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Separation of NbOCl_3 from NbCl_5 in a gas chromatograph by temperature programming*

In recent years considerable interest has been shown in the chromatographic separation of metal halides. A number of separations have been reported in which various partitioning agents, ranging from hydrocarbons to fused salts, have been used¹⁻⁴. A summary of work dealing with the chromatographic separation of metals is given by JUVET AND ZADO in *Advances in Chromatography*⁵. Two principal difficulties are frequently encountered in conventional chromatographic separations of metal halides; *viz.* (1) the metal halides react with the column packing or partitioning agent, and (2) the temperatures required for elution are often sufficiently high to cause the partitioning agent to vaporize or "bleed".

While for many metal halide systems the chromatographic principle of selective sorption is essential to effect a suitable separation, there are a large number of cases where there is a sufficient vapor pressure difference that effective separation can be accomplished by simple temperature programming without using any column packing or absorbent at all. In such separations the problems of reaction with the packing or partitioning agent or vaporization of the partitioning agent are obviously eliminated. Several metal chloride systems, whose vapor pressures differ sufficiently, include SnCl_4 - BiCl_3 , VCl_4 - WCl_6 , MoCl_5 - ZrCl_4 and NbCl_5 - FeCl_3 , to name a few. In addition, the oxyhalides, *e.g.*, NbOCl_3 , which are troublesome impurities in these hygroscopic systems, often exhibit vapor pressure differences which lend themselves to such separations. The separation of NbCl_5 from NbOCl_3 is described here to illustrate the effectiveness of the temperature programming technique.

A sample of NbCl_5 and NbOCl_3 was prepared and sealed in a glass capillary under anhydrous conditions (dry box) and injected into a stream of dry helium at 290° . The carrier gas rate was 160 cc/min as determined with a soap film flowmeter. The capillary was broken inside the injection system and the vaporized sample was totally condensed a short distance downstream in a 1/4 in. O. D. glass condenser tube at room temperature. The length of the empty column was approx. 6 ft.

Separation was then achieved by temperature programming the condensed sample at the rate of $7.5^\circ/\text{min}$ from room temperature to about 230° where vaporization of both NbCl_5 and NbOCl_3 was complete. Detection was made in a standard thermal conductivity cell using a nickel filament. The resulting chromatogram, represented in Fig. 1, shows two separate responses, the first between 100 and 140° and the second between 160 and 220° and are characterized by complete return of the response to the base line between peaks. The scale magnification for the NbOCl_3 response is four times that for the NbCl_5 . The certainty of the separation was ascertained by visual inspection of the condenser zone which confirmed that the yellow NbCl_5 vaporized between 100 and 140° and white NbOCl_3 vaporized at the higher temperatures. No residue remained in the condenser after vaporization.

The vapor pressure curves for NbCl_5 and NbOCl_3 ⁶⁻⁷ are represented in Fig. 2 with the chromatogram of Fig. 1 superimposed to indicate the vapor pressures at

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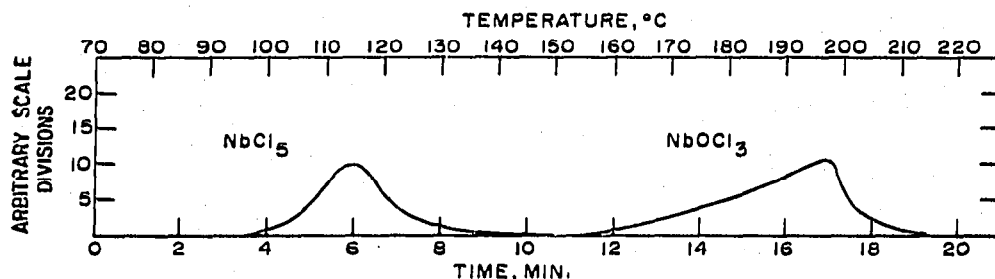


Fig. 1. Chromatogram of NbCl_5 - NbOCl_3 separation (sample estimated to contain less than 25% NbOCl_3).

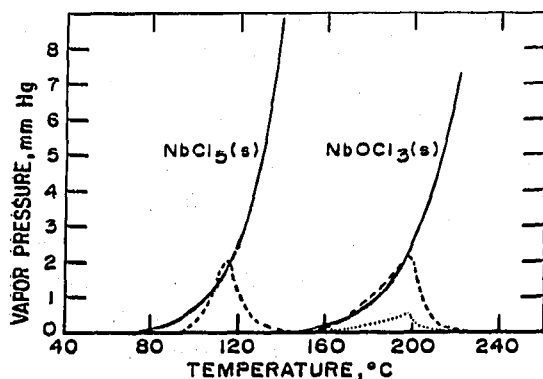


Fig. 2. NbCl_5 and NbOCl_3 vapor pressure curves. Superimposed chromatogram corrected to reflect same attenuation for both responses (dotted curve).

which "elution" occurs. The vapor pressure of NbCl_5 and NbOCl_3 , at the maximum peak heights, is approx. 1.8 and 2.1 mm Hg, respectively. Peak characteristics could no doubt be improved by the application of nonlinear temperature programming to accelerate the vaporization at the respective temperatures at which vaporization takes place.

This example illustrates that complete separation of metal halides as well as oxyhalides may be achieved by temperature programming provided there is a sufficient vapor pressure difference. Where all components to be separated do not have adequate vapor pressure differences, this technique may serve usefully as a preliminary separation or grouping of components prior to separation by more conventional chromatography.

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