

CHROM. 8746

PLASMA CHROMATOGRAPHY OF HEROIN AND COCAINE WITH MASS-IDENTIFIED MOBILITY SPECTRA

F. W. KARASEK*, H. H. HILL, Jr. and S. H. KIM

Department of Chemistry, University of Waterloo, Waterloo, Ontario (Canada)

(Received September 16th, 1975)

SUMMARY

Plasma chromatography detects and identifies compounds in trace quantities at atmospheric pressure through characteristic positive and negative mobility spectra. To facilitate use of the technique to detect gas chromatographic effluents, a number of reference mobility spectra for different classes of compounds have been reported. Reference spectra for two more compounds, heroin and cocaine, are presented in this study. The primary ions found in these mobility spectra were determined to be M^+ , $(M - H_2)^+$, and $(M - CH_3CO_2)^+$ for heroin and M^+ , $(M - C_6H_5CO_2)^+$ and $(M - C_6H_5CO_2 - CO_2CH_3)^+$ for cocaine using a directly interfaced plasma chromatograph-mass spectrometer. The identified ions agree closely with those predicted in the ion mobility spectra using mass-mobility correlation data coupled with chemical ionization mass spectrometry data. Also, an independent check demonstrating the reliability of reduced mobility values reported in earlier reference spectra was made.

INTRODUCTION

Plasma chromatography is an identification technique in which samples in nitrogen or air are ionized in an ion molecule reactor containing a radioactive (^{63}Ni) source. The ions formed are then separated with respect to their mobilities via a drift tube at atmospheric pressure. Their detection after separation produces an ion mobility spectrum *i.e.*, a plot of ionic intensity with respect to drift time. Both positive and negative ion mobility spectra characteristic of a given compound can be obtained. A complete description of the plasma chromatographic technique can be found in a recent review and its references¹.

Plasma chromatography is an extremely sensitive method, capable of detecting and identifying compounds at trace levels. It shows promise as a method for qualitative and quantitative trace analysis of organic compounds, particularly when employed to detect gas chromatographic (GC) effluents. To be useful as a qualitative detector it is necessary to have available a large number of reference mobility spectra as well as a knowledge of the general type of spectra produced by different classes of com-

* Author to whom correspondence should be addressed.

pounds. These reference spectra can be used for "fingerprint" identification of the compounds detected. A number of mobility spectra have been reported previously as part of a general study of the applicability of the plasma chromatographic technique to detection of GC effluents²⁻¹³. While the mobility spectral patterns alone can be used for identification, identity of ionic peaks observed has been postulated based on an approximate mobility-mass relationship, and an apparent relationship of positive mobility spectra to chemical ionization mass spectra¹. In the present study reference spectra for heroin (diacetylmorphine) and cocaine (2 β -carbomethoxy-3 β -benzoxotropane) were obtained with both a simple plasma chromatograph (Beta/VI), and also with another plasma chromatograph directly coupled to a mass spectrometer, (Alpha/II), giving positive identification of the ions associated with each peak in the mobility spectra.

The purpose of this paper is not only to present the mobility spectra of heroin and cocaine, but to identify by using mass-identified mobility spectra the primary ions associated with mobility peaks in each spectrum. Also by obtaining the spectra on different instruments under different conditions an independent check on the accuracy of previously reported reduced mobility data (K_0) was provided.

EXPERIMENTAL

The heroin and cocaine samples were procured from Marsland Engineering (Waterloo, Ontario, Canada) for feasibility studies on their detection and identification by plasma chromatography. Mobility spectra were obtained for each compound separately. Each compound (10 mg) was dissolved in 10 ml of methanol and 1 μ l of this solution was allowed to evaporate on to the tip of a platinum wire. This wire was then inserted into the injection port of a Beta/VI plasma chromatograph (Franklin GNO, West Palm Beach, Fla., U.S.A.) and the ion mobility spectra recorded (Fig. 1). The experimental conditions for these mobility spectra were as follows: 350 ml/min of nitrogen drift gas; 40 ml/min of nitrogen carrier gas; gate widths of 0.2 msec; an electric field gradient of 250 V/cm for cocaine and 214 V/cm for heroin; a drift tube and injection port temperature of 153°C for cocaine and 200°C for heroin; and pressures of 730 and 736 torr for cocaine and heroin, respectively. The drift length of the Beta/VI plasma chromatograph is 6 cm.

Mass spectral (Figs. 2 and 3), total ion mobility spectral (Figs. 4 and 5), and mass-identified ion mobility spectral (Figs. 4 and 5) data were collected using an Alpha/II plasma chromatograph-mass spectrometer (Franklin GNO). The Alpha/II instrument consists of a Beta/VII plasma chromatograph coupled directly to a specially modified Extranuclear Labs. quadrupole mass spectrometer. The mass spectral data were obtained by holding the drift tube gates open, allowing all the ions formed in the plasma chromatograph to continuously drift down the tube and into the quadrupole mass spectrometer. The mass spectrometer was then scanned to determine the m/e values of the ions present. Total ion mobility spectra were obtained by operating the plasma chromatograph's gates in the normal fashion and monitoring the drift times of the ions with the total ion monitor of the mass spectrometer (only ions with masses greater than 100 were monitored). Finally, mass-identified ion mobility spectra were obtained by operating the plasma chromatograph with normal gating but tuning the mass spectrometer to respond only to those ions having a specific m/e .

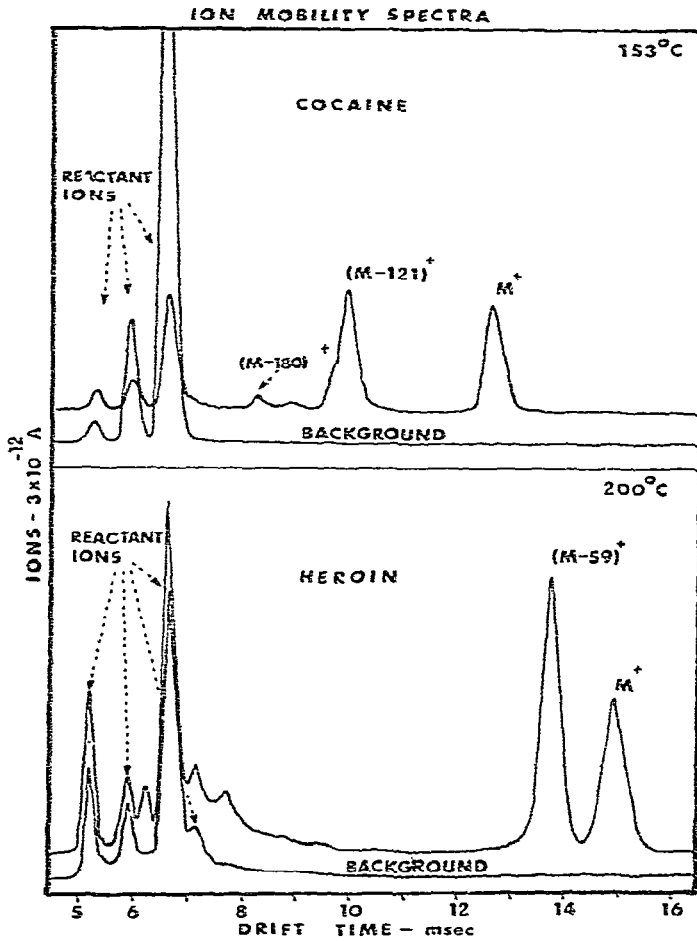


Fig. 1. Beta/VI ion mobility spectra of cocaine and heroin.

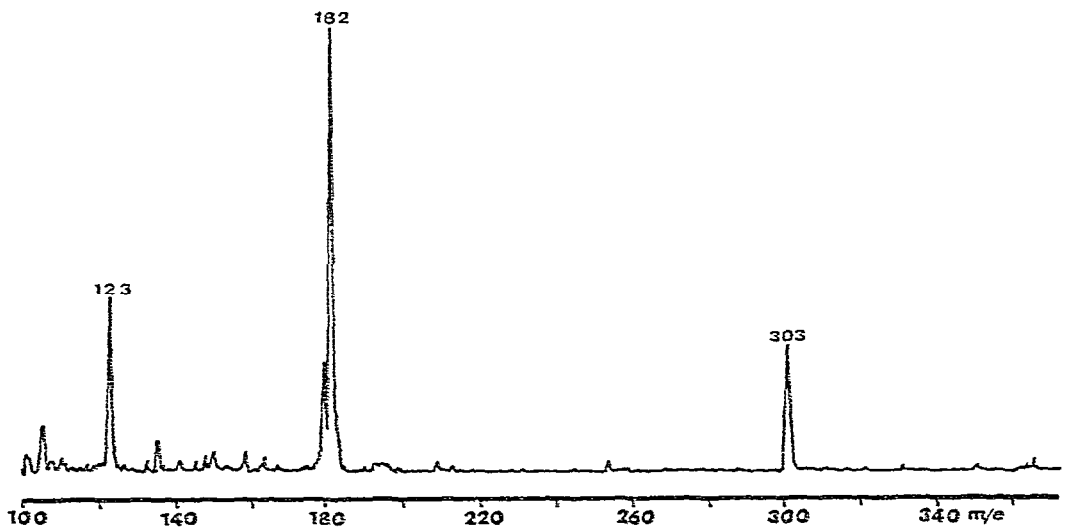


Fig. 2. Alpha/II total ion mass spectrum of cocaine. Data were digitally smoothed 3 times.

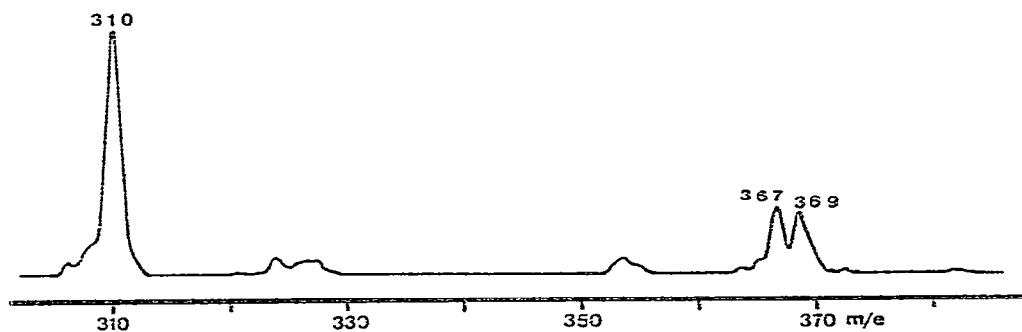


Fig. 3. Alpha/II total ion mass spectrum of heroin. Data were digitally smoothed 20 times.

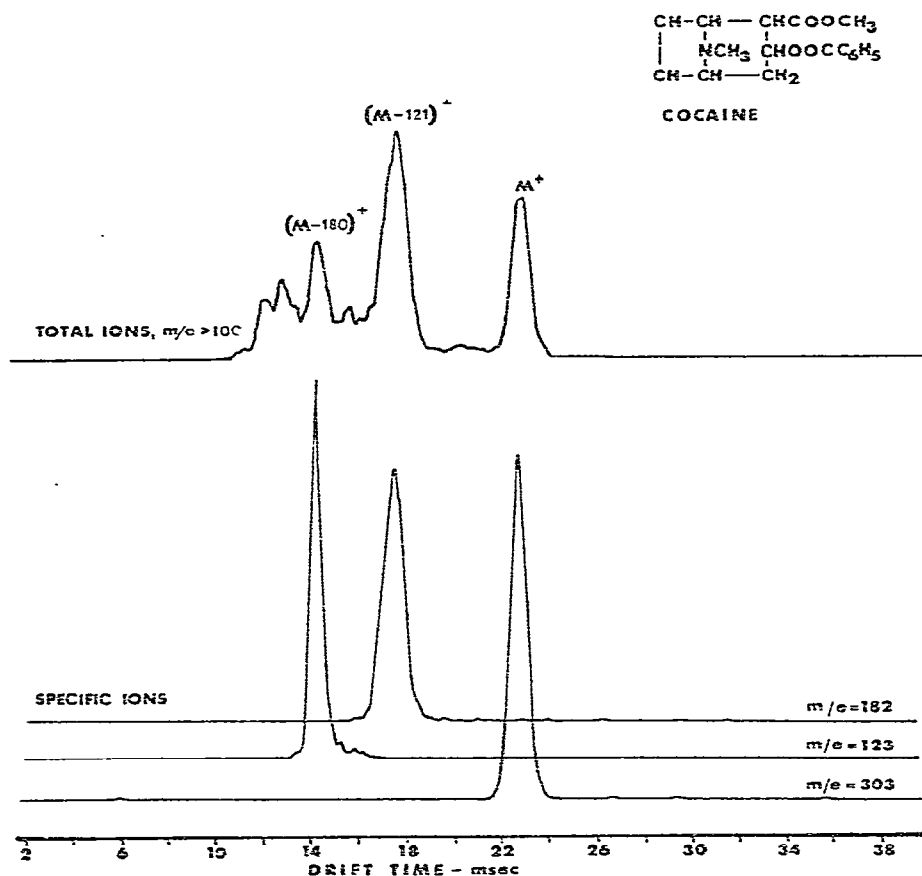


Fig. 4. Upper portion: Alpha/II total ion mobility spectrum of cocaine; only ions with masses greater than 100 are monitored. The averaged data from 4096 continuous 40-msec sweeps were digitally smoothed 5 times. Lower portion: Alpha/II $m/e = 303$, 182, and 123 specific ion mobility spectra of cocaine; the averaged data from 4096 continuous 40-msec sweeps were digitally smoothed 3 times.

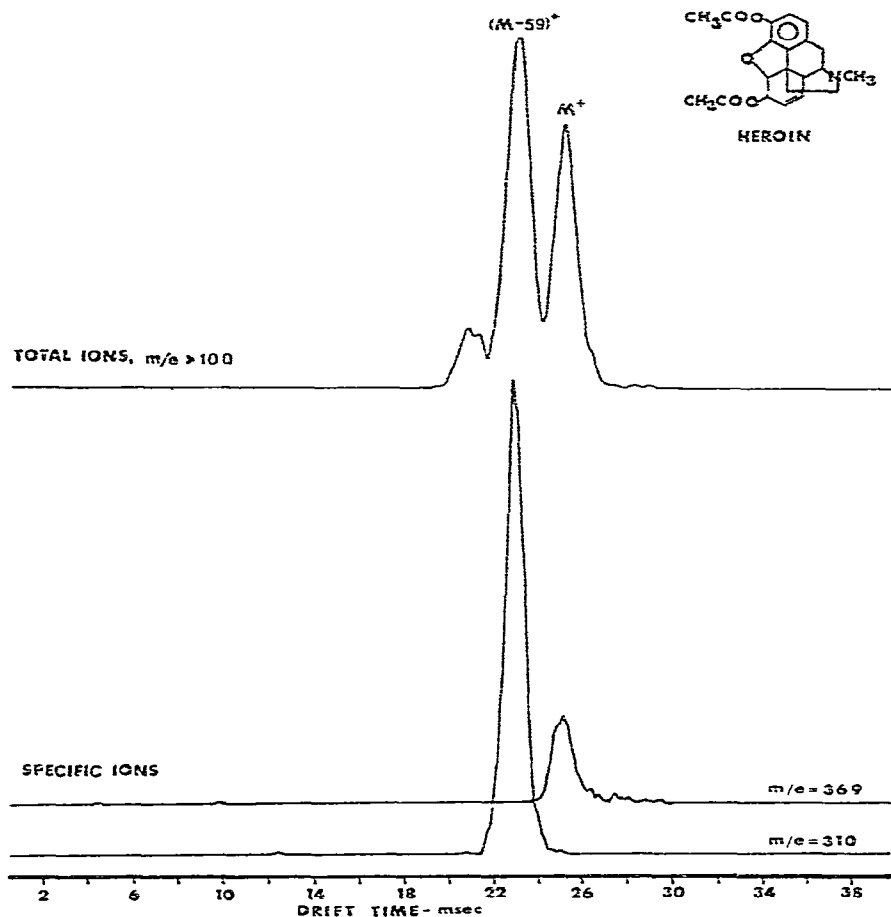


Fig. 5. Upper portion: Alpha/II total ion mobility spectrum of heroin; only ions with masses greater than 100 are monitored; the averaged data from 8192 continuous 40-msec sweeps were digitally smoothed 20 times. Lower portion: Alpha/II $m/e = 369$ and 310 specific ion mobility spectra; the averaged data from 2048 continuous 40-msec sweeps were digitally smoothed 5 times.

The sampling technique used with the Alpha/II instrument was similar to that described above and the operating parameters were as follows: nitrogen drift gas flow-rate, 500 ml/min; nitrogen carrier gas flow-rate, 100 ml/min; gate widths, 0.2 msec; electric field gradient, 214 V/cm; drift tube and injection port temperatures, 204°C; pressure, 763 torr. The drift length of the Beta/VII plasma chromatograph is 8 cm from the injection grid to detector, but the total drift length of the Alpha/II system from the injection grid to the mass spectrometer detector is somewhat longer since the ion lens and orifice interfacing of the mass spectrometer added extra length to the drift space. The mass spectrometer was calibrated using FC-43 and the electron impact ionization source. The standard ionization pattern was accurate to within ± 0.15 a.m.u. from 12 to 600 a.m.u. The calibration was checked prior to running these mass spectra; calibration stability is accurate to within ± 0.1 a.m.u. for any 8-h period¹⁴.

All data reported for the Alpha/II instrument were taken by signal averaging 40-msec scans in a Nicolet signal averaging computer (FT-1072; Nicolet Instruments, Madison, Wisc., U.S.A.). Where indicated in the figures, the data were subjected to multiple 3-point smoothing operations.

CALCULATIONS

In plasma chromatography, mobilities ($\text{cm}^2/\text{V}\cdot\text{sec}$) are used as the qualitative measurement of specific ions. They can be calculated directly from the drift time of the ion, the length of the drift tube, and the strength of the electric field applied. In practice, mobilities are corrected to conditions of standard temperature and pressure allowing comparisons with mobilities obtained under different conditions. These corrected mobilities are termed reduced mobilities, K_0 , and are calculated from the following equation:

$$K_0 = \frac{d}{t \cdot E} \cdot \frac{273}{T} \cdot \frac{P}{760}$$

where d = drift length (cm), t = drift time (sec), E = electric field gradient (V/cm), T = temperature ($^{\circ}\text{K}$), and P = pressure (torr).

The drift length of the Alpha/II plasma chromatograph-mass spectrometer combination was calculated from its drift times and those obtained with the 8-cm drift length of the Beta/VII plasma chromatograph. These calculations give a drift distance of 9.64 cm for the plasma chromatograph-mass spectrometer combination. K_0 values for ion peaks obtained with the Alpha/II instrument were calculated and compared to those obtained with the Beta/VI plasma chromatograph.

RESULTS AND DISCUSSION

Reference ion mobility spectra for heroin and cocaine were obtained with the Alpha/II plasma chromatograph-mass spectrometer. The total ion mobility spectra are shown in the upper portion of Figs. 4 and 5. The reactant ions are not seen in these spectra because the total ion monitor of the mass spectrometer was tuned only to ions with masses greater than 100. For heroin, K_0 values were determined to be $1.05 \text{ cm}^2/\text{V}\cdot\text{sec}$ for the ion at drift time 24.62 msec and $1.15 \text{ cm}^2/\text{V}\cdot\text{sec}$ for the ion at 22.54 msec. Cocaine had three primary ion peaks at drift times of 22.30, 17.26, and 14.06 msec with K_0 values of 1.16, 1.50, and $1.84 \text{ cm}^2/\text{V}\cdot\text{sec}$, respectively. The simplicity of these spectra add to their value as reference spectra since well resolved peaks allow more accurate determination of drift times and reduced mobility values.

Previously in this series, identities of the ionic peaks have been appraised from known chemical ionization mass spectrometry (CIMS) ion fragmentation patterns and K_0 values. However, a more direct identification method is to produce mobility spectra of specific ions with the plasma chromatograph-mass spectrometer.

The ions chosen for specific ion monitoring were determined from a mass spectrum of all the ions produced in the plasma chromatograph. The ions from cocaine gave major mass spectral peaks at m/e values of 303, 182, and 123 (Fig. 2). The ion at mass 303 corresponds to the molecular ion while masses 182 and 123 correspond to

ion fragments $(M - C_6H_5CO_2)^+$ and $(M - C_6H_5CO_2 - CO_2CH_3)^+$, respectively. Similarly, the mass scan for heroin shown in Fig. 3 gave three major peaks with m/e values of 369, 367, and 310. These masses can be respectively assigned to ion fragments M^+ , $(M - H_2)^+$, and $(M - CH_3CO_2)^+$.

Specific ion mobility spectra were obtained for each of the compounds and the drift times of known masses were compared to the total ion mobility spectra. Fig. 4 shows clearly that ions from cocaine with masses of 303, 182, and 123 have drift times of 22.30, 17.26, and 14.06 msec, respectively. Similar data in Fig. 5 show that the two principal peaks in the heroin spectrum are produced by ions with masses of 369 and 310. The ion with $m/e = 369$ corresponded to the peak at drift time 24.62 msec while the ion with $m/e = 310$ corresponded to a drift time of 22.54 msec. The specific ion mobility spectrum was not obtained for the $m/e = 367$ ion observed in the mass spectrum. Since the plasma chromatograph cannot normally resolve ions two mass units apart, this ion would appear along with the $m/e = 369$ ion in the peak at drift time 24.62 msec.

The primary analytical data from the plasma chromatograph consist of "fingerprint" reference mobility spectra. However, the values of these data are greatly enhanced by the identity of the ions associated with each peak in the mobility spectra. Interpretation of peak identity in previously reported reference spectra has been accomplished by postulating the ions expected from a knowledge of those observed for these compounds in chemical ionization mass spectra. Where CIMS data are not available the established ionization pathways of the CIMS technique can be used for guidance. The reasonableness of these ionic assignments can be checked using an established K_0 vs. mass correlation curve¹⁵. This curve has a very low mass resolution, especially at higher masses, and can only be used for an approximation. Following this procedure, the ions postulated for the heroin and cocaine spectra would be those appearing in the CH_4 CIMS spectra shown in Fig. 6. Comparison of these postulated ions with those actually found with the plasma chromatograph-mass spectrometer via the specific ion spectra also appears in Fig. 6. The major difference is that the plasma chromatograph produces the M^+ and $(M - H_2)^+$ ions instead of the MH^- and $(MH - H_2)^-$ observed in CH_4 CIMS. Charge exchange mass spectra using N_2/NO reactant gas gives molecular ions identical to those seen in the plasma chromatographic spectra¹⁷.

These data and their slight differences verify the value of using the approximate method in the absence of an interfaced mass spectrometer. It is clear that the interfaced plasma chromatograph-mass spectrometer gives more detailed and accurate data for reference spectra and is the optimum instrument to use for this purpose.

Finally, as an independent check on the validity of previously reported reference spectra, ion mobility spectra for heroin and cocaine were obtained with the plasma chromatograph used in the earlier studies (Fig. 1). The close agreement of ± 0.02 $cm^2/V \cdot sec$ shown in Table I for the K_0 values calculated from data produced with two completely different instruments and operating conditions is within the reported reproducibility of the Beta/VI instrument. This indicates that K_0 values in previously reported reference spectra have a high degree of reliability. Extensive temperature profiles throughout the drift space of the Alpha/II and Beta/VII instruments have been taken to assure accuracy of the temperature measurement used for the calculation of K_0 values¹⁴.

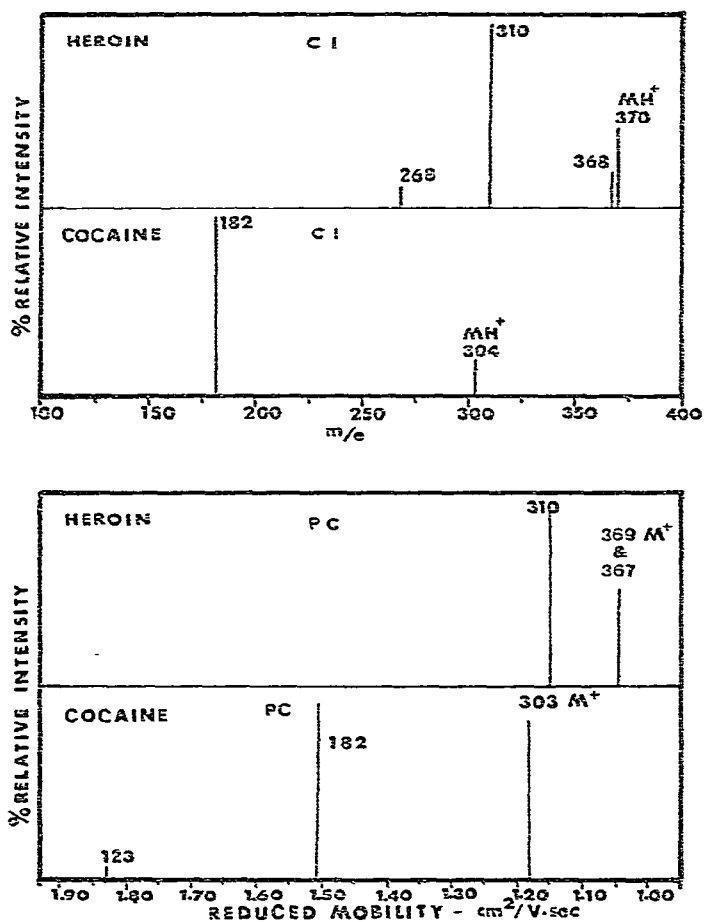


Fig. 6. Comparison of CH_4 CIMS data¹⁶ with ion mobility data for heroin and cocaine. Spectra were normalized to the most intense peak. Reduced mobility values were obtained from the Beta/VI plasma chromatograph.

TABLE I
COMPARISON OF REDUCED MOBILITY VALUES

| Drift time (msec) | | | Reduced mobility ($\text{cm}^2/\text{v}\cdot\text{sec}$) | | | Mass (a.m.u.) |
|-------------------|----------|----------|--|----------|----------|---------------|
| Beta/VI | Beta/VII | Alpha/II | Beta/VI | Beta/VII | Alpha/II | |
| <i>Cocaine</i> | | | | | | |
| 12.47 | 18.50 | 22.30 | 1.18 | 1.16 | 1.16 | 303 |
| 9.77 | 14.16 | 17.26 | 1.51 | 1.52 | 1.50 | 182 |
| 8.07 | | 14.06 | 1.83 | | 1.84 | 123 |
| <i>Heroin</i> | | | | | | |
| 14.88 | 20.60 | 24.62 | 1.05 | 1.04 | 1.05 | 369, 367 |
| 13.70 | 18.80 | 22.54 | 1.14 | 1.14 | 1.15 | 310 |

CONCLUSIONS

Ion mobility reference spectra for heroin and cocaine are reported. The cocaine had three major ion peaks with K_0 values of 1.16, 1.50, and 1.84 $\text{cm}^2/\text{V}\cdot\text{sec}$ while heroin produced two primary ion peaks at K_0 values of 1.05 and 1.15 $\text{cm}^2/\text{V}\cdot\text{sec}$. These reference spectra enable "fingerprint" identification of compounds by plasma chromatography.

Identities of the individual ions in the mobility spectra were obtained with a directly coupled plasma chromatograph-mass spectrometer combination. This instrument was capable of producing three types of spectra: mass spectra of all ions produced in the plasma chromatograph, ion mobility spectra using the total ion monitor of the mass spectrometer, and specific ion mobility spectra by tuning the mass spectrometer to selected m/e values. The combination of these spectra confirmed the masses of ions produced in the plasma chromatography of cocaine to be 303 a.m.u. for $K_0 = 1.16$ corresponding to M^+ , 182 a.m.u. for $K_0 = 1.50$ corresponding to the $(\text{M} - \text{C}_6\text{H}_5\text{CO}_2)^+$ ion and 123 for $K_0 = 1.84$ corresponding to the $(\text{M} - \text{C}_6\text{H}_5\text{CO}_2 - \text{CO}_2\text{CH}_3)^+$ ion. Masses of the ions in the heroin spectrum were 369 and 367 for $K_0 = 1.05$ corresponding to M^+ and 310 a.m.u. for $K_0 = 1.15$ corresponding to $(\text{M} - \text{CH}_3\text{CO}_2)^+$. These values were in good agreement with those predicted from chemical ionization mass spectrometry data and mass-mobility correlation data.

Ion mobility spectra were also obtained for heroin and cocaine with the Beta/VI plasma chromatograph used for previously reported reference spectra. The close agreement between mobility values with the Beta/VI and Alpha/II systems confirms the reliability of earlier spectra.

ACKNOWLEDGEMENTS

The authors wish to thank Marsland Engineering Inc., Waterloo, Ontario, Canada for providing samples of cocaine and heroin. The mass-identified mobility data were obtained through the courtesy and assistance of the personnel and facilities of Franklin GNO Corp., West Palm Beach, Fla., U.S.A. The data were obtained during the reliability test in the "shake-down" period before delivery of the Alpha/II plasma chromatograph-mass spectrometer to the customer. We wish to acknowledge M. J. Cohen, C. Wernlund and R. F. Wernlund for direct assistance in obtaining the data and J. H. Wolfe, R. C. Kindel, D. Taylor, and R. F. Wernlund for design and construction of the Alpha/II. A general acknowledgement for instrument and facilities available is given to H. G. Gibson, Jr.

REFERENCES

- 1 F. W. Karasek, *Anal. Chem.*, 45 (1974) 710A.
- 2 F. W. Karasek and R. A. Keller, *J. Chromatogr. Sci.*, 10 (1972) 626.
- 3 F. W. Karasek and D. M. Kane, *J. Chromatogr. Sci.*, 10 (1972) 673.
- 4 F. W. Karasek, D. M. Kane and O. S. Tatone, *J. Chromatogr.*, 87 (1973) 137.
- 5 F. W. Karasek, D. W. Denney and E. H. DeDecker, *Anal. Chem.*, 46 (1974) 970.
- 6 F. W. Karasek and D. M. Kane, *Anal. Chem.*, 46 (1974) 780.
- 7 F. W. Karasek and D. M. Kane, *J. Chromatogr.*, 93 (1974) 129.
- 8 F. W. Karasek and D. W. Denney, *J. Chromatogr.*, 93 (1974) 141.

- 9 F. W. Karasek and D. W. Denney, *Anal. Chem.*, 46 (1974) 1312.
- 10 F. W. Karasek and S. H. Kim, *J. Chromatogr.*, 99 (1974) 257.
- 11 F. W. Karasek and S. H. Kim, *Anal. Chem.*, 47 (1975) 1166.
- 12 F. W. Karasek, D. E. Karasek and S. H. Kim, *J. Chromatogr.*, 101 (1975) 345.
- 13 F. W. Karasek, A. Maican and O. S. Tatone, *J. Chromatogr.*, 110 (1975) 295.
- 14 R. F. Wernlund, Franklin GNO Corp., private communication, September, 1975.
- 15 G. W. Griffin, I. Dzidic, D. F. Carroll, R. N. Stillwell and E. C. Horning, *Anal. Chem.*, 45 (1973) 1204.
- 16 R. Saferstein and J. Chao, *J. Ass. Offic. Anal. Chem.*, 56 (1973) 1234.
- 17 I. Jardine and C. Fenselau, *Anal. Chem.*, 47 (1975) 730.