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INTEGRATION OF THE DEFORMED PEAK FROM THE HELIUM IONIZATION DETECTOR

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SUMMARY

Chromatographic analysis of permanent gases at the parts-per-million to parts-per-billion (10^9) range is possible only with the helium ionization detector. The detector response to Ne, H_2, Ar, O_2, and N_2 can be positive, negative, or bipolar, depending on the operating conditions, the purity of the carrier gas, and the concentration of the sample analyzed. However, these unusual peak shapes hinder quantitative analysis for these gases.

We have developed a software program for integration of the deformed signal from the helium ionization detector and reconstruction of a symmetrical peak. This program facilitates the use of this detector for measuring these gases. It also allows the linear dynamic range for these gases to be extended without sacrificing sensitivity.

INTRODUCTION

The helium ionization detector is often used for the analysis of permanent gases at trace levels. The detector response to these gases is positive, negative, or bipolar, depending on the operating conditions, including the purity of the carrier gas, and the concentration of the sample analyzed[1–3].

When the carrier gas is of ultra-high purity and the concentration of the sample analyzed is small (less than 100 ppm), the response to these gases is negative. Increasing the concentration of the sample above this level will produce an M-shaped peak[1]. Under normal conditions, this deformed signal could not be used for quantitative analysis.

In order to integrate samples at higher concentration, the helium carrier gas is doped with H_2, Ar, O_2, or N_2 to reach the minimum background current of the detector[2]. At the minimum background current of the detector the response to all compounds and gases is positive. However, this inversion in polarity is accompanied by a loss in sensitivity and decrease in the detector's linear dynamic range[3]. In addition, doping the carrier gas is difficult to control. It takes a long time for equilibration and doping drastically decreases the response to the added gas[3].

To avoid this problem, we looked for another method of integrating the de-~~ned~~ peak. We noticed that the change in response from negative to M-shaped peak is systematic and depends on the concentration of the sample analyzed. This observation suggested a software program for integration of the deformed peak and for plotting a normal symmetrical peak instead of the M-shaped peak.

EXPERIMENTAL

We used a Carlo Erba HRGC 5300 gas chromatograph. The chromatograph was fitted with a flame ionization detector and a helium ionization detector. The helium ionization detector was operated at 150°C and an applied potential of 400 V. The column used was stainless-steel tubing 16 ft. × 0.125 in. O.D., packed with molecular sieve 5A, 60–80 mesh. The column was conditioned at 200°C and operated at 60°C at a flow-rate of 35 ml/min. The sample was introduced via a gas sampling valve with a sample loop of 150 μl.

To generate different concentrations of gaseous samples, we used a glass exponential dilution flask (Varian). The helium used in the flask was the same as that going to the analytical column.

We interfaced the detector with an HP-3357 laboratory automation system for data acquisition. However, the software program was run on the VAX/785 computer (DEC) in batch mode. SAS/GRAPH software was also used to plot the M-shaped peak and the reconstructed peak.

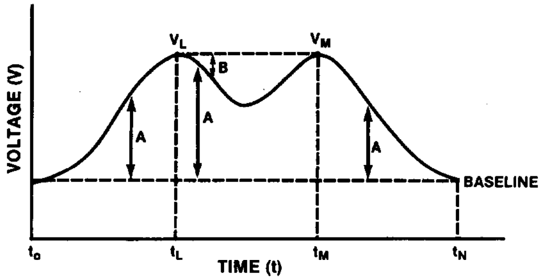

Fig. 1. A typical deformed response from a helium ionization detector. A schematic drawing for baseline correction and unfolding points. t_0 = starting time; t_L and t_M = times at the first and second unfolding points, respectively; t_N = ending time; V_L and V_M = voltages of the first and second unfolding points, respectively.

RESULTS AND DISCUSSION

A typical deformed response for the helium ionization detector is shown in Fig. 1. We wrote a computer program to unfold the middle valley and to integrate the reconstructed peak, assuming a symmetrical Gaussian peak shape. The predicted baseline estimates are based on a linear regression fit from five points at each end of the peak. After baseline correction, the method of peak integration depends on the location of the two unfolding points, (V_L, t_L) and (V_M, t_M), as shown in Fig. 1. These unfolding points are defined by a change of sign of the slope from positive to negative. The peak area is calculated from the following equation:

$$\int_{t_0}^{t_L} \mathrm{A}(t)\,\mathrm{d}t + \int_{t_L}^{t_M} [\mathrm{A}(t) + 2\mathrm{B}(t)]\,\mathrm{d}t + \int_{t_M}^{t_N} \mathrm{A}(t)\,\mathrm{d}t = \int_{t_0}^{t_N} \mathrm{A}(t)\,\mathrm{d}t + 2\int_{t_L}^{t_M} \mathrm{B}(t)\,\mathrm{d}t$$

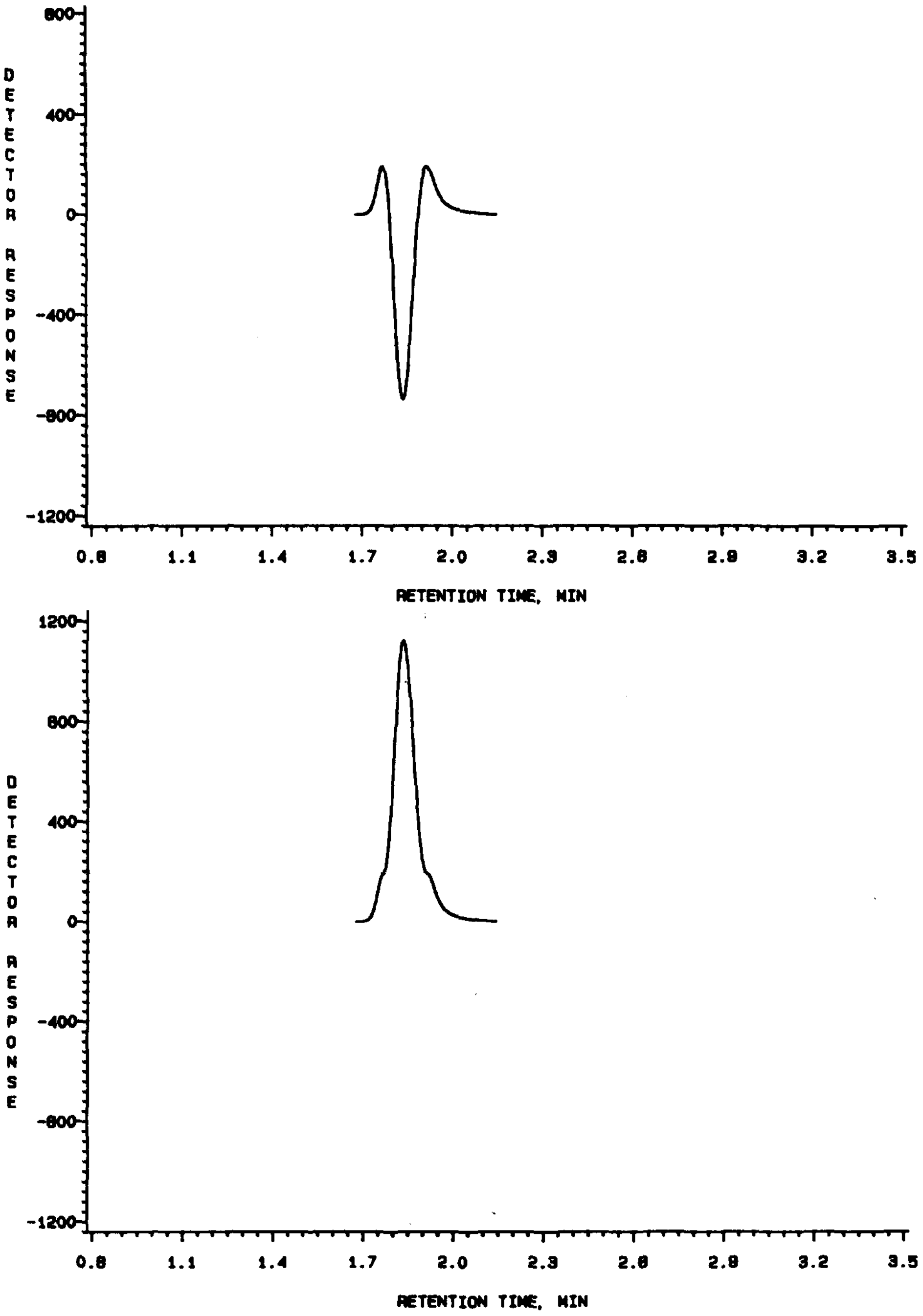

Fig. 2. Deformed detector response to 195 ppm hydrogen (bottom) and reconstructed symmetrical peak (top).

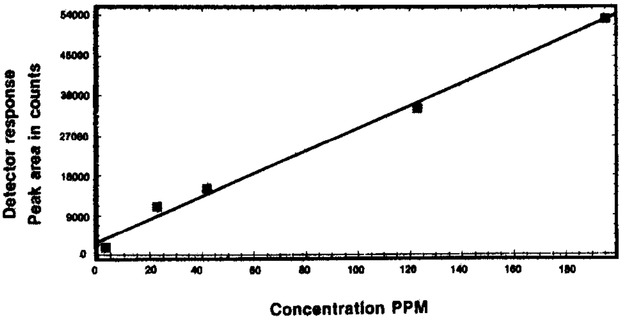

Fig. 3. Hydrogen calibration curve for symmetrical negative and deformed reconstructed peaks.

The total peak area is a sum of area A and twice area B (see Fig. 1).

Fig. 2 shows the M-shaped peak and the reconstructed peak for 195 ppm hydrogen. The inflection points on the reconstructed peak are not very smooth. Fig. 3 shows a calibration curve for hydrogen for symmetrically negative peaks up to 43 ppm and for M-shaped peaks at higher concentrations. The response is linear in the range tested. The irregularity of the inflection points did not seem to effect the linearity. However, if under certain operating conditions, the calibration curve slightly deviates from linearity, the program should be modified to take this into account.

The following is a simple program, written in FORTRAN, for integration of the deformed peak. This program solves some of the problems associated with this sensitive detector. Adjustment of the carrier gas purity to obtain a positive response to these gases is no longer needed. This facilitates the use of this detector and increases the linear dynamic range of the detector for these gases. The program was run on the VAX/785 computer, but it can be converted to run on any other scientific computer.

Integrating program

```
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(400),Y(400),X1(400),Y1(400),NAME(40),X2(10),Y2(10),
     1DYB(2),DXB(2)
100   READ(1,1,END=999) NAME
1     FORMAT(40A2)
      WRITE(5,2) NAME
2     FORMAT(1H1,5X,40A2)
      GO TO 3
999   STOP 'MA966 PROGRAM COMPLETE'
3     CONTINUE
      READ(1,4) TIME,TSN,BS,ES,DB,DE
4     FORMAT(6F)
C     TIME=ACTUAL RUN TIME  TSN=TOTAL SLICE #  BS=START SLICE # OF PEAK
C     ES=END SLICE # OF PEAK  DB=START SLICE # OF DEFORMED PEAK
C     DE=END SLICE # OF DEFORMED PEAK  SCALE=SCALE FACTOR IN FRACTION
      FN=ES-BS+1.0
      N=FN
      READ(1,5) (Y(J),J=1,N)
5     FORMAT(5F)
      ND=2
      N11=N/4
      N21=N-N11
      IF(DB+DE) 6,7,6
```

```
6     ND=1
7     CONTINUE
C     ND=1  DEFORMED PEAK  ND=2 NORMAL PEAK(UNDEFORMED)
      X(1)=BS
      DO 8 I=2,N
8     X(I)=X(I-1)+1.0
      RATIO=TIME/TSN
      DO 9 J=1,N
9     X1(J)=X(J)*RATIO
      GO TO (21,22) ND
21    X2(1)=DB
      X2(2)=DE
      N1=DB-BS+1
      N2=DE-BS+1
      Y2(1)=Y(N1)
      Y2(2)=Y(N2)
      N11=N1+1
      N21=N2-1
      DO 23 I=1,N1
23    Y1(I)=Y(I)
      DO 24 I=N11,N21
      PEAK=Y2(1)+((X(I)-X2(1))*(Y2(2)-Y2(1)))/(X2(2)-X2(1))
      Y1(I)=Y(I)+2.0*(PEAK-Y(I))
24    CONTINUE
      DO 25 I=N2,N
25    Y1(I)=Y(I)
      WRITE(5,101)
101   FORMAT(/5X,'Y1 VECTOR')
      WRITE(5,102) (Y1(J),J=1,N)
102   FORMAT(10X,5F15.5)
      WRITE(5,103)
103   FORMAT(/5X,'X1 VECTOR')
      WRITE(5,102) (X1(J),J=1,N)
      GO TO 26
22    DO 27 I=1,N
27    Y1(I)=Y(I)

26    CONTINUE
      DO 10 J=1,5
      Y2(J)=Y(J)
10    X2(J)=X1(J)
      NN=N-5+1
      DO 11 J=6,10
      X2(J)=X1(NN)
      Y2(J)=Y(NN)
11    NN=NN+1
      WRITE(5,104)
104   FORMAT(//5X,'BASELINE DATA',/10X,'X',20X,'Y')
      DO 105 II=1,10
      WRITE(5,106) X2(II),Y2(II)
106   FORMAT(2X,2E20.8)
105   CONTINUE
      XBAR=0.0
      YBAR=0.0
      DO 12 J=1,10
      XBAR=XBAR+X2(J)
12    YBAR=YBAR+Y2(J)
      XBAR=XBAR/10.0
      YBAR=YBAR/10.0
      SUMX=0.0
      SUMY=0.0
      SUMXY=0.0
      DO 13 J=1,10
      SUMX=SUMX+(X2(J)-XBAR)**2
      SUMY=SUMY+(Y2(J)-YBAR)**2
```

```
13    SUMXY=SUMXY+(X2(J)-XBAR)*(Y2(J)-YBAR)
      B1=SUMXY/SUMX
      B0=YBAR-B1*XBAR
      WRITE(5,107) B0,B1
107   FORMAT(/5X,'EST. COEFF. OF BASELINE  B0=',E20.8,4X,'B1=',E20.8)
C     ADJUSTMENT OF BASELINE FOR DATA
      DO 14 J=1,N
      Y(J)=Y(J)-(B0+B1*X1(J))
14    Y1(J)=Y1(J)-(B0+B1*X1(J))
      WRITE(5,108)
108   FORMAT(/5X,'Y1 VECTOR AFTER BASELINE CORRECTION')
      WRITE(5,102)  (Y1(J),J=1,N)
C     COMPUTES PEAK AREA
      AREA=0.0
      DO 31 J=1,N
31    AREA=AREA+Y1(J)
      AREA=0.25*AREA
C     COMPUTES PEAK R.T.
      DO 32 I=N11,N21
      IF(Y1(I)-Y1(I-1)) 33,32,32
32    CONTINUE
33    RT=X1(I-1)
      WRITE(5,35)
35    FORMAT(////)
      WRITE(5,34) RT,AREA
34    FORMAT(5X,'PEAK R.T.(MIN.)=',F10.6,/5X,'PEAK AREA(UV-SEC)=',F15.6)
      DO 41 K=1,N
      Y(K)=0.25*Y(K)
      Y1(K)=0.25*Y1(K)
      WRITE(15,42) X1(K),Y(K),Y1(K)
42    FORMAT(F12.4,2(1X,F12.4))
41    CONTINUE
      GO TO 100
      END
```

Plotting program

```
DATA RUN1;
INFILE FOR015;
INPUT X1 Y1 Y2;
RUN;
GOPTION HSIZE=10.0 VSIZE=8.0;
PROC GPLOT;
TITLE H=1.5 F=DUPLEX C=GREEN 'HELIUM IONIZATION DETECTOR';
TITLE2 'SAMPLE NO :  SPL LSAV 18';
PLOT Y1*X1 Y2*X1 / OVERLAY HAXIS=1.7 TO 2.06 BY 0.04 VAXIS=0 TO 245 BY 35;
SYMBOL1 I=JOIN C=RED;
SYMBOL2 I=JOIN C=BLUE;
LABEL Y1='DETECTOR RESPONSE';
LABEL Y2='DETECTOR RESPONSE';
LABEL X1='RETENTION TIME, MIN.';
RUN;
ENDSAS;
```

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