

Note

Application of deactivated metal capillaries to the analysis of solvents in varnish

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The analyses of volatile components evolved from varnish while drying is becoming very important from the point of understanding the degree of dryness of the varnish, especially when applied to precision electrical parts, and also from an environmental point of view. For such analysis, the static head space method is a most popular technique, but requires a special attachment on the gas chromatograph and may lack sensitivity towards trace amounts of volatile components and generally towards components having boiling points above 130°C. Some examples^{1,2} of solvents having boiling points above 130°C have been analysed by heating the sample, but the necessity of an exclusively designed attachment has prevented general acceptance of the method as a practical technique.

The dynamic head space method is superior in sensitivity to the static head space method because all the volatiles that are trapped are subjected to gas chromatographic (GC) analyses. Some volatiles from solid materials have been analysed by the dynamic head space method using a combination of a capillary column and a capillary cold trap^{3,4}. Special devices were designed in each case for cooling and heating the trap, showing that the method is not yet routine. A special technique for focusing was reported⁵ for the head space method, by cooling the column head prior to passage of the sample to the capillary column. There is also a report⁶ on focusing with the dynamic head space method in which the volatiles trapped in a Tenax TA cartridge were focused in a fused-silica capillary trap prior to passage to a fused-silica capillary column. Also in this method, special devices must be used for cooling and heating the trap. For the method to become routine, a simple technique for cooling the trap by liquid nitrogen and for rapid heating of the trapped solvents prior to passage to the column should be developed.

The analyses of volatiles in paint has been performed either for the purpose of analysing the solvents in the paint itself or for the purpose of analysing the remaining volatiles in the film^{1-5,7,8}. The latter has been performed only in the case of simple components, and, to our knowledge, there is no report on the analyses of the complex mixture of remaining volatiles including alcohols.

Here, a new approach to the dynamic head space method was devised to trace

the decrease of solvents in varnish. First we will describe how easy cooling and heating is achieved by using a deactivated metal capillary tube^{9,10} as a cold trap; secondly, by using a deactivated metal capillary column¹¹ as a separation column, it was very easy to remove the column from the oven, which enables the ready cooling of the column and facilitates the separation of low boiling solvents; finally, by utilizing the above advantages, it becomes possible to monitor changes in the components of solvents remaining in the varnish during drying which have a complex composition including alcohols.

EXPERIMENTAL

Instrument and sample

For gas chromatography, an Okura Model 701 was used with flame ionization detection (FID), a deactivated metal capillary column, 20 m \times 0.25 mm I.D., coated with 0.4 μ m OV-1 and a Shimadzu Chromatopac C-RIA as an integrator. The "RAS" metal capillary^{9,10} used for the trap capillary, 40 cm \times 14 cm \times 1 mm I.D. \times 2 mm O.D. was supplied by Nippon Chromato (Tokyo, Japan) with the metal capillary column mentioned above. The rapid heating apparatus for the trap capillary included an insulating transformer having an output of 5 V, 15 A, two lead wires between the transformer and both ends of the trap, and an element for measuring the temperature of the trap which was heated electrically as shown in Fig. 1.

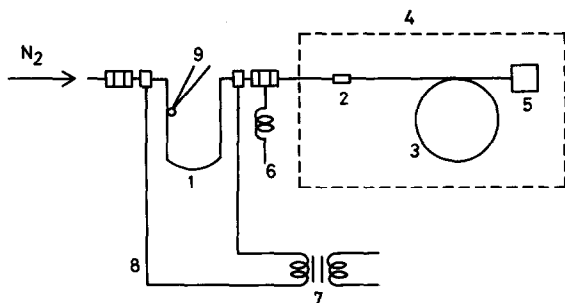


Fig. 1. Method of GC analysis for the samples collected in the trap. 1 = Trap; 2 = PTFE tube; 3 = "RAS" capillary column; 4 = oven; 5 = flame ionization detector; 6 = split; 7 = transformer; 8 = lead wire; 9 = AC thermocouple.

A cylindrical glass vessel, 10 cm \times 30 mm I.D., was used as the sample container, to which a glass pipe (10 cm \times 6 mm O.D.) is welded to one and an inner joint (29/42) with a glass cap to the other end. A stainless-steel joint (6 mm/2 mm) was used to connect the pipe to the end of the trap.

Collection and GC analyses of volatile components

Onto an aluminium foil (2 cm \times 2 cm) was coated a sample of varnish (5–20 mg). After drying for an appropriate time, the foil was put into the sample container. The container was connected to the collection line as shown in Fig. 2, and was evacuated at 1 mmHG for 1 h with the trap dipped in liquid nitrogen so as to collect the volatile components.

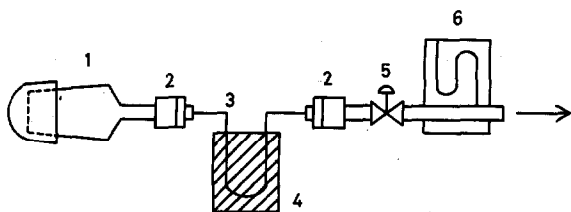


Fig. 2. Collection of volatiles from varnish. 1 = Sample container; 2 = metal joint 6 mm / 2 mm; 3 = trap capillary; 4 = liquid nitrogen; 5 = vacuum cock; 6 = manometer.

The trap with volatile components was connected to the chromatograph as shown in Fig. 1. While cooling the trap, the baseline of the chromatogram was recorded, and then the trap was directly heated by the electric current at 150°C for 5 min in order to transport the volatiles to the chromatograph. Count numbers, which are proportional to peak areas, were measured by the integrator. GC analyses was conducted under the following conditions; nitrogen pressure 1.1 kg/cm²; column temperature after removal from the oven, held at room temperature for 10 min after the trap heating, then placed in the oven at 60°C followed by programming at 10°C/min; sensitivity $8 \cdot 10^{-11}$; splitting ratio 320:1; velocity 36.6 cm/s.

Calculation of degree of drying and composition of volatiles

When W_0 mg of undried varnish was analyzed by GC to give a total count number, C_0 , the count number for 1 mg of the sample is C_0/W_0 . For S_0 mg of undried varnish, total count numbers, C_s , can be obtained by $C_s = S_0 C_0/W_0$. When S_0 mg of the above undried sample was partly dried to S_1 mg, and the total count number for S_1 mg was obtained, C_d , the degree of drying can be calculated as:

$$\text{Degree of drying} = (1 - C_d/C_s) \cdot 100\%$$

The composition of the volatiles was calculated from the area per cent.

RESULTS AND DISCUSSION

Blank test of the system

A blank test was performed without varnish in the sample container. The trap was heated in order to transport anything trapped for GC analysis. Many large peaks were obtained but there was no reproducibility. By washing the apparatus and joints, and also applying grease to the nearest part of the sample container to the cap, the problem was solved, giving a blank test chromatogram which was almost flat.

Collection time and length of trap

After an hour's collection, the trap was changed to a new one, but another one hour's collection did not give a further appreciable amount, which means that an hour's collection is sufficient. Two traps were connected in series to estimate the necessary trap length; it was confirmed that no appreciable amount of sample was collected in the second trap, suggesting that one trap is enough.

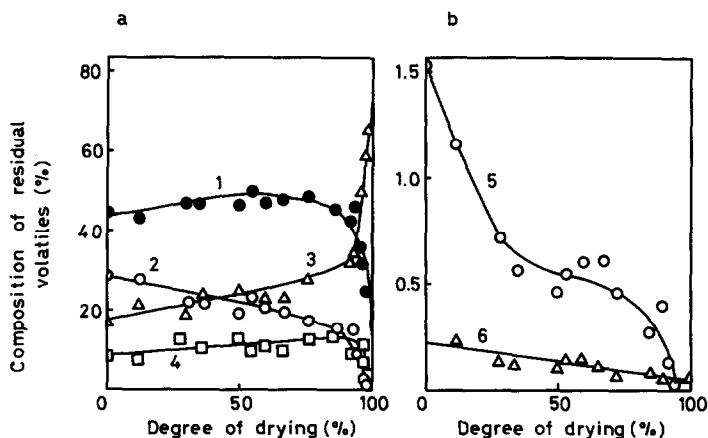


Fig. 3. Residual volatiles in the varnish vs. degree of drying: (a) major components; (b) minor components. Curves: 1 toluene; 2 ethyl acetate; 3 isobutanol; 4 isobutyl acetate; 5 methyl acetate; 6 methanol.

Drying time and residual volatiles in the varnish

The drying time was changed to determine the effect on the composition of the residual volatiles. The results are shown in Fig. 3. They show that, at the initial stage, ethyl acetate and methyl acetate vaporize rapidly. Isobutanol becomes predominant in the residual volatiles at the final stage. Fig. 4 shows the chromatogram at 98.4% drying.

Degree of drying

The degree of drying was calculated according to the method described in the Experimental section. It can also be obtained from the weight change of the varnish.

$$\text{Degree of drying} = [1 - (W - W_{100}) / (W_0 - W_{100})] \cdot 100\%$$

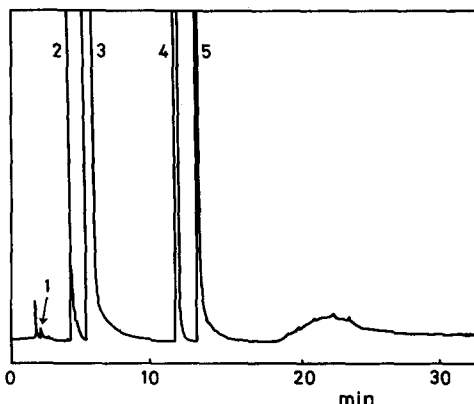


Fig. 4. Chromatogram of the volatiles in the varnish. For GC conditions see Experimental. Degree of drying = 98.4%. Peaks: 1 = methyl acetate; 2 = ethyl acetate; 3 = isobutanol; 4 = toluene; 5 = isobutyl acetate.

where W = weight of varnish after an appropriate drying, W_0 = weight of varnish just after coating and W_{100} = weight of completely dried varnish. The correlation of these two values is as follows:

$$\text{Degree of drying (weight change)} = 0.88 \cdot \text{degree of drying (calculated)}$$

Deactivated metal capillary tube as a cold trap

A naked stainless-steel capillary tube was used as a cold trap¹², and also, desorption was conducted by electrically heating the tube¹³. According to our experiment, however, cold trapped samples, even hydrocarbons, became very hard to recover as the carbon number increased to more than 12, which suggests that quantitative recovery of hydrocarbons that have more than 16 carbons is questionable. We have also found that polar solvents such as alcohols cannot be recovered at all, even those of low molecular weight. The difference between our results and those reported can be attributed to the difference in surface activity of naked stainless-steel capillaries, but considering the fact that the metal surface is active, naked stainless-steel is by no means a good choice for a cold trap.

An alternative is the use of a fused-silica capillary tube as a cold trap^{4,5}. However, fused silica has the disadvantage that it is hard to bend to an U shape, especially that of 0.53 mm I.D., and is easy to break.

A solution of this problem was achieved by using a completely inert, deactivated metal capillary tube⁹. The tube can be bent in any way and can be electrically heated. For transport of the trapped volatiles into the capillary column, special devices are necessary with glass or fused-silica capillary. With a metal capillary, the trapped volatiles are easily transferred by only electrically heating of the trap.

Advantage of deactivated metal capillary column

The deactivated metal capillary column withstood continuous use at 450°C in the case of polymethylsiloxane as the stationary phase and retained sufficient mechanical strength for column exchange after use. Thus the column is advantageous as a high-temperature GC column compared with a fused-silica capillary¹¹. It also has an advantage in the analysis of samples including low boiling compounds. In such analyses, it is desirable to set the initial temperature below 50°C, which is usually difficult due to the remaining heat of the oven and also due to the heat transfer from the flame ionization detector. The metal capillary has a great advantage in that it can be used very easily at initial temperatures of below 50°C, because it can be removed from the oven easily without disconnecting to operate at or below room temperature, and then returned to the oven for further temperature programming. Though fused-silica capillary is flexible to some extent, the elastic limit and the break point are the same, and treatment in this way may lead to breakage of the column.

Potential of dynamic head space method

In the above experiment, volatiles were collected under a vacuum. If gas can be passed through the sample container, the conventional dynamic head space method can be applied. In the case that a small quantity of volatiles is to be analysed, the dynamic head space method¹⁴ is possible, in which the capillary column is removed from the oven, and inlet side of the column is disconnected from the gas chromatograph to

connect it to the sample container and the column is cooled to collect volatiles. Also in this method, a metal capillary has an advantage over a fused-silica one because metals do not break.

CONCLUSIONS

Tracing of the decrease in solvents in varnish was carried out satisfactorily by using a deactivated metal capillary tube as a cold trap and a deactivated metal capillary column as a GC column. The metallic cold trap was rapidly heated directly with an electric current and the capillary column was removed from the oven while it was connected to the gas chromatograph to be chilled to obtain the peaks of the separated low volatile solvents and after an appropriate time it was replaced in the oven for further temperature programming.

ACKNOWLEDGEMENT

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