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ANALYSIS OF LIQUID SAMPLES BY CAPILLARY GAS CHROMATOGRAPHY AND HELIUM IONIZATION DETECTION

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SUMMARY

Misunderstandings and misconceptions have held back the use of the sensitive helium ionization detector, particularly for the analysis of liquid samples. Some recent work on this detector and the development of fused-silica capillary columns have led to new applications utilizing both tools.

In this report we evaluated helium ionization detector applications for the analysis of liquid samples. The water content of various solvents and reagents was determined using a split injection technique and a Carbowax fused-quartz column. We used both isothermal and temperature-programmed conditions. Concentrations as low as 2 ppm of water were detected. The system is linear up to 700 ppm although the lower detection level is dependent upon the water present in the system blank.

Other potential applications as well as the advantages and limitations of the helium ionization detector will be discussed.

INTRODUCTION

In gas chromatography (GC) today, while many areas in the field have matured, the development of ultra-sensitive universal detectors such as photoionization and helium ionization have lagged behind. To improve the sensitivity and therefore decrease the limits of detection, sample concentration techniques and derivatization methods are generally used. Recent reports on the helium ionization detector[1–3], however, indicate an expanded potential for making ultra-low-level determinations. A detection limit in the ppb range can be achieved with the helium ionization detector if the proper operating parameters are used[1–3].

Most analyses using the helium ionization detector have been performed on gaseous samples utilizing packed columns. In fact, there are only two reports on the analysis of liquid samples[1,4]. In order to expand the applications of the helium ionization detector, it has to be adapted to gas–liquid chromatographic separations of liquid samples. It was generally thought that the bleed obtained from liquid phases would prohibit use of the detector[5,6]. New developments in column technology (*i.e.*, fused-quartz capillary columns), however, have resulted in high resolution–low bleed columns that can be used with the helium ionization detector. This report illustrates

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the suitability of these columns for helium ionization detection of traces of water in liquid samples.

Traditionally, water has been analyzed by GC using packed columns and thermal conductivity detectors. The use of porous polymer materials in water analysis of liquid samples has been reported[7–9], but it has been recently shown that these polymers are the source of systematic errors[10]. Additionally, the thermal conductivity detector typically used for water analysis by GC, has a modest detection limit of only a few micrograms. Water has an ionization potential of 12.59 eV, therefore the helium ionization detector is more powerful in this respect. We recently reported the analysis of traces of water in gaseous samples[11]. In the present report the analysis of trace quantities of water in liquid samples using both the helium ionization detector and capillary columns will be described, advancing this difficult analysis well beyond current chromatographic capabilities. Other potential applications will be discussed, and the performance of the helium ionization detector will be evaluated.

EXPERIMENTAL

A Varian 3700 gas chromatograph with both capillary and packed-column injection ports was used in this work. The chromatograph was fitted with a Varian 1700 electrometer, a Varian helium ionization detector and an Ortec high-voltage power supply (Model 446). The bucking-current circuit of the electrometer was modified to measure directly the actual value of the current as previously reported[2]. The detector was operated at an applied potential of 200 V, and was maintained at 200°C. The helium carrier gas used was of ultra-high purity (99.999%) grade and was further purified over a heated converter tube (Supelco purifier, Supelco, U.S.A.).

Packed and capillary columns were used in this work. When a capillary column (WCOT) was used make-up gas was added to the detector cell using a "T" connection. The capillary end of the column was extended through the T connection to the base of the detector to minimize any dead volume, the total flow through the detector being adjusted to 28 ml/min. The capillary columns used were 30 m × 0.25 mm I.D. and 50 m × 0.25 mm I.D. fused-silica coated with Carbowax 20M (Durawax-Dx4, J & W Scientific).

The packed columns used were glass-lined stainless-steel, 2.4 m × 2.0 mm I.D., packed with Porapak Q, Super Q, Chromosorb 101, Carbosieve S, or Carbopack C with 0.2% CW 1500. All columns were conditioned for 48 h with dry helium at 175°C except for the Carbosieve S column which was conditioned at 250°C. To evaluate the column background current, the column was heated overnight at 160°C before the background current was measured. The column was then cooled to 130, 100, 50 and 20°C sequentially. The flow-rate was adjusted at each temperature, and the background current was measured after it had stabilized at each step.

For trace water analysis, a well-conditioned molecular sieve, type 4A, 8–12 mesh, was used to dry solvent from water. Only freshly opened bottles of solvent were employed and each bottle was filled up to one-third with the dry sieves. The bottle was then allowed to stand overnight prior to use. A 50-ml Wheaton serum bottle was used as a sampling container to minimize atmospheric contamination. The bottle was washed with the dry solvent, filled and then sealed with a crimper using a rubber septum. Filling the bottle minimizes the effect of atmospheric contamination.

Standards of water were prepared by transferring water to the dry solvent with a syringe through the septum cap. Adding 5 μl water to a solvent bottle (*ca.* 70 g of methylene chloride) generated a standard solution containing about 70 ppm of water. This standard was used to generate lower concentrations by further dilution into other bottles while higher concentrations were prepared by sequential additions of water into the same bottle with analysis following each addition. Each standard was mixed in an ultrasonic bath for 1 min. All sample and standard preparations were carried out in a glove box. The box was filled with dry nitrogen and a dry molecular sieve kept the box dry.

For the analysis of formaldehyde, a 37% formalin solution was used (Baker analyzed grade). This solution was further diluted with deionized water to generate lower concentrations.

The chromatographic signal was recorded at 1 mV full scale on an Omega strip chart recorder, and was integrated on a Hewlett-Packard 3390A integrator.

RESULTS AND DISCUSSION

Performance evaluation of the helium ionization detector

The helium ionization detector utilizes a metastable atomic state for the ionization of eluted substances. The complete ionization mechanism behind the helium ionization detector is not fully elucidated[12,13], however metastable helium has sufficient energy to ionize all compounds, thus making it a universal detector. The high sensitivity of this detector is recognized only for the analysis of some permanent gases. Recent work, however, indicates that the helium ionization detector can be used for the detection of a wide range of organic and inorganic compounds.

In order to obtain the usual good response from this detector, it is necessary to understand the principles behind the helium ionization detector and just as important to evaluate the performance of this detector prior to use for routine analysis.

The performance of the helium ionization detector depends on: (1) the activity of the source used; (2) the applied potential; (3) the carrier gas purity at the detector cell; (4) the cleanliness of the detector cell, and (5) the carrier gas flow-rate. In the saturation region of the detector field intensity (between 20 and 250 V applied potential), the number of metastable helium atoms available for ionization is constant, and can be affected by any impurities in the detector cell, thus increasing the detector background current. For example, atmospheric leakage, column bleed, carrier gas impurities etc. will all shorten the linear dynamic range and decrease the detection signal. The ideal background current in the saturation region is between 9 and 12 nA[1]. A good evaluation of the detector performance can be obtained from the analysis of a gas mixture containing H_2, Ar, O_2, N_2 and CH_4 (about 5 ppm each) on a molecular sieve column[2]. The polarity of the response to CH_4 is always positive. The magnitude of this response (if the detector performance is good) should be more than 0.5 mV at an attenuation of 64 (detection limit is about 5 ppb)[1]. The rest of the mixture will provide a full positive to a full negative response depending on the purity of the carrier gas at the detector cell[2,12,13].

The helium ionization detector response is best illustrated in Fig. 1, which shows the magnitude of the detector response, the polarity of this response, and the detector background current as a function of the carrier gas purity (H_2, Ar, O_2 and N_2 as impurities).

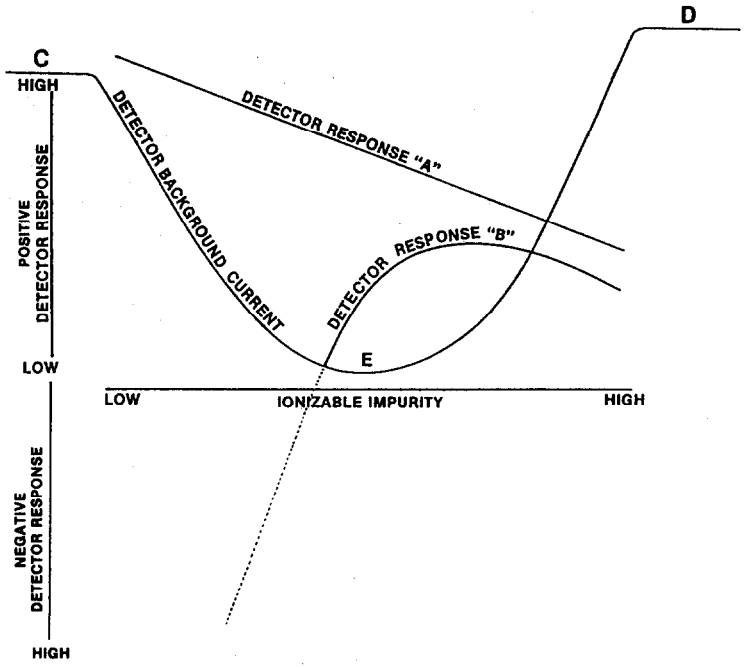

Fig. 1. The effect of the helium purity on the detector performance. Dotted line indicates negative response.

At high purity level (region C), the detector response is high to all compounds; any increase in the level of impurity will decrease detector response.

For the class of compounds that characteristically produces positive response (all compounds except Ne, H_2, Ar, O_2 and N_2), this relationship is straightforward as shown in curve "A".

For the compounds that characteristically produce negative response such as Ne, H_2, Ar, O_2 and N_2[2,12,13], the magnitude of this response will become less negative as the impurity level increases to approach the minimum background current (region E). At the minimum background current the detector response is fully inverted to positive for all these gases except for neon which remains negative. This class of compound is presented as in Fig. 1, curve A.

Fig. 1 shows that while the absolute magnitude of the detector's background is comparable for regions C and D, the detector response is higher at region C.

In general, negative response to H_2, Ar, O_2 and N_2 is a good indicator of high-purity helium at the detector cell. A high performance can be expected when other columns are substituted, provided minimum column bleed occurs.

Evaluation of columns for helium ionization detector applications

It is possible to control the purity of the helium carrier gas cleanliness of the system and the amount of atmospheric leakage, but column bleed is largely an inherent property of the chromatographic phase and the column used. It is generally understood that heating chromatographic columns will cause an amount of bleed and this can easily be detected with the helium ionization detector due to its sensi-

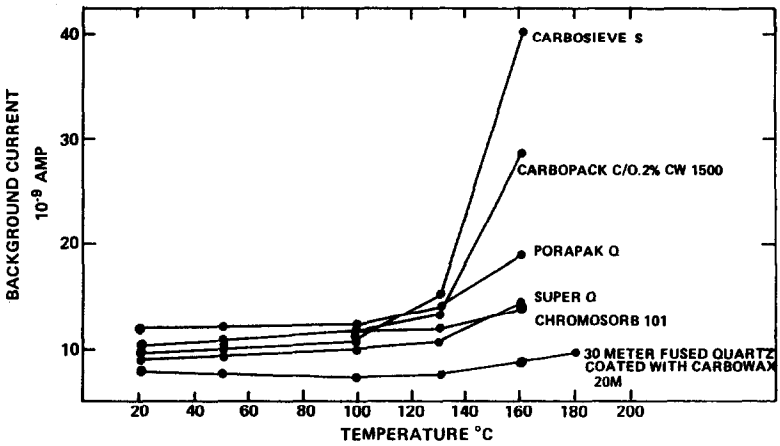

Fig. 2. Effect of column temperature on the detector background current.

tivity. But there is no data on the magnitude of this bleed for different columns and no comparative data on column bleed for capillary *versus* packed columns. The helium ionization detector has been used primarily for the analysis of gaseous samples using adsorption columns at relative low temperatures (below 80°C). The use of WCOT columns was briefly reported[3,14], but there is little information on the suitability of these columns for practical and routine analyses.

For preliminary evaluation of the chromatographic columns for helium detection applications, we chose five packed columns and one capillary column (WCOT). We were concerned only with the magnitude of detector background current at different column temperatures because ultimately the detector's background current influences the lower detection limit.

Fig. 2 shows a summary for column evaluation at the capillary column that exhibits the lowest background current from the six columns tested. In fact, the background current of the capillary column at 180°C is lower than the background current of all the packed columns at 20°C. It seems from Fig. 1 that the background current is dependent on the surface area of the column material. The surface areas for Carbosieve S, Carpoback C, Porapak Q, Super Q and Chromosorb 101 are 1000, 12, 840, 840 and 35 m^2/g, respectively. The surface area for a 30 m × 0.25 mm I.D. capillary column is 0.0118 m^2. Moreover, the amounts of liquid stationary phase in the capillary column are very small (< 10 mg). The background current for the Carbopack column is somewhat higher than expected; this is due to the presence of the liquid phase.

Other factors which will influence the magnitude of the background current include cleanliness of the packing (note the difference between Porapak Q and Super Q) and the temperature at which the column has been conditioned. It also appears from Fig. 2 that the capillary column can be used quite adequately and without significant loss in sensitivity at least up to 180°C. We did not exceed this temperature although higher temperatures are possible.

Analysis of traces of water

When a capillary column was used for sample analyses, we observed that the

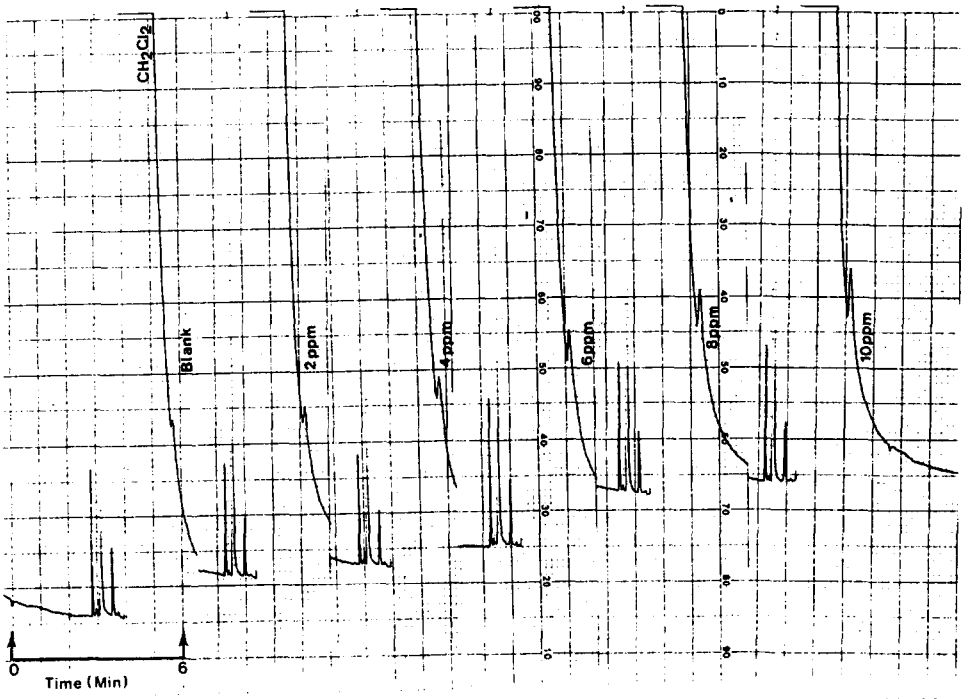

Fig. 3. Detector response to sample blank and 2, 4, 6, 8 and 10 ppm of water in methylene chloride. Column: 30 m × 0.25 mm I.D., coated with Carbowax 20M. Split ratio 385:1. Injector temperature 250°C. Sample size 1 μl. 50°C isothermal.

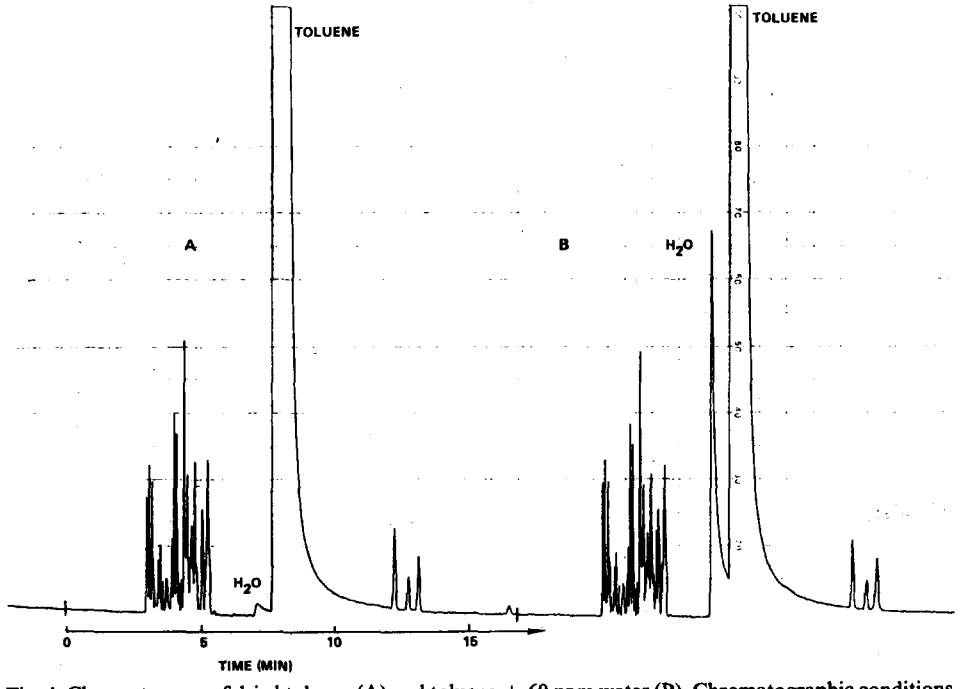

Fig. 4. Chromatogram of dried toluene (A) and toluene + 60 ppm water (B). Chromatographic conditions as in Fig. 2.

effect of split injection on the helium ionization detector response is minimal. Switching the split injection valve to the "ON" position caused a *ca.* 10% increase in the detector's background current. This increase is due to decreased column flow and minimal atmospheric leakage through the injection splitter.

In our early work water was detected in all the solvents and reagents tested. Due to the ubiquitous nature of water it is difficult to obtain a completely dry solvent or reagent. Even if a dry solvent could be found, sample transfer by syringe to the GC would cause contamination if it is carried out in the open atmosphere.

For calibration work we dried methylene chloride with an excess of well-conditioned molecular sieve. A dried syringe was injected into the septum of the solvent bottle and the syringe needle remained in the bottle at all times, except when a sample was injected into the gas chromatograph. In order to obtain a small and constant blank, the length of time the syringe was exposed to the atmosphere was standardized and kept at a minimum. Several dried methylene chloride bottles were tested for their blank values and a small water peak was usually detected. The bottle that contained the lowest blank was used for preparation of standards. The water level in the dry solvent, when analyzed, reached a constant value after a few injections. The initial injections gave a higher response due to the thermal desorption of water from the syringe needle in the hot injection port. A typical blank is shown in Fig. 3. The relative standard deviation for six blank injections was *ca.* 6%. For a 30-m Carbowax column and split ratio of 385:1, Fig. 3 shows the detector response to 2, 4, 6, 8 and

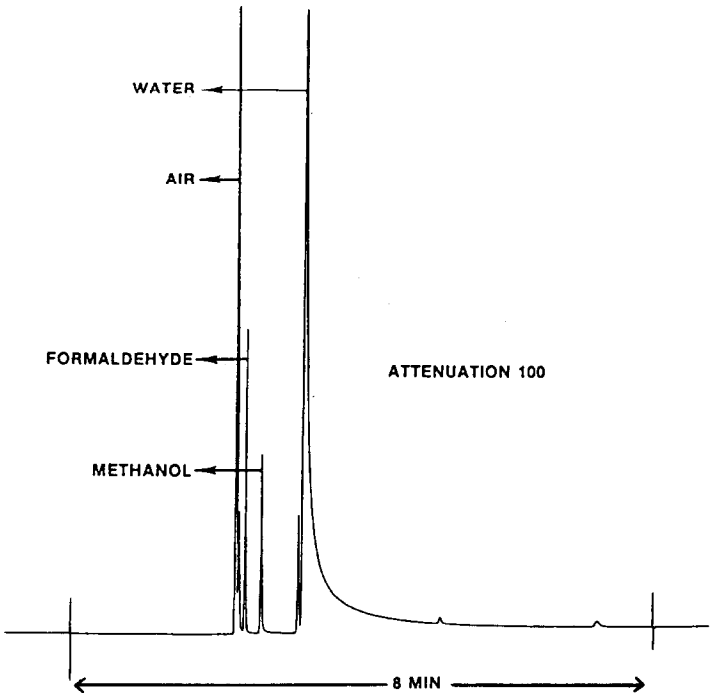

Fig. 5. Chromatogram of formalin solution vapor. Column 50 m × 0.25 mm I.D., coated with Carbowax 20M. Temperature 70°C isothermal, split ratio 110:1. Sample size 2 μl.

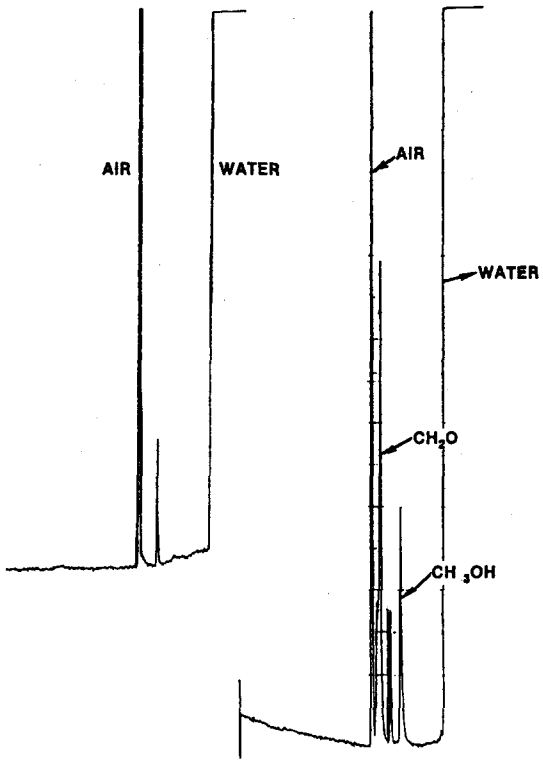

Fig. 6. Chromatogram of standard of formaldehyde in water. GC conditions as in Fig. 5. The figure to the left is for the water blank.

10 ppm of water in methylene chloride. The detector response is linear up to 700 ppm. The lowest detectable amount is highly dependent on the response of water in the sample blank rather than on the detector sensitivity.

Water content was determined in a number of solvents and reagents. Fig. 4 shows the isothermal analysis of dried toluene and toluene containing 60 ppm of water. The R.S.D. of six injections was 4.5%. When ethanol was analyzed for water, the reproducibility for six injections was 11.3%. This relatively poor reproducibility is due to atmospheric contamination. It is expected that solvents which are highly miscible with water will extract more moisture from air than non-miscible solvents. Solvents such as methanol, ethanol, acetone, etc., therefore, must be handled in a dry atmosphere.

Analysis of traces of formaldehyde

Although the helium ionization detector is a truly universal ultra-sensitive detector, it is especially important for the detection of classes of compounds that are poorly detected with other detectors. These include some inorganic and organic gases, some halocarbons, water, ammonia, formic acid and formaldehyde. We briefly investigated the detection of formaldehyde in liquid samples.

Some recent findings indicate that traces of formaldehyde are potentially toxic. This compound gives a very poor response with commonly used detectors, making

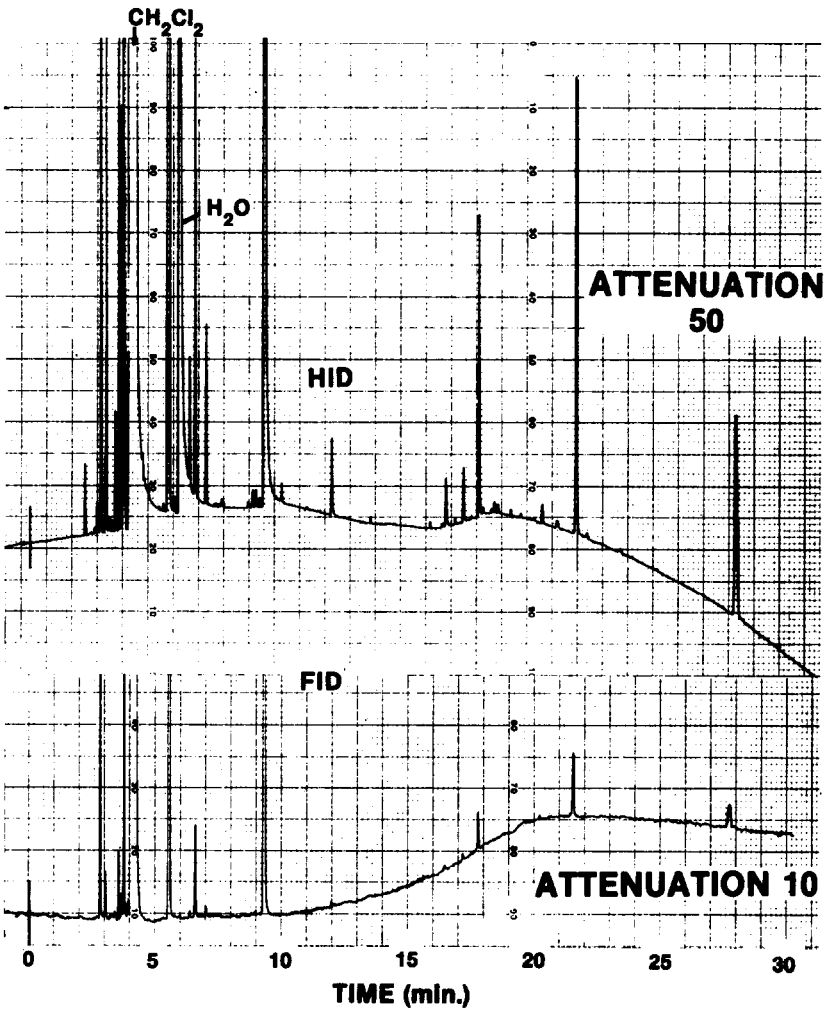

Fig. 7. Chromatograms of technical grade methylene chloride with FID and HID. Column as in Fig. 5. Split ratio 385:1. Initial temperature 50°C for 2 min, then programmed at 5°C/min to 180°C.

indirect methods of detection necessary. Presently, formaldehyde is determined using concentration and chemical derivatization by colorimetric methods, chromatographic methods, or gas chromatography combined with mass spectrometry. Concentration and derivatization techniques, however, have certain general limitations, particularly interference from other compounds present and high blank values.

In this work we evaluated the detection of formaldehyde in liquid and vapor samples using a 50-m fused-silica column and split injection technique. Fig. 5 shows the analysis of formaldehyde vapor (37%) indicating that the separation of formaldehyde from air and water is quite adequate. Fig. 5 also shows the presence of five impurities.

Fig. 6 shows the magnitude of response to 18.5 ppm formaldehyde in aqueous

samples using a split injection technique. Less than 1 ppm formaldehyde can be detected as shown from the magnitude of the response in Fig. 6.

The two applications reported in this work provide little or no response with flame ionization detection (FID). A comparison between FID and HID has been briefly reported[14,15]. During this work we analyzed a technical grade of methylene chloride with both FID and HID under the same conditions. Fig. 7 shows the response on both detectors: the helium ionization detector is about thirty to fifty times more sensitive than the flame ionization detector for the compounds that provide response with FID.

Fig. 7 shows a temperature-programmed run. This run shows an increase followed by a decrease in the baseline. This is due to: (1) column bleed which causes an increase in the column's background current; (2) removal of impurities trapped on the front end of the column, causing an increase followed by a decrease in the column's background, and (3) heating the column which causes a decrease in the column's flow resulting in an increase or decrease in the detector's background current; (4) the net results of these factors will produce the final shape of the baseline.

From the examples cited here and from the data reported on the column's evaluation for HID applications, this detector is suited for analysis of liquid samples using fused-quartz columns. One must maintain a high purity level of helium at the detector cell. This is best evaluated by analyzing a sample containing some of the gases that characteristically produce a negative response.

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