

CHROM. 11,031

## SUITABILITY OF PLATINUM AS A MATERIAL FOR INTERFACES

FRANZ ETZWEILER

*Givaudan Forschungsgesellschaft AG, CH-8600 Dübendorf (Switzerland)*

---

### SUMMARY

The advantages of using capillaries of platinum or its alloys for interfaces in gas chromatographic systems has been reported previously. Special attention must be paid to the behaviour of the inner surface. Any adsorption or decomposition of the substances eluting from the gas chromatographic column must be avoided. Investigations on surface activity were performed by Grob and in this laboratory. Grob observed that under certain experimental conditions a deactivated platinum-iridium capillary was converted into a very highly activated state. However, we were unable to reproduce Grob's findings. Based on our observations, we can still recommend the use of platinum (platinum alloy) as a material for interfaces.

---

### INTRODUCTION

The use of metal tubing to connect gas chromatographic columns to injectors, detectors and auxiliary components such as splitting and back-flushing valves is well known. It has found additional application in the design of gas chromatograph-mass spectrometer (GC-MS) interfaces<sup>1-3</sup>. We have used platinum-iridium capillaries for effluent-splitting of glass capillary columns, avoiding a dead volume<sup>4</sup>. This technique led to interesting applications in simultaneous multi-detection<sup>5</sup> and separation cassettes<sup>6</sup>. Grob<sup>7</sup> referred to an adsorption effect due to the noble metal surface. He observed an increasing activity of the inner surface of a deactivated platinum-iridium capillary upon column exchange. His work prompted us to make a more comprehensive investigation of the behaviour of platinum-iridium capillaries, although several outlet splitters (prepared from this material), preceded by different columns, performed well in our laboratories. We also conducted experiments involving the same types of column and stationary phases as those used by Grob. Our aim was to find a set of conditions resulting in an activity increase as he described.

### EXPERIMENTAL

The experimental arrangement is shown in Fig. 1<sup>1,7</sup>. The metal capillary of interest was mounted between a glass capillary column and the flame-ionization detector (FID). The inlet of the column was connected to the injection port and the outlet to one end of the metal capillary (attached at each end to a ca. 3-cm long

piece of AR-glass capillary) by means of PTFE shrink-tubing. The other end was connected with PTFE to a 12-cm piece of AR-glass capillary, which led into the flame tip of the FID. Any contact of the metal capillary with the oven wall must be avoided. Unless stated otherwise, the column used for deactivation was a glass capillary column (20 m  $\times$  0.3 mm I.D.) coated with UCON HB 5100. Subsequently we replaced the UCON capillary column with a PEG-20M glass capillary column (18 m  $\times$  0.35 mm I.D.). A helium flow-rate of 3 ml/min was applied and the system was heated at 240° for different periods of time. Chromatograms were recorded with a 25 m  $\times$  0.3 mm I.D. glass capillary column coated with PEG-20M to which was connected the heated platinum-iridium capillary. This change of column was necessary as heating the PEG-20M column for days and even weeks at 240° destroyed the stationary phase. With this arrangement, the metal capillary and glass capillary column were held at the same temperature. Commercially available helium 4.6 was used as the carrier gas (Sauerstoff- und Wasserstoff-Werke AG, Lucerne, Switzerland).

The valves employed were regular pressure controllers purchased from H. Lüdi & Co. (Zürich, Switzerland) and Carbagas, Div. Scientifique (Zürich, Switzerland).

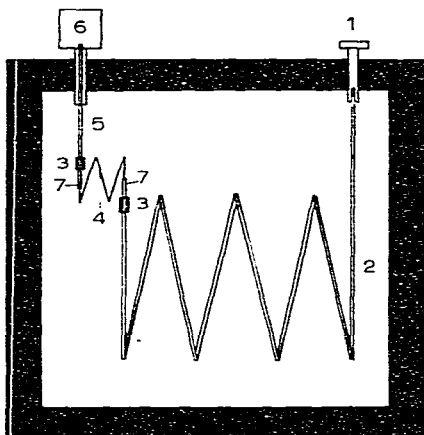


Fig. 1. Scheme of experimental arrangement. 1 = Injection port; 2 = glass capillary column; 3 = PTFE shrink-tubing; 4 = platinum-iridium capillary; 5 = ca. 12-cm AR-glass capillary; 6 = FID; 7 = pieces of AR-glass capillaries attached by fusing to the metal capillary.

All glass capillary columns used were about 20 m long and had an inner diameter of 0.3 mm. They were coated with UCON HB 5100, OV-101, silicone ASI 100 methyl, OV-17 and PEG-20M.

The noble metal capillaries were made of platinum-iridium (9:1), 30–50 cm long, O.D. 0.3 mm, I.D. 0.15 mm, supplied by Degussa (Hanau, G.F.R.).

All connecting glass capillaries were made of untreated AR-glass. As a very high activity for hydrocarbons was stated by Grob<sup>7</sup>, we chose a test mixture containing 1-octanol, *n*-dodecane, 1-dodecanol and *n*-heptadecane (dissolved in *n*-hexane).

*Gas chromatographic conditions.* The glass capillary column (25 m  $\times$  0.3 mm) was prepared and coated with PEG-20M according to the method of Grob and Grob<sup>8</sup> and used in the temperature-programmed analysis. The temperature programme was 3 min isothermal at 60°, then from 60° to 180° at 6°/min. The flow-rate

of helium carrier gas was adjusted in all experiments (with or without a metal capillary) to 3 ml/min measured at 100°. The injection port and the detector were maintained at 200°. The amount injected was always 2  $\mu$ l in the splitless mode.

## RESULTS AND DISCUSSION

A complete investigation of all parameters influencing the behaviour of the surface obviously required too many experiments. Therefore, we decided first to attempt to reproduce Grob's results.

### *Influence of stationary phase*

*Carbowax.* A new platinum-iridium capillary, 50 cm long, was heated until red-hot while flushing with oxygen. This procedure converted the surface into a highly activated state. This activity of the metal capillary disappeared very rapidly (in less than 1 h) on heating it together with a UCON column while maintaining a flow of helium<sup>1,7</sup>. In our experiment, we heated the oven for 16 h at 170°, replaced the UCON column with the PEG column, and heated at 240° for 23 h and 47 h. Fig. 2 shows gas chromatograms obtained after exchange of the PEG column (A) without and (B)

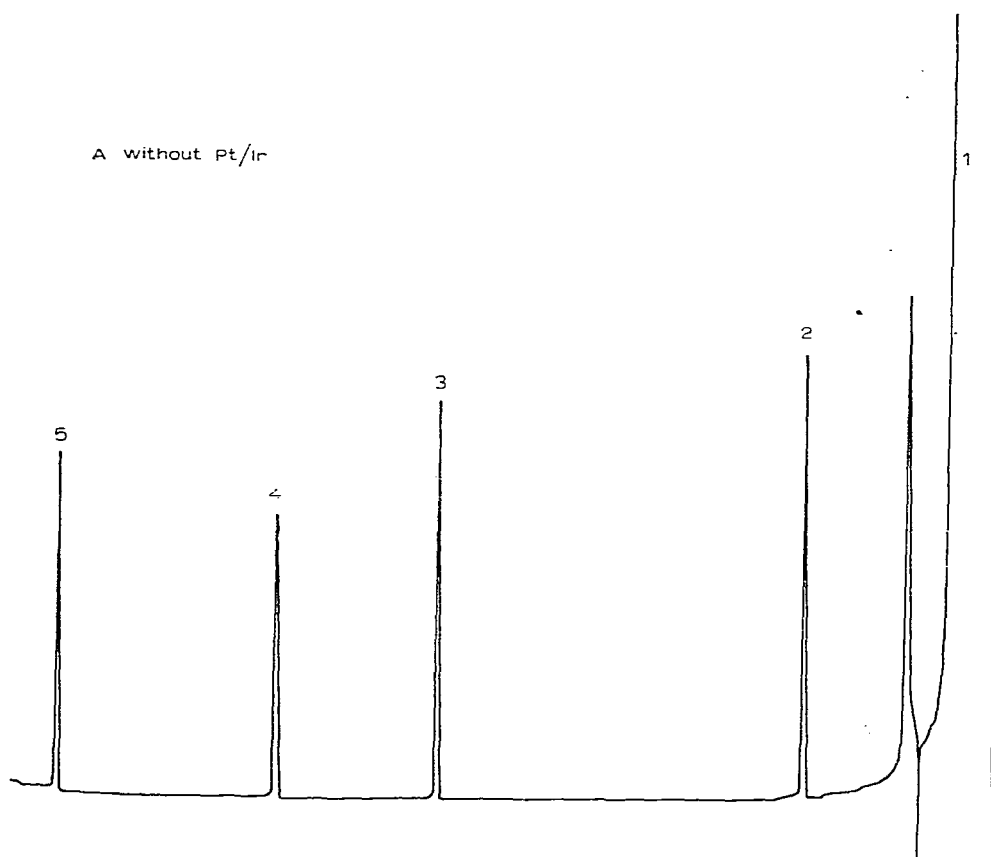


Fig. 2A.

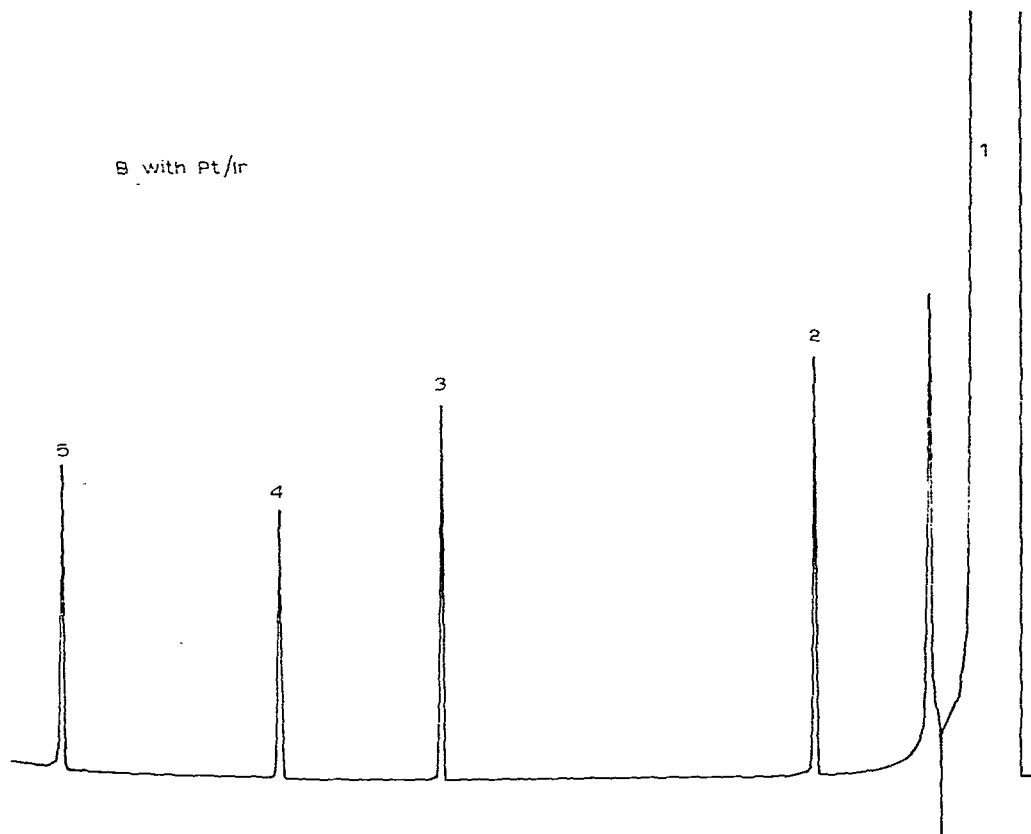


Fig. 2. Chromatogram of test mixture on a 25 m  $\times$  0.3 mm I.D. glass capillary column coated with PEG-20M. Peaks: 1 = *n*-hexane; 2 = *n*-dodecane; 3 = 1-octanol; 4 = *n*-heptadecane; 5 = 1-dodecanol. A, Column connected directly to the FID; B, column connected via platinum-iridium capillary to the FID. The metal capillary was heated for 47 h at 240° together with a PEG-20M column.

with a platinum-iridium capillary. In contrast to Grob's findings, no adsorption was observed.

*UCON*. Under the conditions described above, a platinum-iridium capillary (50 cm  $\times$  0.15 mm I.D.) was deactivated. Heating it together with the *UCON* column for several days at 180° while maintaining a flow of helium resulted in no activity. This result agreed well with earlier experiments obtained by Grob<sup>7</sup> and in this laboratory<sup>1,2</sup>.

*OV-1, OV-101 and OV-17*. From earlier experiments, it was known that deactivation by silicone oil-coated capillary columns required more time (at least 12 h) than those coated with *UCON*. Based on this observation, it was expected that some activity of the metal capillary in connection with these stationary phases would occur.

In this laboratory, platinum-iridium capillaries are used routinely as interfaces for several GC-MS systems. After heating the platinum-iridium capillary until red-hot

in a flow of oxygen, the capillary was fused to a glass capillary column coated with OV-1, helium carrier gas was applied, the oven heated to 200° and the interface temperature maintained overnight at 250°. Under these conditions, daily trace analyses were run during several months. This capillary certainly can be considered as "used". The OV-1 column had to be replaced with a freshly prepared column coated with ASI 100 methyl, as it showed severe tailing with alcohols. On this ASI column, we ran the test mixture and increased the interface temperature stepwise from 250° to 300°, while recording gas chromatograms after each temperature increase. Upon reaching 300°, the interface was heated for 60 h. Comparison of these chromatograms with those recorded directly with the FID showed no activity that could be attributed to the platinum-iridium capillary. Other experiments with capillaries coated with OV-17 and OV-101 gave the same results.

#### *Influence of flame temperature*

With the above results, we searched for differences between Grob's and our treatment of the capillaries. All of our capillaries were heated until red-hot in a luminous flame of butane while maintaining a flow of oxygen<sup>1</sup>. Grob used the same treatment, except that he applied a hotter blue flame. Carrying out the same treatment in this laboratory, followed by deactivation for 1 h at 100° with a UCON column and subsequent heating for 4½ days at 240° with a PEG column, a thoroughly deactivated platinum-iridium capillary was obtained. This result is contradictory to Grob's finding, as he obtained poor results after 2 days.

#### *Influence of impurities in helium carrier gas*

It was suspected that the oxygen content of the helium carrier gas could be a possible cause of the change in activity. Only the two extremes were examined, namely pure air and "pure" helium.

*Air.* A platinum-iridium capillary employed in previous experiments was heated in the GC oven for 2½ days at 240° without a gas flow. Recording gas chromatograms with this capillary showed that no adsorption had occurred.

*"Pure" helium.* All of our gas chromatographs are equipped with standard valves and connected by means of steel tubes to 45-l steel cylinders, provided with Lüdi pressure controllers. This type of pressure controller uses rubber membranes and hence diffusion of water and air into the carrier gas may occur. Therefore, one of these controllers was replaced with an Air Liquide controller, which features a metal membrane. The Carlo Erba pressure controller was removed, the carrier gas line attached directly to the injection port and the septum replaced with a piece of PTFE of thickness 4 mm. The platinum-iridium capillary was fused to the PEG-20M column on one end and the other to a 12-cm long AR-glass capillary which led to the FID. This set-up ensured minimal impurities in the carrier gas. A platinum-iridium capillary from previous experiments and a freshly purchased capillary were heated for 5 days at 240° while maintaining a flow of helium. Subsequently recorded gas chromatograms of the test mixture showed no adsorption effect.

*Water.* Water is the second important impurity in helium and we assumed that its presence in the carrier gas could affect adsorption. In order to investigate this assumption, a filter-drier filled with water was placed in the carrier gas line between the steel cylinder and the injection port. The platinum-iridium capillary was mounted

between the injector and detector (without columns), a flow of helium gas containing water (about 3 ml/min) applied and the oven heated for 24 h at 280°. Examination of the capillary with the test set-up showed no adsorption.

#### CONCLUSION

There seems to be no reason to avoid the use of platinum capillaries as interfaces in gas chromatographic systems. We were unable to reproduce the activation of an inactive surface as described by Grob.

#### ACKNOWLEDGEMENTS

The author is indebted to Dr. K. Grob for stimulating discussion and for the gift of a capillary column. Discussions on the manuscript with Dr. W. Achermann are gratefully acknowledged.

#### REFERENCES

- 1 N. Neuner-Jehle, F. Etzweiler and G. Zarske, *Chromatographia*, 6 (1973) 211.
- 2 K. Grob and H. J. Jaeggi, *Chromatographia*, 5 (1972) 38.
- 3 D. Henneberg, U. Henrichs and G. Schomburg, *Chromatographia*, 8 (1975) 449.
- 4 F. Etzweiler and N. Neuner-Jehle, *Chromatographia*, 6 (1973) 509.
- 5 M. Hrivnac, W. Frischknecht and L. Cechova, *Anal. Chem.*, 48 (1976) 937.
- 6 R. E. Kaiser, *Chromatographia*, 7 (1974) 688.
- 7 K. Grob, *Chromatographia*, 9 (1976) 509.
- 8 K. Grob and G. Grob, *J. Chromatogr.*, 125 (1976) 471.