

CHROM. 10,860

SORPTION EFFECTS IN COLUMNS IN THE GAS CHROMATOGRAPHY OF COPPER TRIFLUOROACETYLACETONATE

D. N. SOKOLOV, A. V. DAVYDOV, S. YU. PROKOFYEV, S. S. TRAVNIKOV,
E. V. FEDOSEEV and B. F. MYASOEDOV

V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, U.S.S.R. Academy of Sciences, Moscow, and Section of the Institute of Chemical Physics, U.S.S.R. Academy of Sciences, Chernogolovka, Moscow Province (U.S.S.R.)

(Received December 21st, 1977)

SUMMARY

The distribution of copper trifluoroacetylacetonate during the conditioning of a gas chromatographic column has been studied. It was found that the sorption of the copper chelate in the column depends on the amount of the compound injected, the content of liquid phase in the bed, the nature of the solid support and the temperature. Substantial sorption of the copper chelate by glass- and PTFE-wool plugs was observed. It is shown that the sorption of the copper chelate by the bed is partly a reversible process. The results obtained indicate the necessity for further investigations of inert phases and solid supports and for the suppression of sorption effects in the chromatographic column.

INTRODUCTION

In the gas chromatography of β -diketonates of metals, several effects occur that cause some difficulties in the application of the method for analytical purposes. Of particular importance is the necessity for conditioning the column in order to overcome adsorption of the chelate during the injection of the first portions of the compound being analysed in a column that is new or has not been used for a long period^{1,2}, displacement of earlier sorbed chelate from the column by other chelates^{1,3} or by pure β -diketone⁴, difficulties in the determination of small amounts of β -diketonates connected with their losses in the column⁵⁻⁹, etc. Similar effects have been observed with other compounds¹⁰. In most papers on the gas chromatography of chelates of metals, sorption effects in columns are rarely considered, except for two papers^{1,3}.

This paper describes a study of the sorption of bis-(1,1,1-trifluoro-2,4-pentadionato)copper(II) (copper trifluoroacetylacetonate) in columns depending on the conditions used in the gas chromatographic determination. This compound was chosen because the behaviour of copper trifluoroacetylacetonate (CuL_2) in columns is typical of most β -diketonates of metals (an exception are the fluorinated β -diketonates of

beryllium, aluminium and chromium, for which the above effects occur only slightly or not at all). Also, we chose the method of radioactive tracers as the main method of investigation and the isotope copper-64 has nuclear physical characteristics that are convenient for radiometric measurements.

EXPERIMENTAL

Equipment

A gas chromatograph of special construction was used, with which it is possible to detect the compound being chromatographically determined by measuring its γ -radiation at any point along the column and also to record automatically the distribution of γ -radioactive substances during their sorption in the column without cooling and removing it from the chromatograph. In order to measure γ -radiation, a scintillation detector with a NaI(TL) crystal was used that was connected with an intensimeter, the response of which was recorded with an electronic potentiometer. Tsvet-5 and Tsvet-102 gas chromatographs with a katharometer and a flame-ionization detector and an LHM-8 MDP with a detector for γ -radiation of our own construction were used.

For the determination of copper in the liquid phase and separately in the solid carrier a Saturn atomic-absorption spectrophotometer with a Perkin-Elmer NSA-74 graphite furnace atomizer was used.

Columns

Glass or PTFE columns of dimensions 30×0.4 cm (40×0.4 cm in some instances) were used. Various amounts (5–10%) of SE-54 silicone and 5PUE polyphenyl ether on the solid supports Chromaton NAW (0.1–0.125 mm), Chromaton NAW DMCS (0.25–0.315 mm) and Polychrome-1 were used as liquid phases. The beds were fixed in the columns by two plugs of PTFE- or glass-wool. The carrier gas was high-purity helium at a flow-rate of 30 ml/min. The temperature of the columns and the evaporator was varied with the range 120–160°. Before chromatographic operations the columns were purged with helium for 2 h at 180°.

Reagents

Copper trifluoroacetylacetonate was synthesized from trifluoroacetylacetonone (Serva, Heidelberg, G.F.R.) according to Berezkin *et al.*¹⁰. In order to obtain a compound labelled with copper-64, special-purity copper (content of impurities $10^{-4}\%$), irradiated in a reactor with neutrons, with a specific activity of 5 mCi/mg was used. The copper trifluoroacetylacetonate was purified by sublimation in a current of argon at 200°. The radiochemical purity of the compound obtained was controlled by the γ -spectrometric method.

Methods of investigations

Copper trifluoroacetylacetonate in the form of a 2.5–3.0% solution in benzene or toluene ("pure for analysis") was injected into the columns with a 10- μ l microinjector. The volume of the samples injected was 2–10 μ l. The amount of the compound sorbed in the column was determined within 5 min of the detection of the last chromatographic peak.

With copper trifluoroacetylacetonate labelled with copper-64, the distribution of γ -radioactivity along the column was recorded and the area of the radiogram obtained was measured in order to determine the amount of the copper compound sorbed in the column. The amount of copper was calculated from the calibration graph of the area of the radiogram *versus* the copper content, which was plotted by measurement of the γ -activity of standard samples. If necessary, a correction for decay of copper-64 (half-life = 12.8 h) was introduced. For the preparation of standards, aliquots of the solution of copper trifluoroacetylacetonate (labelled with copper-64) with a known copper content (12.9–49 μg) were taken, 1 ml of diethyl ether was added and the solutions obtained were applied to strips of filter-paper that were 3 mm wide and of a length equal to that of the chromatographic column (30 cm). The strips were dried and placed in glass tubes analogous to the chromatographic columns. The relative standard deviation of the determination of copper in the column by the given method was 0.05 at $\alpha = 0.95$.

The determination of copper in the liquid phase and separately in the solid carrier was accomplished as follows. The bed was removed from the column, the liquid phase with the sorbed copper trifluoroacetylacetonate was extracted twice with chloroform, the chloroform solutions were combined, brought to a volume of 5 ml and the copper in the solution obtained was determined by atomic-adsorption spectrophotometry with electrothermal atomization. The solid carrier remaining after the removal of the liquid phase was dried and then boiled for 1 h with concentrated nitric acid. The solution was separated by centrifugation and diluted with water to a volume of 5 ml, and the copper in this solution was determined by atomic-absorption spectrophotometry. In order to carry out blank experiments, a bed from a column that had only been purged with helium was used.

RESULTS AND DISCUSSION

The sorption of copper trifluoroacetylacetonate in the column during conditioning was first studied. Fig. 1 shows the curves of the distribution of copper-64 over the length of the column for various amounts of CuL_2 injected into the column, using Chromaton NAW and Polychrome-1 containing 5% of SE-54 as beds. The temperatures of the columns were 120° and 140°, respectively. The conditions selected for the chromatographic analysis were the optimum for observing most clearly the process of column conditioning. When the first portion of copper chelate (25 μg of CuL_2 or 4.3 μg of Cu) was injected the compound was completely sorbed in the column, mainly in the top part. During subsequent injections a gradual equilibration of the concentration of sorbed compounds along the length of the column occurred. On injection into the column packed with 5% SE-54 on Chromaton NAW (and also on Chromaton NAW DMCS) of more than 400 μg of CuL_2 at 140°, stabilization of the form and area the peaks of copper trifluoroacetylacetonate was observed, although chelate sorption in the column was not completed.

In the study of the distribution of the copper compound in the column, significant sorption of the compound by glass-wool plugs was observed, reaching 25–30% of the total amount of the compound sorbed. Replacement of glass-wool with PTFE-wool resulted in less sorption of the chelate (10–12%) on the plugs. The maxima on the curves of the distribution of copper-64 (Fig. 1a and 1b) correspond to

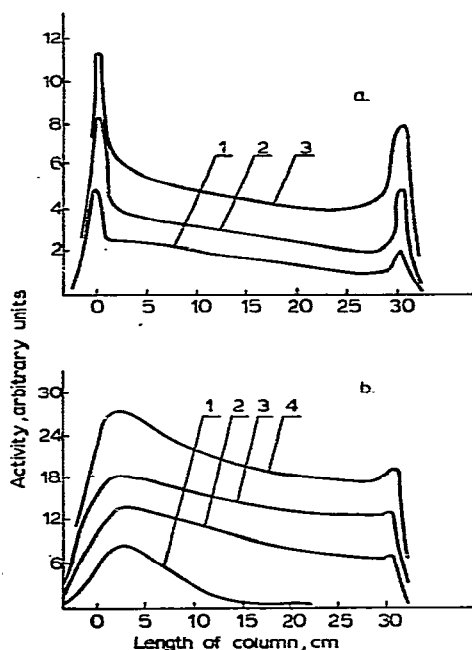


Fig. 1. Distribution of copper-64 in a chromatographic column containing 5% of SE-54 on (a) Chromaton NAW and (b) Polychrome-1 during conditioning. Amount of copper trifluoroacetylacetonate injected into the column: (a) 1 = 25 μg ; 2 = 50 μg ; 3 = 250 μg ; (b) 1 = 25 μg ; 2 = 125 μg ; 3 = 250 μg ; 4 = 1000 μg . Temperature of column: (a) 120°; (b) 140°. Amount of the bed in the column: (a) 1 g; (b) 2 g.

sorption of the chelate by PTFE-wool plugs at each end of the column. This substantial sorption of copper trifluoroacetylacetonate by glass-wool and even of PTFE-wool plugs is not only of interest from the methodological point of view, but may also explain some of the anomalous effects that have been observed during the gas chromatography of chelates of metals. Thus, Uden and Jenkins¹ noticed that during displacement of aluminium trifluoroacetylacetonate, sorbed in a column, by a corresponding iron chelate, the retention time of the complex being displaced during a series of successive injections of iron chelate did not change. The same effect was observed on replacement of the bed of the column, silanization of the solid carrier and use of PTFE instead of a diatomite carrier. This effect may be explained by the sorption of the aluminium chelate by glass-wool in the top part of the column.

Figs. 2 and 3 give data that illustrate the influence of various factors upon the sorption of copper trifluoroacetylacetonate in the column, namely the amount of chelate introduced into the column, the content of the liquid phase on the carrier, the nature of the carrier and the temperature. With an increase in the amount of chelate introduced into the column, gradual saturation of the bed occurs, a gradual decrease in the amount of compound sorbed with respect to the amount of chelate introduced being observed. Table I gives data that characterize the sorption in a column packed with 5% of SE-54 on Chromaton NAW (140°) on the successive introduction of various amounts of chelate. The values given were obtained by taking into account sorption of the chelate by PTFE-wool plugs.

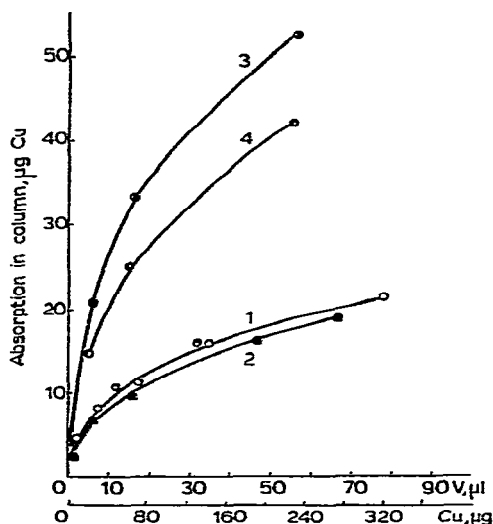


Fig. 2. Sorption of copper trifluoroacetylacetonate in columns containing SE-54 on (1) and (4) Chromaton NAW, (2) Chromaton NAW DMCS and (3) Polychrome-1 (2 g) supports at 140°. SE-54 content: (1) and (3) 5%; (4) 20%. Curve 1 was constructed according to data obtained on two columns. Abscissa: total volume of solution under investigation and total amount of copper injected into the column.

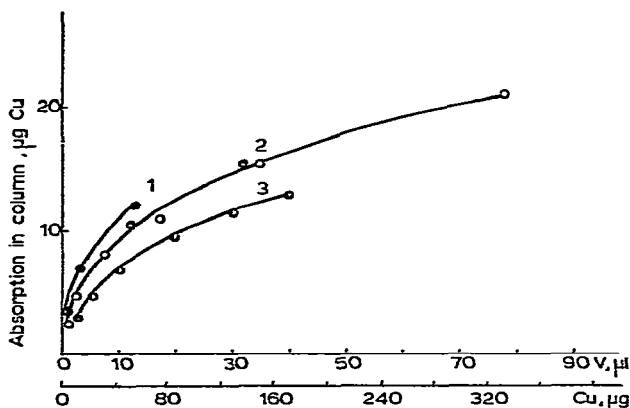


Fig. 3. Influence of temperature on sorption of copper trifluoroacetylacetonate. Temperature: (1) 120°; (2) 140°; (3) 160°. Abscissa: as in Fig. 2.

The adsorption of copper trifluoroacetylacetonate in the column occurs as a result of its interaction with the bed. This was also confirmed by radiometric measurements on the portion of the tube in the evaporator: the amount of copper found in this portion was less than 1% of the amount injected.

As can be seen from a comparison of curves 1 and 4 in Fig. 2, the sorption of copper trifluoroacetylacetonate depends on the amount of liquid phase in the column. With an increase in the content of SE-54 from 5 to 20% (on Chromaton NAW), the sorption of the chelate increased almost 2.5-fold.

TABLE I
SORPTION IN COLUMN PACKED WITH 5% OF SE-54 ON CHROMATON NAW

<i>Volume of solvent injected (μl)</i>	<i>Amount of CuL_2 injected into the column (μg)</i>	<i>Sorption of CuL_2 (% of amount injected)</i>
3	15	100
2	50	34
5	125	20
10	250	7.8
2×10	500	6.1
4×10	1000	3.5

The nature of the solid carrier also influences the sorption of the copper chelate in the column. Although the difference in extent of sorption of the chelate when non-silanized and silanized Chromaton NAW is used as the carrier was not great, when polychrome-1 was used a significant increase in sorption was observed. This effect was unexpected because Polychrome-1 is usually considered as the most inert solid support.

The determination of copper in the bed by atomic-absorption spectrophotometry showed that after removal of the liquid phase by treating the bed with chloroform a noticeable amount of copper remained in some form on the solid support, and could be removed from the support only by treating it with concentrated nitric acid. This appears to indicate partial decomposition of the copper chelate in the column. Using 5% of SE-54 on Chromaton NAW DMCS, the weight of the bed being 1 g, 770 μ g of CuL_2 being injected into the column and the temperature of the column being 140°, the amount of copper determined in the liquid phase was 12.1 μ g by atomic-absorption spectrophotometry and 13.4 μ g by the radiometric method.

Experiments on the influence of temperature on the sorption of copper trifluoroacetylacetonate (Fig. 3) showed that as the temperature was increased the extent of sorption decreased. On purging the column, conditioned with a fixed amount of chelate at 140°, with a carrier gas for 1–2 h at the same temperature, no decrease in the amount of copper in the column was observed. However, on purging at 160° the amount of copper in the column rapidly decreased to a level corresponding to the extent of sorption during conditioning of the column at 160°. From this result it can be concluded that the sorption of the chelate in the column is not completely irreversible. Further experiments were carried out in order to elucidate the question of whether purging from the column of a reversibly sorbed chelate at a constant temperature of the column occurs. For this purpose, columns with removable glass tubes at the ends were used. After injection into the column of a series of samples of copper chelate labelled with copper-64 (ten injections, each of 5 μ l or 1250 μ g of CuL_2), the removable tube at the end of the column was replaced with an exit tube to the cold zone and provided with a plug of glass-wool. The column was purged with carrier gas at a flow-rate of 30 ml/min for 5 h and then radiometric measurements on the removable tube with the plug were made.

The results showed that during this period 5–10% of the chelate sorbed in the column was purged from the column. Thus sorbed chelate is continuously purged from the column, liberation of active centres of the bed occurring which may sorb

the chelate again on subsequent injection of a sample. This effect probably explains the "disappearance" from columns of small amounts of chelates of metals such as copper, iron and rare earths making their determination in microamounts impossible.

The question of the role of the liquid phase in the gas chromatography of chelates of metals has previously been poorly studied. In most instances silicone phases of the type SE-30, XE-60, OV-17 or OV-1 were used. In this work, the silicone SE-54 was studied, and also for comparison, the sorption of copper chelate on 5PUE polyphenyl ether, which contains hydrogen bridges in the chain. Such phases are considered to be unsuitable for the gas chromatography of chelates of metals. Experiments have shown that, when 1500 μg of copper chelate are injected into a column packed with 5PUE on Chromaton NAW (Fig. 4), the compound is completely absorbed in the column and a strongly pronounced dependence of the amount of chelate sorbed on the amount of liquid phase in the column is observed.

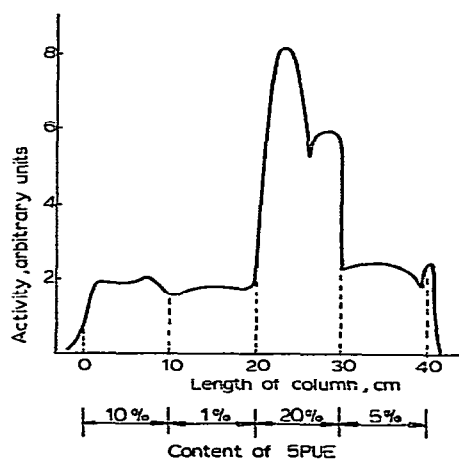


Fig. 4. Distribution of copper trifluoroacetylacetonate during sorption in a column containing 5PUE on Chromaton NAW. Temperature of column, 140°; amount of copper chelate injected into the column, 1500 μg .

REFERENCES

- 1 P. C. Uden and C. Jenkins, *Talanta*, 16 (1969) 893.
- 2 D. N. Sokolov and G. N. Nesterenko, *Zavod. Lab.*, 39 (1973) 939.
- 3 C. A. Burgett and J. S. Fritz, *J. Chromatogr.*, 77 (1973) 265.
- 4 K. Utsunomiya, *Anal. Chim. Acta*, 59 (1972) 147.
- 5 R. Belcher, W. I. Stephen, I. J. Thomson and P. C. Uden, *J. Inorg. Nucl. Chem.*, 33 (1971) 1851.
- 6 C. A. Burgett and J. S. Fritz, *Anal. Chem.*, 44 (1972) 1738.
- 7 C. A. Burgett and J. S. Fritz, *Talanta*, 20 (1973) 363.
- 8 R. Belcher, R. J. Martin, W. I. Stephen, D. E. Henderson, A. Kamalizad and P. C. Uden, *Anal. Chem.*, 45 (1973) 1197.
- 9 H. Kaweguchi, T. Sakamoto, Y. Tuji and A. Mizaike, *Bunseki Kagaku (Jap. Anal.)*, 22 (1973) 1434.
- 10 V. G. Berezkin, V. P. Pakhomov and K. I. Sakodinsky, *Solid Carriers in Gas Chromatography*, Khimia Moscow, 1975, p. 128.