	187	100	172	26	55
25	165	434	24	187	100	172	29	67
26	240	569	35	166	100	151	10	17
27	210	429	29	166	100	151	43	49

The observed values are the mean of triplicate of the measurements.

4) K. G. Das, P. T. Funke, and A. K. Bose, *J. Amer. Chem. Soc.*, **86**, 3729 (1964).

TABLE 3. HIGH RESOLUTION MASS MEASUREMENTS OF YMP-1 AND -10

Standard ion structure	YMP-1 Formula	YMP-1 Calcd mass	YMP-1 Obsd mass	YMP-10 Formula	YMP-10 Calcd mass	YMP-10 Obsd mass
Ar(Ai)–N=N–CH(COCH$_3$)–CO–NH$^{+\cdot}$–Ar(Bj)	$C_{16}H_{15}N_3O_2$	281.116	281.116	$C_{17}H_{14}N_4O_4Cl_2$	408.039	408.040
Ar(Bj)–NH$_2^{+\cdot}$	C_6H_7N	93.058	93.060	$C_6H_5NCl_2$	160.980	160.983
Ar(Ai)–N=N–CH(COCH$_3$)–CO$^+$	$C_{10}H_9N_2O_2$	189.066	189.069	$C_{11}H_{10}N_3O_4$	248.067	248.065
Ar(Bj)–N=C=O$^{+\cdot}$	C_7H_5NO	119.037	119.035	$C_7H_3NOCl_2$	186.962	186.960
Ar(Bj)–NH–CO$^+$	C_7H_6NO	120.045	120.043	$C_7H_4NOCl_2$	187.970	187.968
Ar(Ai)$^+$	C_6H_5	77.039	77.041	$C_7H_6NO_2$	136.040	—[a]
Ar(Ai)–N=N$^+$	$C_6H_5N_2$	105.045	105.047	$C_7H_6N_3O_2$	164.046	164.044
Ar(Bj)–NH–CO–CH(COCH$_3$)$^+$	$C_{10}H_{10}NO_2$	176.071	176.070	$C_{10}H_8NO_2Cl_2$	243.993	243.993
Ar(Ai)–NH$_2^{+\cdot}$	C_6H_7N	93.058	93.060	$C_7H_8N_2O_2$	152.058	152.057
Ar(Ai)–NH$^+$	C_6H_6N	92.050	92.048	$C_7H_7N_2O_2$	151.050	151.048

a) An ion of this formula was not observed.

group in β-diketone[5] and that of both sides of the azo group in substituted azo benzene[6] have also been reported.

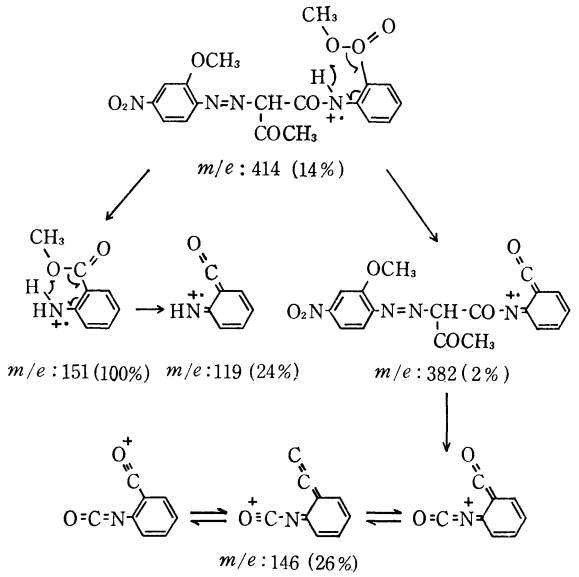
All the apparent peaks in each spectrum were examined by the high-resolution method; some of them are shown in Table 3 in the cases of YMP-1 and -10. The mean intensities of the ions were as follows (the intensity obtained is shown in parentheses):

Ar(Ai)–N=N–CH(COCH$_3$)–CO$^+$ (1)
Ar(Ai)$^+$ (<1)
Ar(Ai)–N=N$^+$ (1)
Ar(Bj)–NH$_2^{+\cdot}$ (100)
Ar(Bj)–N=C=O$^{+\cdot}$ (5)
Ar(Bj)–NH$^+$ (<1)
Ar(Bj)–NH–CO–CH(COCH$_3$)$^+$ (1)
Ar(Bj)–NH–CO$^+$ (2)
(M–43)$^+$ (3)
Ac$^+$ (49)
(M–17)$^+$ (<1)
Ar(Ai)–NH$^+$ (2)
Ar(Ai)–NH$_2^{+\cdot}$ (3)

The last ion, Ar(Ai)–NH$_2^{+\cdot}$, is assumed to be produced from the enol form of M$^+$ with hydrogen scrambling.[7] The formation of these ions can be similarly explained by the scission described in the above literature.[4-6]

When Am$^+$ has a methoxy group at the *ortho* or *para* position, Ad$^+$ was observed in every case at a position of 15 mass units lower than Am$^+$. Compounds possessing a carbomethoxy group at the *ortho* position showed two typical ions at *m/e*: 119 and 146. The formation of these unusual ions can reasonably be explained by the fragmentation process shown in Scheme 1. The transformation of Am$^+$ (*m/e*: 151) into Ad$^+$ (*m/e*: 119) is known as the *ortho* effect.[8]

Analytical Method of YMP. As has been mentioned above, M$^+$, Am$^+$, Ad$^+$, and Ac$^+$ are typical ions in the mass spectra of YMP. Ac$^+$ is a specific ion by which YMP can be distinguished from other types of organic pigments. The only exceptions are Water-insoluble Yellow Disazo Pigments, but they can easily be differentiated by their high molecular weights (over 600).



Scheme 1. Fragmentation process of YMP-7.

Usually YMP are synthesized from two aromatic amines. For example, a pigment with the general formula is synthesized from two amines, Ar(Ai)–NH$_2$ and Ar(Bj)–NH$_2$. If these amines are limited to substituted anilines, such as anisidine or toluidine, the structure of YMP can be decided on the basis of low-resolution mass-spectrometric measurements alone. The substituents, Ai and Bj, can be easily deduced from the following equations. The correlation in the mass among M$^+$, Am$^+$, and substituents is given by Eqs. (1) and (2), where M(X) represents the mass of X, and where m and n represent the number of substituents:

$$\sum_{i=1}^{m} M(\mathrm{Ai}) + \sum_{j=1}^{n} M(\mathrm{Bj}) = M(\mathrm{M}^+) - 281 + m + n \quad (1)$$

5) C. Beard, J. M. Wilson, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, **86**, 248 (1964).
6) J. H. Bowie and G. E. Lewis, *J. Chem. Soc., B*, 621 (1967).
7) R. G. Cooks, I. Howe, and D. H. Williams, *Org. Mass Spectrom.*, **2**, 137 (1969).
8) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco (1967), pp. 197, 279, 516, 636.

$$\sum_{j=1}^{n} M(\mathrm{Bj}) = M(\mathrm{Am}^+) - 93 + n \quad (2)$$

Equations (3) and (4) are obtained from Eqs. (1) and (2):

$$\sum_{j=1}^{n}(M(\mathrm{Bj}) - 1) = M(\mathrm{Am}^+) - 93 \quad (3)$$

$$\sum_{i=1}^{m}(M(\mathrm{Ai}) - 1) = M(\mathrm{M}^+) - M(\mathrm{Am}^+) - 188 \quad (4)$$

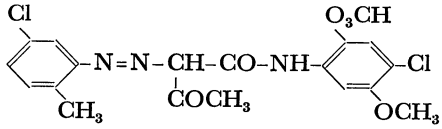
If Ai or Bj is the chlorine or bromine atom, the number and kind of these halogen atoms can be decided from the intensities of the isotope peaks of these ions. The methoxy or carbomethoxy group can be deduced from Ad^+, and the number of nitrogen atoms also be easily deduced by the application of the nitrogen rule.[9] If no appropriate combination can be found, the amines seem not to be simple substituted anilines. In this case, a precise mass determination would be very useful.

The position of the substituent cannot usually be decided on the basis of the mass spectrum, except in the cases of the methoxy and carbomethoxy groups mentioned above. However, the positions of the substituents are limited to some extent because of the difficulty of synthesis and the inferiority of the physical properties. We surveyed the literature and can now presume the position of the substituent from its structure with some statistical probability. In the case of the dimethylamino group, for example, *p-N,N*-dimethylaminoaniline alone has been used as the starting material.

Application to Unknown Samples (Fig. 2). *X-1*: M^+ and Am^+ were observed at *m/e*: 423 and 187 respectively. M^+ contains two chlorine atoms, and Am^+ contains one chlorine atom, showing that both substituents, Ai and Bj, contain one chlorine atom. Equations (3) and (4) give the following values:

$$\sum(M(\mathrm{Bj}) - 1) = 94, \quad \sum(M(\mathrm{Ai}) - 1) = 48$$

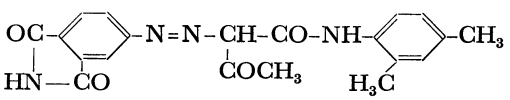
It is conclusively deduced that Ai consists of one chlorine atom and one methyl group, and that Bj consists of one chlorine atom and two methoxy groups, one of which is considered to be at the *ortho* of *para* position from the presence of Ad^+ at *m/e*: 172. The following structure was, then, considered most probable from the statistical viewpoint; it was confirmed by comparison with the compound synthesized.



X-2: M^+ and Am^+ were observed at *m/e*: 378 and 121 respectively. Neither ion contains a halogen atom. As Ad^+ was not observed, the methoxy and carbomethoxy groups are absent. The summation of the mass of substituents may be given as follows:

$$\sum(M(\mathrm{Bj}) - 1) = 28, \quad \sum(M(\mathrm{Ai}) - 1) = 69$$

Obviously Bj consists of two methyl groups or one ethyl group, but ethyl aniline has never been used as a starting material. As an appropriate combination of substituents for 69 mass units could not be found, the amine, $Ar(Ai)-NH_2$, used as the starting material seemed not to be a simple substituted aniline. The elemental composition of M^+ was determined to be $C_{20}H_{18}N_4O_4$ (calcd: 378.135, obsd: 378.133) by a precise mass determination. Therefore, the 69 mass units corresponding to $C_2H_{-1}NO_2$ may be presumed to be an imide group or acetylene plus a nitro group. The latter can, however, be rejected because of the absence of the 2200 cm^{-1} band in its infrared spectrum. Thus, the –CO–NH–CO– grouping appears to be most probable. Although the positions of methyl groups cannot be decided on the basis of the experimental results, 2,4-dimethylaniline seemed to be the most probable starting material. The following structure was, then, suggested; it was confirmed by comparison with the compound synthesized.



X-3: M^+ is an ion at *m/e*: 450 and contains two chlorine atoms. Am^+ is an ion at *m/e*: 221 or 194 and contains no chlorine atoms. Therefore, two chlorine atoms are contained in Ai. If Am^+ is an ion at *m/e*: 221, $\sum(M(\mathrm{Ai})—1)$ must be 41 mass units, which conflicts with the foregoing result. Therefore, Am^+ must be an ion at *m/e*: 194, and the mass numbers of the substituents may be calculated as follows:

$$\sum(M(\mathrm{Ai}) - 1) = 68, \quad \sum(M(\mathrm{Bj}) - 1) = 101$$

Ad^+ was observed at *m/e*: 166 and 165, which correspond to the loss of an ethylene and an ethyl radical from Am^+ respectively. From this fact, it was assumed that Am^+ contains an ethoxy group at the *ortho* or *para*

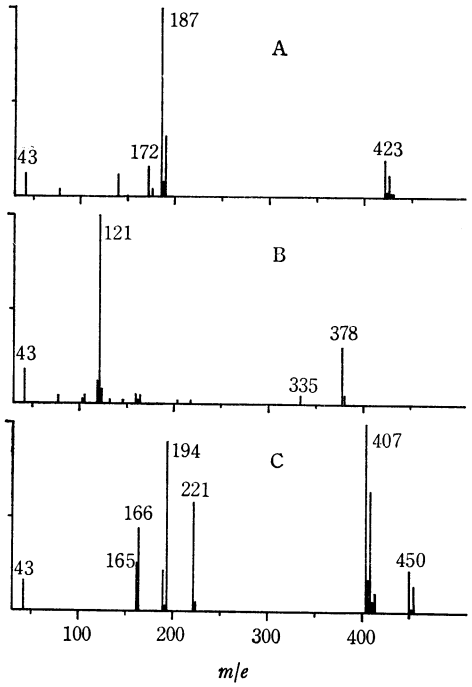


Fig. 2. Mass spectra of unknown samples.
A: X-1, B: X-2, C: X-3

9) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley & Sons, New York (1963), p. 11.

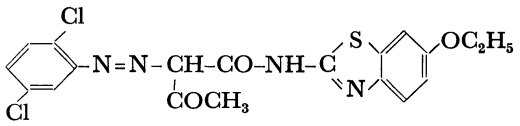
TABLE 4. HIGH RESOLUTION MASS MEASUREMENT OF X-3

Observed mass	Formula	Calculated mass	Standard ion structure
450.032	$C_{10}H_{16}N_4O_3SCl_2$	450.032	M^+
221.040	$C_{10}H_9N_2O_2S$	221.038	$Ar(Bj)-NH-CO^+$
194.053	$C_9H_{10}N_2OS$	194.051	Am^+
166.019	$C_7H_6N_2OS$	166.020	$Ad^+:Am^+-C_2H_4$
165.010	$C_7H_5N_2OS$	165.012	$Ad^+:Am_+-C_2H_5$

position.[10] By subtracting the mass of the ethoxy group from 101, the total mass of Bj becomes 57 mass units, which corresponds to methyl plus an amide group. As the combination of ethoxy, methyl, and amide groups has never been used, the elemental composition of M^+ was examined. The elemental composition of M^+ was $C_{19}H_{16}N_4O_5Cl_2S$ (Table 4); the 57 mass units described above corresponded to $CH_{-1}NS$, suggesting a thioisocyanate or thiazole ring.

10) K. Kobayashi, unpublished work (1970).

The former was rejected on the basis of its high reactivity. The following structure was, then, proposed as the most probable one and was confirmed by comparison with the compound synthesized:



Ions at *m/e*: 407 and 211, corresponding to $(M—43)^+$ and $Ar(Bj)-NH-CO^+$ respectively, were observed as intense peaks in this case alone.

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