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## Note

### Corrosion of stainless steel by mixtures of carbon tetrachloride and 2-propanol

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During the development of liquid chromatographic procedures in our laboratory, it was noted that mixtures of carbon tetrachloride (LC grade; Burdick and Jackson, Muskegon, Mich., U.S.A.) and 2-propanol (HPLC grade; Fisher Scientific, Fair Lawn, N.J., U.S.A.) react severely and rapidly with stainless steel. Within a 24-h period after having run a step gradient, a dark green fluid was observed in the purge lines of the liquid chromatograph. This occurred even though the system was flushed with 2-propanol at the end of each daily series of runs. Carbon tetrachloride was never left in the instrument overnight. It seemed that once the reaction was initiated, flushing was not effective in removing carbon tetrachloride from the stainless-steel surfaces. Within a few days, all of the stainless-steel flow lines that had contacted the mixed mobile phase were plugged with corrosion.

Some of the metal had a brown crust on it, and other parts had a pinkish crust which turned green when exposed to air. Since the solvents were mixed inside the mixing chamber of the liquid chromatograph, it would seem that light is not necessary for the corrosive reaction.

In order to observe these effects in a less costly manner, 1-in. lengths of 1/8-in. 316 stainless-steel rods (6.4 g) were placed in 10%, 25%, 50%, 75% solutions of carbon tetrachloride in 2-propanol, and also in 100% carbon tetrachloride. No sign of a reaction was observed in pure carbon tetrachloride after 50 days. The tubes containing the stainless-steel samples are shown in Fig. 1, at 30 days.

A noticeable green color developed in the liquid phase at 50 and 75% carbon tetrachloride in about two days. In three days a brownish crust had formed on the surface of the rods, and there was obvious gas evolution. Within five days, the liquid phase in the 75% sample separated into two phases, an upper dark green phase, and a lower yellow phase containing the dispersed crust.

The liquid phase in the 25% sample began to develop a green color in about 8 days, and the 10% sample took approximately 32 days. Once the green color began to develop the reaction took place rapidly with a crust forming in two days.

All of the samples in which corrosion was observed evolved a gas which was found to be acidic by placing moist pH test paper over the tube. The gas also gave a positive test with phosgene test paper<sup>1</sup>, indicating that it was probably HCl, since phosgene test paper gives a positive response to HCl. Phosgene would not be stable in the presence of the large amounts of alcohol.

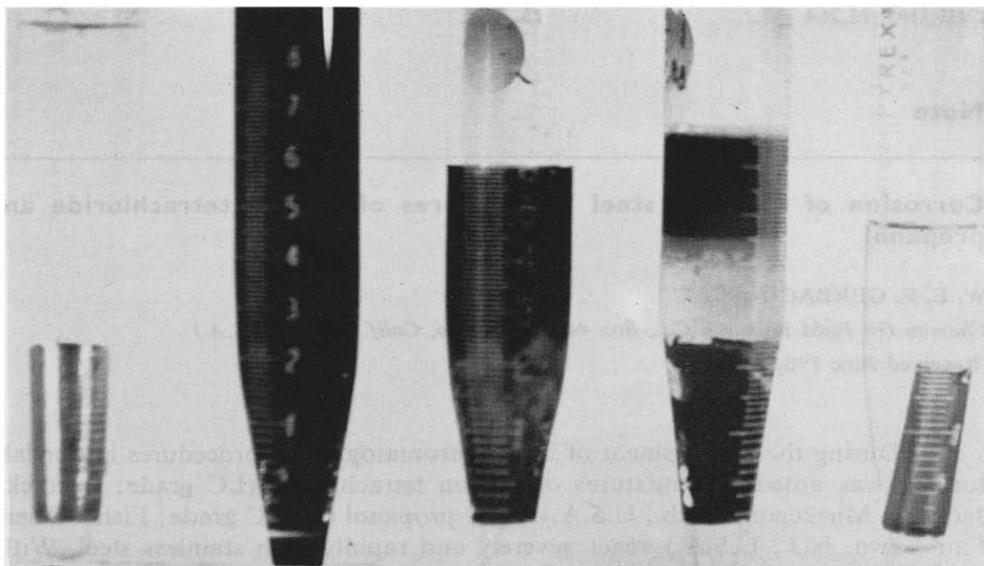


Fig. 1. 316 stainless-steel cylinders in carbon tetrachloride-2-propanol; left to right: 10%, 25%, 50%, 75%, 100% carbon tetrachloride.

The solid corrosion products were analysed by X-ray-scattering and spectroscopy. Iron(II) chloride was found to be the predominant product. The ratio of iron to other metals was essentially the same as that in the original stainless steel.

Ku and Freeman<sup>2</sup> have reported the corrosion of stainless steel by mixtures of carbon tetrachloride and acetone, tetrahydrofuran, diethyl ether, or isopropyl ether. They found that it was necessary to have carbon tetrachloride present for the reaction to occur, while the other solvents were ascribed the role of catalysts. They observed a 10% weight loss from 316 stainless-steel samples in carbon tetrachloride-tetrahydrofuran (1:1) after 10 days. While this represents a severe decrease in weight, the most drastic results were observed when two solvents were combined with carbon tetrachloride. For example, a viscous brown colored liquid was observed when 316 stainless steel was immersed in a mixture of carbon tetrachloride, diethyl ether and acetone for 10 days.

In light of our observations and those of Ku and Freeman, it would seem best to avoid using any halogenated hydrocarbon when its use would bring it into contact with stainless steel. In addition to the corrosion problem, the instability of these solvents could lead to reactions with injected samples changing their nature. These effects could give rise to spurious analytical results.

#### REFERENCES

- 1 *Merck Index*, 9th ed., Merck and Co., Rahway, N.J., 1976, p. 955.
- 2 A. Y. Ku and D. H. Freeman, *Anal. Chem.*, 49 (1977) 1637.