Journal of Chromatography, 190 (1980) 133–135

CHROM. 12,545

Note

Analysis errors following hydrogen cleaning of an electron capture detector

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(Received November 16th, 1979)

A potential source of error in analyses by gas chromatography with electron capture detection (GC–ECD) is described here which occurs following a procedure for cleaning a ^{63}Ni ECD. This cleaning method (recommended by the manufacturer of our instrument) involves passing a mixture of carrier gas and hydrogen through the detector at high temperatures for a period of at least 0.5 h. This procedure does, indeed, clean the detector very rapidly (where the measured baseline of the ECD is taken as a measure of detector cleanliness), as compared to the time required for cleaning a contaminated detector by using carrier gas alone. However, for a significant period of time immediately following the cleaning procedure, the responses toward oxygen and several chlorinated hydrocarbons are significantly diminished.

EXPERIMENTAL

The gas chromatograph used is a Varian 3700 Aerograph with constant current operation of a ^{63}Ni detector. This instrument is described in detail elsewhere[1]. A 10 ft. × ⅛ in. stainless steel column packed with 10% SF-96 on Chromosorb W was used at an oven temperature of 30°. The flow-rate of nitrogen carrier is 30 ml/min. The detector temperature during analyses is 300°. The gaseous sample is introduced to the GC using a 2-ml volume sample loop (Carle 8030).

The hydrogen cleaning procedure is as follows. The nitrogen carrier flow is reduced to about 20 ml/min. Hydrogen gas flow of about 50 ml/min is added to the carrier flow just prior to the detector and after the column. This is done using the "make-up" gas ports supplied with our instrument. The detector temperature is set to 400°, while the hydrogen mixture flows through it for a period of one-half to a few hours.

RESULTS AND DISCUSSION

In Fig. 1 are shown several chromatograms of the same standard analyzed repeatedly before (A) and at various times after (B–H) the hydrogen cleaning treatment. In chromatogram A, three peaks are indicated. These are due to oxygen, ethyl chloride, and chloroform, where their concentrations are 15, 0.3, and 0.003 ppm, respectively, in nitrogen gas. The detector was relatively clean when chromatogram A was obtained, but to test the effect of the cleaning process, hydrogen cleaning was

then performed for 0.5 h. After re-establishing the identical conditions of chromatogram A, analyses of the same standard were then performed at the various times indicated in Fig. 1. It is seen that the oxygen and chloroform peaks do not appear at all until about 1.5 h after cleaning. These peaks then grow gradually in intensity, but after 2 h still have not yet reached their original values. The ethyl chloride peak is also strongly affected by the cleaning process, but its recovery occurs more rapidly.

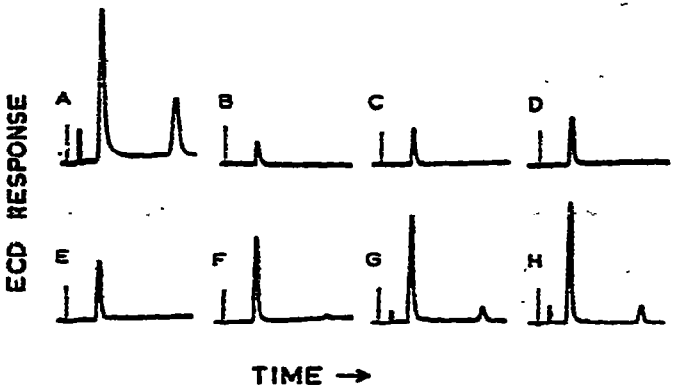

Fig. 1. GC–ECD chromatograms of a gaseous sample containing three components eluding in the order: oxygen, ethyl chloride, and chloroform. Their concentrations are 15, 0.3, and 0.003 ppm, respectively. Chromatogram A was obtained prior to hydrogen cleaning. The other chromatograms were obtained at the following times after hydrogen cleaning was stopped: B, 15; C, 30; D, 50; E, 65; F, 85; G, 105; and H, 140 min.

Two potential explanations of these observations have been considered. One is that the hydrogen cleaning procedure activates the stainless steel tubing through which the carrier gas passes enroute to the ionization region of the ECD. The compounds examined here are possibly reduced upon contact with this activated surface. Exposure to some stainless tubing is unavoidable with our instrument, because stainless tubing is an inherent part of the detector (see ref. 1). In support of this interpretation, the use of hydrogen-activated metallic surfaces has been suggested by Lovelock[2] for the intentional removal of unwanted traces of oxygen and halocarbons in carrier gas supplies.

Another possible explanation is that the suppression of response is due to some type of involvement of small amounts of hydrogen gas in the ion chemistry within the ionization region of the ECD. This latter possibility, however, has been ruled out, by our observation that the suppression of the responses shown in Fig. 1 cannot be caused by simply doping the nitrogen carrier gas with small amounts of hydrogen. The effects of hydrogen cleaning on subsequent analyses, therefore, are thought to be due to surface reactions within the transfer lines.

In order to avoid analysis errors caused by hydrogen cleaning, we have found it necessary to wait several hours following cleaning until responses of the compounds of interest stabilize at a maximum value. Alternatively, we have found that the period of waiting can be reduced greatly by passing oxygen-doped carrier gas through the detector immediately following hydrogen cleaning. In recent articles[3,4] we have reported the use of intentionally O_2-doped carrier gas for improving the ECD response

to monochlorinated hydrocarbons such as ethyl chloride. In those studies undesireable variations of response following hydrogen cleaning were not observed, presumably because the transfer line is maintained in a deactivated state by the continuous presence of oxygen. An obvious remedy for the detrimental effects of hydrogen cleaning under all conditions is the use of non-reactive materials for the transfer lines within the cell.

ACKNOWLEDGEMENT

This material is based upon work supported by the National Science Foundation under Grant No. CHE-7824515.

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