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The application of repeated wide-range zero shifting in gas chromatography*

Gas chromatography has repeatedly proved to be a powerful tool in trace analysis¹. Trace constituents that are present in some mixtures, however, frequently exhibit a retention behavior similar to that of the matrix component of these products. This problem is frequently encountered in the analysis of flavors, solvents and impurities in monomers.

Even when the retention time of a trace constituent is 30 % longer than that of the matrix component, its peak appears only on the shoulder of the matrix component peak; under high-sensitivity conditions, the shoulder extends over many times the full-scale range of the recorder. Under such conditions most of the shoulder of the matrix-component peak remains unrevealed in the "off-scale" portion. As a consequence trace constituents appearing on the shoulder of the "off-scale" portion of the matrix peak remain undetected. If the sample size or the sensitivity of the detection system is decreased so that a greater portion of the matrix peak appears on the chart, the detection of the trace peaks will again not be possible: the size of these trace peaks also decreases, and they frequently become smaller than the minimum needed for detection. The problem of detecting trace constituents appearing on the shoulders of large gas chromatographic peaks was solved by use of a method which can be called "wide-range zero shifting". A high-sensitivity flame-ionization system consisting of a Keithley 410 electrometer and a modified flame-ionization detector² was used. The electrometer was operated at the 3×10^{-10} A range; only about 1 % of the output was fed to a 1-mV Honeywell recorder.

The zero shifting method involves the following procedure: slightly after the matrix peak reaches "off-scale", the baseline position is shifted from + 0.1 mV (which is the original position of the baseline) to about -10 mV. This shift brings into the range of the 1-mV recorder the range which without the shift would be ten times "off-scale". A 1-mV portion of the matrix peak shoulder is then recorded. The baseline position is immediately shifted to -9 mV, and the portion of the peak which without the shift would be nine times "off-scale" is then recorded. This procedure is repeated until the baseline reaches its original position.

Samples of alcoholic beverages in which ethanol is the matrix component were analyzed by gas chromatography, with the zero shifting method. A typical chromatogram is shown in Fig. 1. Peaks 11, 12, and 13 remained in the "off-scale" of the chromatogram when the sample was run without zero shifting. A large peak (No. 10) remained undetected even with zero shifting, because its retention time was too close to that of ethanol. When the sensitivity of the system was decreased 10 times so that the greater portion of the matrix peak shoulder was recorded on the chart, peaks 11, 12, and 13 remained undetected in most of the samples. In later experiments application of a Keithley model 261 picoampère source proved to be superior for wide-range zero shifting to the zero shifting achieved through the use of the original zero control knob of the electrometer. The suppression currents are delivered by the picoampère source

* Part of this work was carried out at the Department of Plant Science, University of Manitoba, Canada.

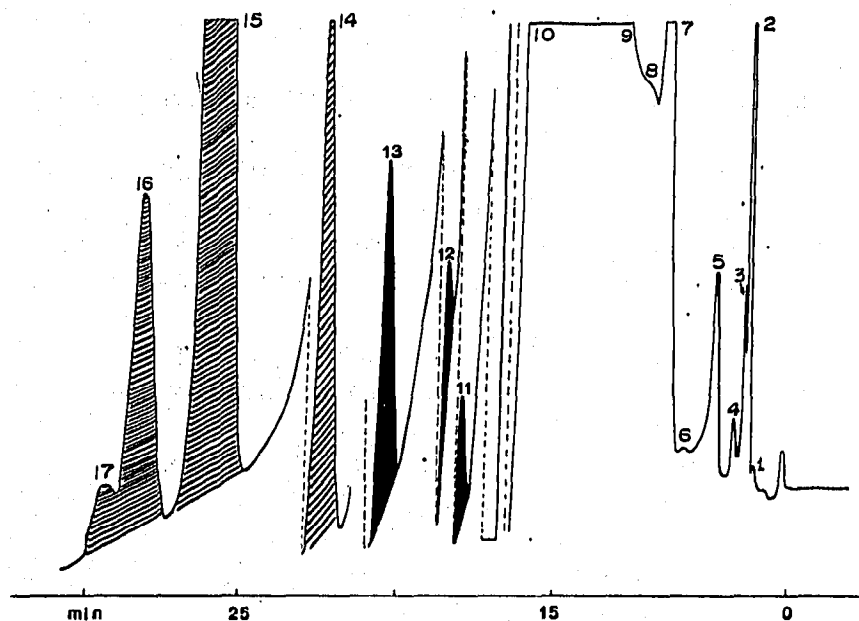


Fig. 1. Chromatogram of an alcoholic beverage which reveals trace flavor constituents on the shoulder of the ethanol peak by high sensitivity and repeated zero shifting.

in a stepwise mode; in turn, this permits reproducible shifting of the zero position to be achieved by switching rather than by rotation.

The zero shifting procedure permits the detection of trace constituents by exposing on the recorder chart a greater portion of the matrix peak. It was successfully applied in the analysis of trace flavor constituents in alcoholic beverages.

Midwest Research Institute, Kansas City, Mo. 64110 (U.S.A.)

RAM L. LEVY

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