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Short communication

Gas-phase electron diffraction as a detection method in capillary gas chromatography

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Abstract

The effectiveness of gas-phase electron diffraction as a method of detecting and identifying isomers in capillary gas chromatography has been examined. Illustrative results for solutions of *ortho*- and *meta*-dichlorobenzene are presented. The sensitivity and dynamic range of this technique were tested under the nonoptimal experimental constraints imposed by the existing diffraction camera. Methods to improve sensitivity of detection to perhaps 100 pg or better are discussed. © 1998 Elsevier Science B.V.

Keywords: Electron diffraction detection; Detection, GC; Dichlorobenzenes

1. Introduction

Since the pioneering work of Golay [1,2], capillary gas chromatography (cGC) has been developed into a high-resolution chemical separation method with distinct advantages over gas chromatography (GC) using columns packed with fine particles. Among the detectors applied so far, mass spectrometry (MS) and Fourier transform infrared (FTIR) have proven to be the most effective in identifying GC effluents. Because of its high sensitivity and universal detectability, MS is particularly widely used. Its inability to distinguish between isomers is a drawback in some applications, however.

Several years ago electron diffraction was demonstrated to be able to discriminate between isomers in the effluent of GC columns [3]. It is the purpose of the present research to determine the effectiveness of electron diffraction as a detection method in separations of isomers carried out in capillary chromatographic columns.

2. Experimental

In all but a small fraction of investigations of gases by electron diffraction, the patterns of diffracted electrons have been recorded upon photographic plates. Such a time-consuming method would be useless in chromatography. Therefore the development of direct recording in real-time on photodiode arrays (PDAs) by Ewbank et al. [3] made it worthwhile to explore the feasibility of carrying out cGC separations with electron diffraction detection. In the present investigation a gas electron diffraction unit described elsewhere [4] was modified as illustrated schematically in Fig. 1. The original photographic camera was replaced by a digital recording unit consisting of an aluminized P20 phosphor screen and photodiode array (Princeton

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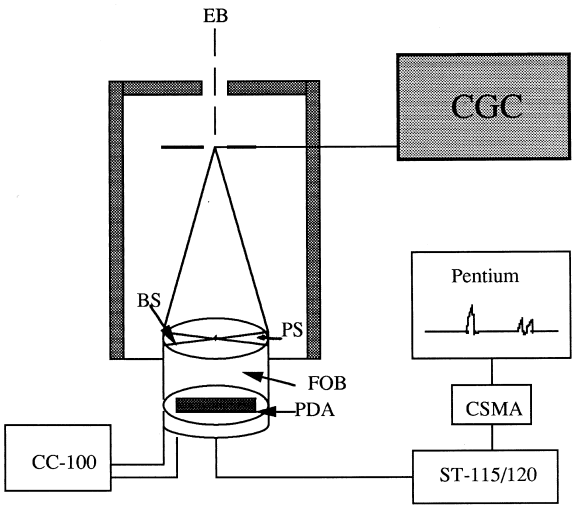

Fig. 1. Schematic diagram of capillary gas chromatography apparatus (cGC) with an electron diffraction detector. EB, 40-kV electron beam; PS, phosphor screen; BS, butterfly slit; FOB, fiberoptic bundle; PDA, photodiode array.

Instruments). Diffracted 40-kV electrons striking the phosphor each induces the emission of hundreds of photons which are led by a fiber-optic bundle through an optical couplant (Dow Corning Q2-3067) to the photodiode array. The array has 1024 elements, each with an area of 25×2500 μm, and is cooled thermoelectrically to ca. −40°C to reduce noise. Before diffracted electrons reach the phosphor they are masked by a 'butterfly slit' (opening proportional to the square of the radius of the electron pattern). This masking avoids saturating the inner diodes while counts are accumulated in the more weakly illuminated outer diodes. Undiffracted electrons are stopped by a graphite beam trap. In experiments to be described, the electrons intersected the effluent gas from the cGC system 9.5 cm above the phosphor, allowing diffraction patterns to be recorded out to about $s=9$ Å^{-1}, or 0.72 Å^{-1} in the scattering variable $\sin\theta/\lambda$.

Experiments were carried out with a Hewlett-Packard 5790 Series GC system with a capillary column, 30 m×250 μm I.D. This capillary was inserted directly into the electron diffraction chamber about 0.5 mm from the electron beam after its end was covered by a grounded aluminum tube 0.02 in. I.D. to prevent the build-up of charge on the glass column (1 in.=2.54 cm).

The interface between the PDA and a Pentium computer to process the data was achieved through an ST-115/120 controller using CSMA software from Princeton Instruments. Minimum readout times for individual diodes are 5 μs, and a readout of the 1024 elements can be achieved in a little over 5 ms. For longer integration times the array was scanned once, then allowed to accumulate light from the phosphor for the remainder of the exposure period.

In the present experiments, the systems selected consisted of solutions of isomers of dichlorobenzene (1,2-dichlorobenzene, ODCB, and 1,3-dichlorobenzene, MDCB) in the solvent acetone. To test sensitivity and dynamic range, a series of solutions was prepared with ODCB to acetone volume ratios of 1.0, 0.1, 0.01, and 0.001. Helium maintained at a pressure of 1.3 bar served as the carrier gas. The column and injector temperatures were set at 120 and 180°C, respectively, for the tests of sensitivity and dynamic range. For experiments to identify isomers an optimized temperature program was used to separate the isomers from the solvent and from each other. It started with a column temperature of 80°C for 1 min, followed by a heating rate of 5°C/min to a maximum of 120°C. For comparison, a cGC–MS analysis was carried out on an acetone solution of 10% ODCB and 8% MDCB in a Finnigan cGC–MS instrument imposing a similar programming of temperature.

3. Results

The chromatograms from three different concentrations of ODCB are plotted in Fig. 2. For the present operating conditions the dynamic range to ODCB is about 10^4, and the detection limit ca. 1.3 μg. If it is desired to distinguish between structures under the present operating conditions it is helpful if the concentrations of the analytes in 1 μl of solution are at least 5%. Fig. 3 illustrates the appearance of a chromatogram from an acetone solution with concentrations of 10% in both ODCB and MDCB. The first peak corresponds to acetone and the next two, to the dichlorobenzenes. A search of the GC–MS literature did not indicate which isomer should elute

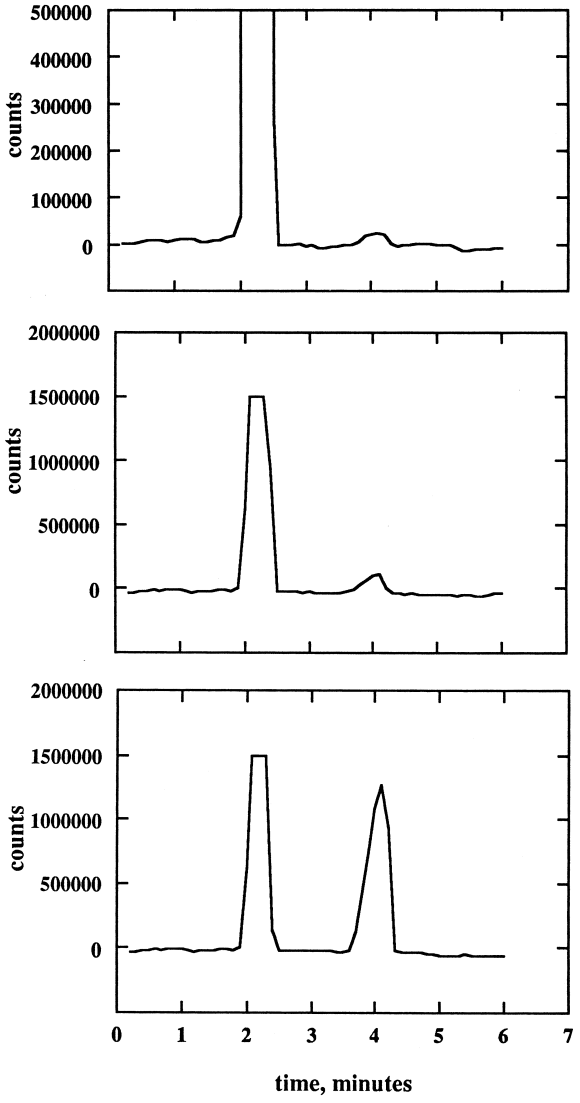

Fig. 2. Chromatograms of solutions of 1,2-dichlorobenzene (ODCB) in 1 μl of acetone. ODCB/acetone ratios, by volume: top, 0.001; middle, 0.01; bottom, 0.1. Electron diffraction detection.

first. On the other hand, the electron diffraction patterns from the second and third peaks (Fig. 4) and, more intuitively, the radial distribution curves (Figs. 5 and 6) clearly reveal which isomer is associated with which peak. The Cl–Cl interatomic distances show that MDCB is the first effluent after the solvent.

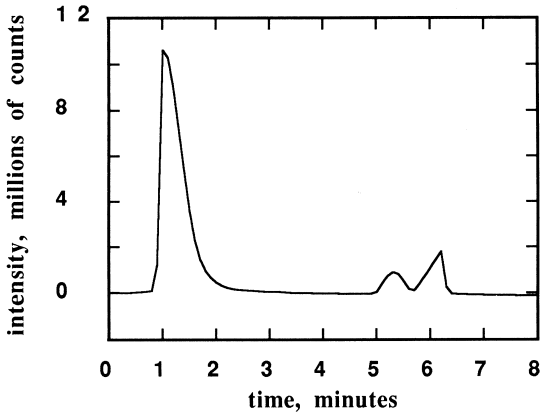

Fig. 3. Chromatogram of 1 μl of acetone solution 10% in both 1,2-dichlorobenzene, and 1,3-dichlorobenzene. Electron diffraction detection.

4. Discussion

Results of this preliminary investigation show that electron diffraction is at least as applicable to cGC as to GC, and that it can distinguish between isomers, particularly when the structures differ in the positions of heavy atoms. In structural chemistry, gas-phase electron diffraction has a long history of determining relative concentrations of isomers and conformers in a mixture, recent examples including Refs. [5–7]. Alternative detection schemes capable of discriminating between isomers in GC include various spectroscopic methods. As mentioned above, IR detectors have been used for many years. Recently the use of UV spectrometers has been described [8].

Amounts of material detected in the present cGC–electron diffraction investigation were for the most part substantially smaller than those in the GC–electron diffraction study of Ref. [3]. Although the detection limit for ODCB of 1.3 μg obtained in the present preliminary exploration is not particularly impressive, it was obtained under conditions very far from optimal inasmuch as the present diffraction unit was designed for entirely different purposes. In the following we will discuss how a substantial increase in sensitivity by electron diffraction can be obtained. One consequence of the comparatively low sensitivity in the present investigation is the conspicuously

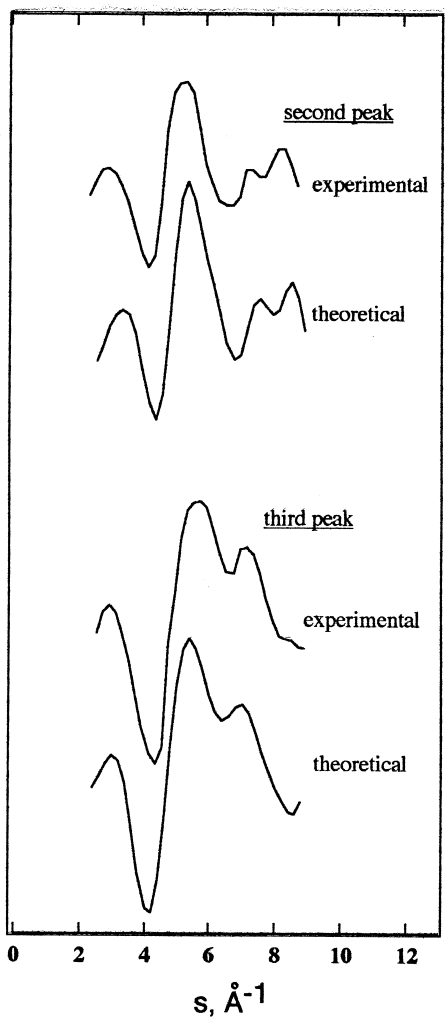

Fig. 4. Electron diffraction intensity curves of cGC effluents recorded during the run of Fig. 3.

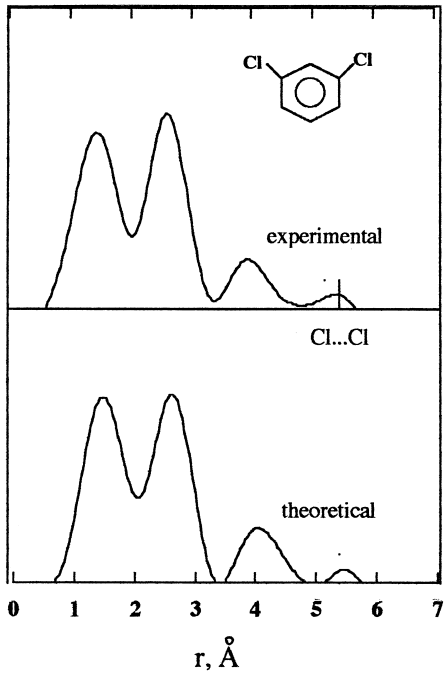

Fig. 5. Radial distribution curves of the effluent corresponding to peak 2 of Fig. 3. Top, calculated from the experimental intensity curve of Fig. 4; bottom, calculated from the theoretical intensity curve.

broad peaks in Figs. 2 and 3 resulting from an overloaded column. A possible additional contributing factor may be the unheated part of the transfer line into the diffractometer where the temperature falls substantially below the boiling point of the samples. A heated transfer line would pose no particular difficulty in the design of a unit to be devoted to analytical chemistry.

Steps to increase the sensitivity would include the following. A stronger electron beam current would amplify the signal in proportion to the current. The beam current of only 0.2 μA used in the illustrated experiments was over two orders of magnitude weaker than that used in the GC–electron diffraction research. Although it would be trivial to raise the current correspondingly in the present diffraction unit, our beam at that current is insufficiently stable for the present purposes. A redesign could remedy the flaw. The current PDA detector intercepts only about 6% of the circularly symmetric diffraction pattern. Replacing that detector by a charge-coupled device (CCD) which would accept the entire circumference of the circularly symmetric gas diffraction patterns, and which would give a considerably higher signal-to-noise ratio per pixel, would also add an additional several orders of magnitude increase in sensitivity. Still further improvements could be obtained with a more efficient beam trap (to reduce the background noise) and a modified tip of the column to direct the effluent gas into the probing electron beam. In comparison with the present diffraction unit which was constructed to maintain a vacuum during the injection of an intense supersonic jet, an electron

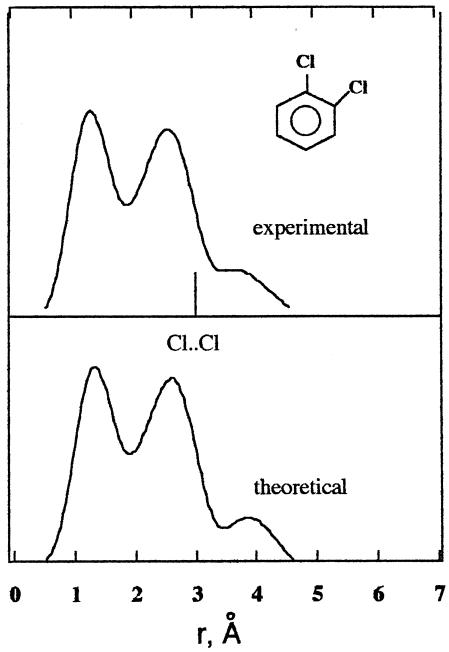

Fig. 6. Radial distribution curves of the effluent corresponding to peak 3 of Fig. 3 Top, calculated from the experimental intensity curve of Fig. 4; bottom, calculated from the theoretical curve.

diffraction unit designed expressly for application in cGC analyses would be relatively simple to construct in view of the very modest pumping demands imposed by the gas flow through the capillary. The vacuum requirements for gas-phase electron diffraction are roughly two orders of magnitude less stringent than for mass spectrometry. Under optimized conditions, such a unit could probably achieve a sensitivity better than, and possibly appreciably better than, 100 pg of analyte and would yield considerably narrow peak widths.

Acknowledgements

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