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Analysis of waterborne paints by gas chromatography–mass spectrometry with a temperature-programmable pyrolyzer

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Abstract

Gas chromatography–mass spectrometry (GC–MS) with a temperature-programmable pyrolyzer was used for the analysis of waterborne paints. Evolved gas analysis (EGA) profiles of the waterborne paints were obtained by this temperature-programmed pyrolysis directly coupled with MS via a deactivated metal capillary tube. The EGA profile suggested the optimal thermal desorption conditions for solvents and additives and the subsequent optimal pyrolysis temperature for the remaining polymeric material. Polymers were identified from pyrograms with the assistance of a new polymer library. The solvents were identified from the electron ionization mass spectra with the corresponding chemical ionization mass spectra. The additive was identified as zinc pyrithione by comparison with authentic standard. Zinc pyrithione cannot be analyzed by GC–MS as it is. However, the thermal decomposition products of zinc pyrithione could be detected. The information on the decomposition temperature and products was useful for the identification of the original compound. © 2001 Published by Elsevier Science B.V.

Keywords: Paints; Pyrolysis; Evolved gas analysis; Polymers; Zinc pyrithione

1. Introduction

Painting gives an object beauty and protection against various kinds of corrosion. Paint generally consists of polymer, pigment, solvents, and additives such as dispersing agent, plasticizer, antifungal substance, rust inhibitor, and drying agent. Recently, waterborne paints have come into wide use on account of protecting the health for workers and the environment. As for the analysis of paints, it is important to analyze each component without interference of the other components. In the conventional

analytical methods, paint solvents are analyzed by gas chromatography (GC) after dilution of the paint with an appropriate solvent [1]. However, GC is contaminated with non-volatile compounds such as polymer and pigment. Polymer analysis is performed by pyrolysis–GC after drying of the paint, or by Fourier transform infrared spectrometry after removal of solvents and pigment from the paint [2]. Additives are analyzed after being separated from solvents and polymer by thin-layer chromatography, liquid chromatography, fractionation based on solubility, or the like [3,4]. Hence, we need to develop a rapid and convenient method for their analysis. On the other hand, evolved gas analysis (EGA), which is a kind of thermal analysis, is an analytical method which tracks chemical species produced during

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temperature-programmed heating of a sample. Especially, by using mass spectrometry (MS) as a detection method, it becomes possible to directly obtain chemical information on the thermal desorption and/or thermal decomposition products. The EGA–MS system which directly connected thermogravimetry (TG) with MS has been applied to the analysis of the polymeric materials [5]. However, this generally needs a sample amount of as much as 10 mg. Additionally, organic substances with strong polarities and/or high boiling points caused serious problems; they were adsorbed at active and/or cooler spots in the interface which combined TG with MS. Recently, a micro-furnace pyrolyzer with a temperature programming capability was developed [6], and a new EGA–MS system, where the pyrolyzer is directly connected to the MS system through a deactivated metal capillary tube, was also developed [7,8]. The serious adsorption problems were substantially improved and the necessary sample size was reduced down to several hundreds of micrograms with the new EGA–MS system. The EGA profile obtained suggested the optimal thermal desorption temperature for volatile components such as residual solvents and additives and the subsequent optimal pyrolysis temperature. Therefore, on the basis of these conditions, this pyrolysis–GC–MS system enabled us to analyze volatile components separately, and to subsequently analyze the remaining polymer without interference of the volatile components [9,10]. The new pyrolysis system allows us not only to obtain information on the polymer itself and on the volatile compounds contained therein, but also to acquire thermal characteristics of a polymer. In addition, a new library for polymer identification was included in this system. The original polymeric material can often be identified using the new polymer library of mass spectra for standard polymers based on average spectra over a selected region of the EGA profile [11].

In this study, the new EGA–MS system was applied to waterborne paints. The EGA profile enabled us to separately analyze solvents, additives, and polymer without interference of the other components. Polymers in the waterborne paints were identified from pyrograms with the assistance of the new polymer library. In addition, significant data were obtained for zinc pyrithione which was used as antifungal substance in paints.

2. Experimental

2.1. Materials

Two kinds of waterborne paints for home use were commercially available. In this paper, we call one of them paint A and the other paint B. About 1.0 mg of the waterborne paint was directly analyzed by EGA–MS. About 0.3 mg of the sample was directly analyzed by pyrolysis–GC–MS.

2.2. Instrumentation

2.2.1. EGA

A double-shot pyrolyzer (Frontier Labs., Fukushima, Japan) attached to an Agilent 6890 GC system equipped with an Agilent 5973 MS system (Agilent Technologies, Palo Alto, CA, USA) was used for EGA. This pyrolyzer is a vertical micro-furnace type and has temperature-programming capability. A deactivated metal capillary tube (2.5 m × 0.15 mm I.D.; Frontier Labs.) kept at 300°C was used to connect the pyrolyzer directly with the MS system for EGA–MS. During heating the sample from 60 to 700°C at 20°C/min, the resulting evolved gas was directly detected by MS. The temperature of the GC injection port was 300°C. Helium was used as carrier gas for the capillary tube with a flow-rate of 0.8 ml/min, and the split ratio was set at 50:1. MS was operated in the electron ionization (EI) mode at 70 eV electron energy and with a scan range of m/z 10 to 700. The EGA–MS Polymer Library (Frontier Labs., mass spectra of 136 kinds of polymers), which works with library search for an average mass spectrum of any range of the EGA profile, was used for the assistance of polymer identification.

2.2.2. Thermal desorption and pyrolysis

The apparatus used for thermal desorption and pyrolysis was basically the same as that for EGA except for the tube. The deactivated capillary tube was replaced with a separation column. The thermal desorption temperatures were from 60 to 190°C at 20°C/min for solvents and from 190 to 280°C at 20°C/min for additives and the pyrolysis temperature was 550°C. An Ultra Alloy-1 metal capillary column (30 m × 0.25 mm I.D., 0.25 μm film thickness; Frontier Labs.) was used for the separation of thermally desorbed components and/or pyrolysis

products. The temperature of the column was maintained at 35°C for 3 min, raised to 320°C at 10°C/min, and held for 5 min. The GC injection port temperature was 300°C. The tip of the metal capillary column was dipped into liquid nitrogen to trap the vaporized compounds during the thermal desorption process. Helium was used as carrier gas with a column flow-rate of 1 ml/min in the constant flow mode and the split ratio was set at 50:1. MS was operated in the EI mode at 70 eV electron energy and with a scan range of m/z 10 to 700. For the assistance of solvents identification, an Agilent 5971 MS system was operated in the positive chemical ionization (PCI) mode served with methane as the reagent gas and with a scan range of m/z 75 to 650.

3. Results and discussion

3.1. EGA profile

EGA profiles indicate thermal characteristics of the waterborne paints similar to those obtained by thermal analysis. Fig. 1 shows EGA profiles detected by MS. Regarding paint A, two peaks with their peak maxima at 100 and 400°C were observed. The first peak will be related to solvents and the second peak will be related to polymer decomposition at higher temperatures. Regarding paint B, three peaks with their peak maxima at 120, 220, and 400°C were observed. The first peak will be related to solvents, the second peak will be related to volatile compounds such as additives and the last peak will be related to polymer decomposition.

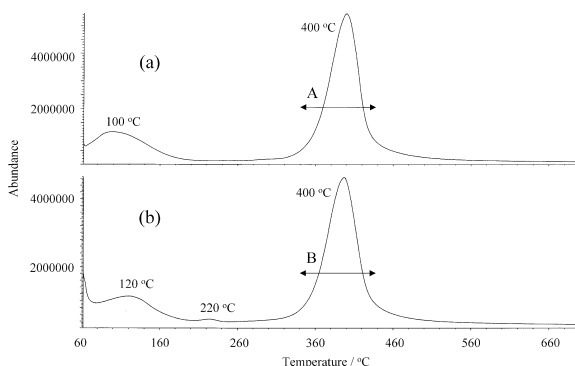


Fig. 1. EGA total ion profile obtained (a) from the paint A and (b) from the paint B by EGA-MS.

Using these EGA profile data, the thermal desorption temperature for solvents and additives was empirically determined as from 60 to 190°C and from 190 to 280°C, respectively, to prevent interference of main polymer decomposition. The subsequent pyrolysis temperature was fixed at 550°C, about 50°C higher than the ending temperature (500°C) of thermal decomposition for the polymer component. In effect, the optimum pyrolysis temperature was determined as 550°C, 150°C higher than the peak maximum temperature (400°C), in order to obtain the characteristic pyrogram.

3.2. Identification of polymer

As for paint A, an average mass spectrum corresponding to the specific EGA profile from 340 to 440°C (A) shown in Fig. 1a was used for the identification of polymeric materials. Using the EGA-MS Polymer Library, the polymer was identified as acrylonitrile-acrylate-styrene copolymer. The observed mass spectrum for A is shown in Fig. 2 together with the reference spectrum in the library. Fig. 3A and B show the pyrograms obtained at 550°C of the polymer components in paints A and B, respectively. The pyrogram in Fig. 2A showed a pattern of acrylic resin. The main decomposition products were identified as the monomeric compounds acrylonitrile, styrene, and 2-ethylhexyl acrylate. Therefore, it was found that the polymer

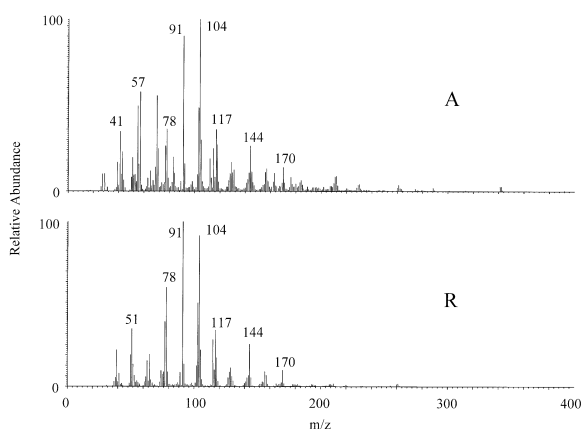


Fig. 2. Comparison of (A) average mass spectrum corresponding to the specific EGA profile for paint A from 340 to 440°C and (R) reference mass spectrum of acrylonitrile-acrylate-styrene copolymer.

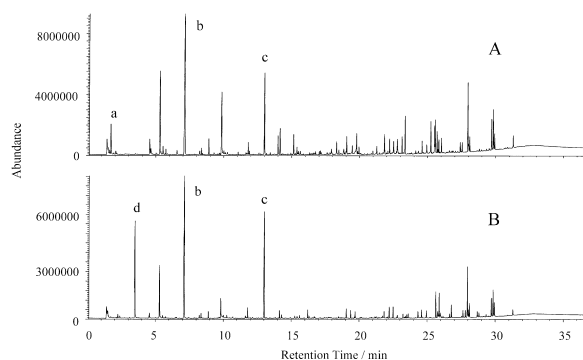


Fig. 3. Pyrograms of (A) the polymer components in paint A and (B) those in paint B. a=Acrylonitrile; b=styrene; c=2-ethylhexyl acrylate; d=methyl methacrylate.

components in paint A were acrylic resins comprised of acrylonitrile, styrene and 2-ethylhexyl acrylate. In the same manner, the polymer component in paint B was identified as styrene–methyl methacrylate copolymer using the EGA–MS Polymer Library. An average mass spectrum corresponding to the specific EGA profile from 340 to 440°C (B) shown in Fig. 1b was used for the identification. The observed mass spectrum for B is shown in Fig. 4 together with the reference spectrum in the library. The pyrogram (B) showed a pattern of acrylic resin. The main decomposition products were identified as the monomeric compounds methyl methacrylate, styrene, and 2-ethylhexyl acrylate. Therefore, it was found that

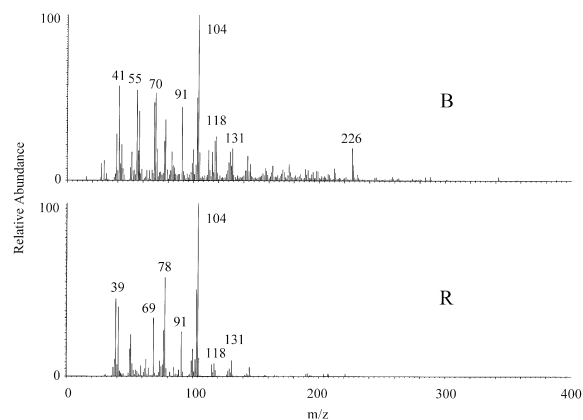


Fig. 4. Comparison of (B) average mass spectrum corresponding to the specific EGA profile for paint B from 340 to 440°C and (R) reference mass spectrum of styrene–methyl methacrylate copolymer.

the polymer components in paint B were acrylic resins comprised of methyl methacrylate, styrene, and 2-ethylhexyl acrylate.

3.3. Solvent analysis

Figs. 5 shows total ion chromatograms (TICs) of the thermally desorbed components from 60 to 190°C for paints A and B. The solvents could be identified by EI mass spectra with the corresponding PCI mass spectra. In these alcoholic solvents, since the EI mass spectra did not provide molecular mass information, it was difficult to identify the solvents only by the EI mass spectra. The PCI mass spectra are shown in Fig. 6 together with the EI mass spectra. Molecular masses of the alcoholic compounds were determined with the assistance of PCI mass spectra. For paint A, it was found that water, ethylene glycol, 2-butoxyethanol, *N*-methyl-2-pyrrolidone, 2-(2-butoxyethoxy)ethanol, and isomers of hydroxyoctyl isobutylacetate were used as solvents. For paint B, it was found that water, ethylene glycol, 2-butoxyethanol, and isomers of hydroxyoctyl isobutylacetate were used as solvents.

3.4. Additive analysis

Fig. 7 shows TICs of the thermal desorption and/or thermal decomposition products from 190 to 280°C. Although trace amounts of 2-ethyl hexanol

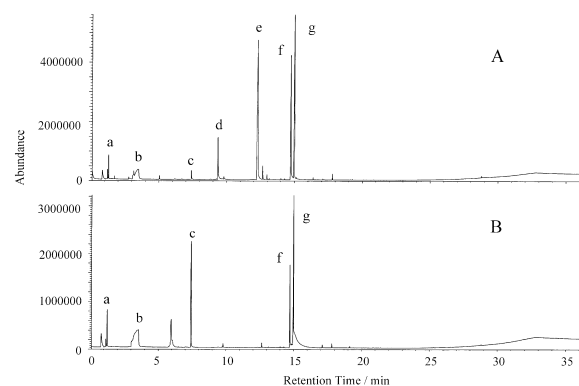


Fig. 5. Thermal desorption chromatograms from 60 to 190°C for solvents in (A) paint A and (B) paint B by pyrolysis–GC–MS. a=Water; b=ethylene glycol; c=2-butoxyethanol; d=*N*-methyl-2-pyrrolidone; e=2-(2-butoxyethoxy)ethanol; f=hydroxyoctyl isobutylacetate; g=hydroxyoctyl isobutylacetate.

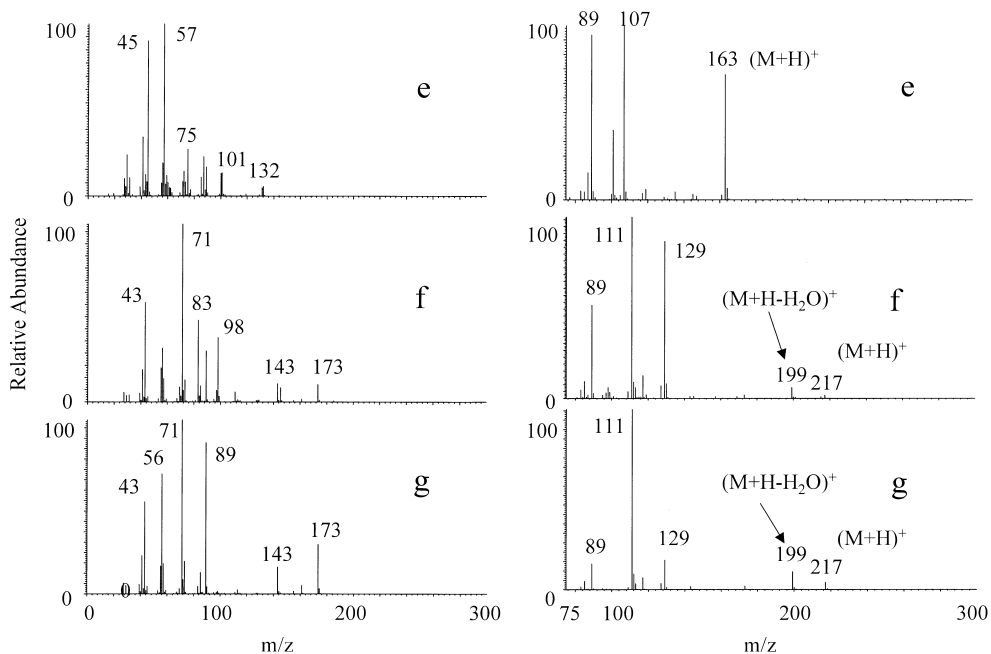


Fig. 6. EI mass spectra (left) of solvents together with the corresponding PCI mass spectra (right). (d) 2-(2-Butoxyethoxy)ethanol; (e) hydroxyoctyl isobutylacetate; (f) hydroxyoctyl isobutylacetate.

were detected from paint A, this compound will be a decomposition product from the polymer at around 280°C. As for paint B, 2,2'-dithiobispyridine was detected; this compound might be derived from zinc pyrithione as antifungal substance. Fig. 8 shows EGA profiles of paint B and zinc pyrithione standard from 60 to 460°C. The decomposition temperature of

zinc pyrithione standard was the same as the temperature observed for paint B. Fig. 9 shows the TIC of thermal decomposition products of zinc pyrithione standard from 190 to 280°C. The main decomposition products were identified as pyridine, 2,2'-thiobispyridine, and 2,2'-dithiobispyridine. These compounds were also found in thermal desorption and decomposition products from paint B. Taking

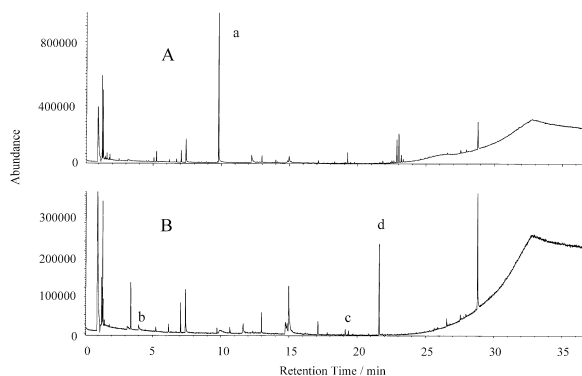


Fig. 7. Thermal desorption and/or thermal decomposition chromatograms from 190 to 280°C for additives in (A) paint A and (B) paint B by pyrolysis-GC-MS. a=2-Ethyl hexanol; b=pyridine; c=2,2'-thiobispyridine; d=2,2'-dithiobispyridine.

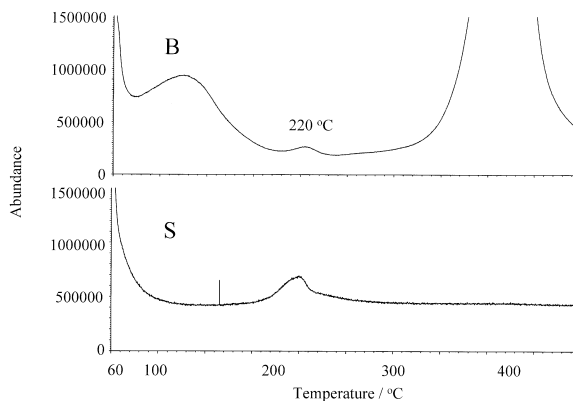


Fig. 8. EGA total ion profile of (B) paint B and (S) zinc pyrithione standard from 60 to 460°C by EGA-MS.

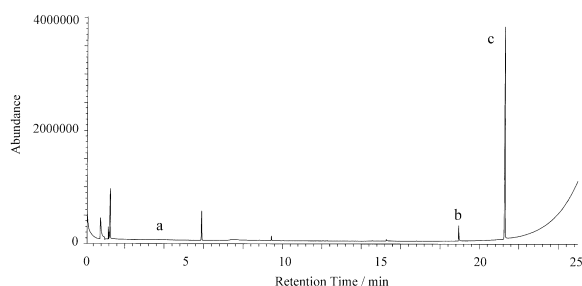


Fig. 9. TIC of thermal decomposition products of zinc pyrithione standard from 190 to 280°C. a=Pyridine; b=2,2'-thiobispyridine; c=2,2'-dithiobispyridine.

into account that this additive was for paints, it was decided that paint B contained zinc pyrithione as an antifungal substance.

4. Conclusions

The EGA–MS system suggested the optimal thermal desorption condition for solvents and additives and the subsequent optimal pyrolysis temperature for the remaining polymeric material. Under the suggested conditions, the solvents, additives, and polymer could be analyzed separately by this temperature-programmed pyrolysis–GC–MS system. Furthermore, this study has proved the following: the PCI mass spectra were helpful for the identification of the alcoholic solvents in the waterborne paints; the

information on the decomposition temperature and products was useful for the identification of zinc pyrithione; the polymer library proved helpful in the identification of polymers.

This method was also applied to the analysis of solvent-based paints, and provided good results: the EGA profile indicated thermal characteristics of the samples; solvents and polymers could be identified without interference of the other components.

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