VERSITA

Cent. Eur. J. Chem. • 7(3) • 2009 • 312–316
DOI: 10.2478/s11532-009-0004-4

Central European Journal of **Chemistry**

Improving the selectivity of non-polar alkanes, alkenes, and aromatic hydrocarbon compounds by the application of acetonitrile as a CI reagent

Research Article

Fadel Alwedian*, Khalid Abu-Shandi

Department of Chemistry, Faculty of Science, Tafila Technical University, Tafila 66110, Jordan

Received 31 May 2008; Accepted 04 November 2008

Abstract: The selective enhancement of membrane introduction mass spectrometry for non-polar alkanes, alkenes, and aromatic hydrocarbon compounds by the application of acetonitrile as a chemical ionization reagent was investigated. Acetonitrile CI is able to produce specific fragment ions for many of the compounds test and this can be used to identify and quantify the parent neutrals. This method provided relatively high detection limits of the test compounds. This method could potentially be useful for analytical applications such as the detection of non-polar hydrocarbons for environmental studies if CH_3CN CI/MIMS is coupled with a preconcentration method.

Keywords: *Membrane introduction • Chemical ionization • Acetonitrile • Hydrocarbon compounds*

1. Introduction

In membrane introduction mass spectrometry (MIMS), non-polar semi permeable membranes are used to allow for the selective introduction of volatile and semi-volatile analytes into the ion source of a mass spectrometer *via* a process known collectively as pervaporation [1-3]. Permeated analyte is usually ionized with electron ionization (EI) or chemical ionization (CI), and the parent and fragment ions are then mass analyzed and detected. MIMS has proven to be valuable for the direct online analysis of volatile organic compounds (VOCs) in aqueous [4-7] and air [4,8-10] samples by demonstrating promising simplicity, speed, and trace-level detection. MIMS has also been used in biological applications [11-13] and online environmental monitoring of industrial processes [14].

The major disadvantage of the MIMS approach is the inherent inability to physically separate sample mixtures [15]. For mixtures of VOCs, especially hydrocarbons, extensive ion fragmentation tends to produce very complicated mass spectra and this leads to quantitation problems due in part to the fact that different parent compounds have common fragment ions. The missing unique molecular fragments or ions for each analyte in the mixture makes it difficult to identify individual parent neutral species and to conduct a quantitative analysis based on their mass spectra. To solve this problem, several techniques have been investigated including selective chemical ionization [9,13,16], tandem mass spectrometry [17], ozone reaction pretreatment [18], and multivariate calibration methods [15,17,19].

A variety of selective chemical ionization reagents have been used in combination with the MIMS technique; including isobutene [16], methane [13], ammonia [13], water vapor [20], oxygen [21], and nitric oxide [22]. The two important advantages of chemical ionization are the molecular ion production (or pseudo-molecular ions) and the control over the ion fragmentation of analytes. Both of these advantages result in reducing the complexity of the mass spectrum. Although the above CI reagents showed enhanced sensitivity and/or selectivity for polar organic compounds, only nitric oxide showed the same augmentation for alkanes and alkenes.

Prior work by Traldi *et al.* [23] showed that when a mixture of long chain hydrocarbons containing of

* *E-mail: alwedfad@yahoo.com*

docosane (C22), 3-methylheneicosane, and 1-docosene was introduced into a ion trap and analyzed using acetonitrile as the CI reagent at a manifold temperature of 110°C, the mass spectra of the test compounds was dominated by the formation of abundant ions corresponding to $[M+CH_2CN]^+$ and $[M+H]^+$, $[M+H]^+$ formed the base peak of the mass spectra. This result demonstrated the advantage of using acetonitrile as CI reagent for analyzing long chain hydrocarbon mixtures.

In this paper, acetonitrile was investigated as a suitable chemical ionization reagent to aid in the measurement and improvement of the selectivity of the membrane introduction mass spectrometric method for volatile hydrocarbons in complex gaseous matrixes.

2. Experimental Procedures

The experimental setup was described previously by Wedian *et al*. [22]. In brief, the MIMS system used in these experiments is similar in design to commercially available systems. It consists of an ion trap mass spectrometer (Magnum, Finnigan MAT, San Jose, CA) that is configured to accept a 2.2 cm diameter direct insertion capillary membrane probe through a vacuum adapter installed in the GC transfer line inlet port. The capillary membrane used in this work was Silastic laboratory tubing, 2.16 mm. o.d., 1.02 mm. i.d. (Dow Corning, Midland, MI). The exposed length of the capillary membrane (within a glass and Teflon adapter) was 15 cm. A small helium flow (~ 2 mL min^{-1}) is used to help transfer permeated analytes from the adapter into the ion trap and to supply the ion trap buffer gas requirement. The entire MIMS system is typically held at 130ºC.

Different gas mixtures were prepared in 56 L Tedlar bags (Alltech Associates, Inc) by injecting a known volume of test compounds into a helium filled bag and allowing the bag to equilibrate for at least half an hour before use. Further dilutions of gas solutions were made to reach concentrations of 80 ppb-1.2 ppm. Between mixtures, the bags were flushed and filled with C.P. nitrogen (purity 99.985%) several times before they were used again. All gas samples were made and stored at room temperature. The test compounds toluene (EM Science, 97%), pentane (Allied Signal, 99%), p-xylene (Matheson Coleman & Bell, 98%), hexane (Aldrich, 97%), cyclohexane (Aldrich, 99%), cyclohexene (Fluka, 99%) were all used as delivered.

A small test tube containing liquid acetonitrile was connected to the inlet for the CI reagents on the rear of the Magnum ion trap. The operating conditions for acetonitrile was optimized and monitored using the Magnum ion trap software supplied by the manufacturer. Under acetonitrile CI operation conditions, the spectrum consists of three major peaks at m/z 41 $(CH_3CN)^+$, 40 $(CH_2CN)^+$, and 39 $(CHCN)^+$, and is independent of manifold temperature. The mass spectra were recorded using the chemical ionization/chemical reaction mode. The mass spectral data (40-200 m/z) were collected using Magnum ion trap control software in the GC mode (mass spectra as a function of time).

3. Results and Discussion

Fig. 1 compares the mass spectra obtained for a three-compound mixture (hexane, cyclohexene, and toluene) using electron ionization (EI) and CH_3CN chemical ionization modes. Fig. 1A was obtained using EI mode, and shows significant fragmentation and severe overlapping of ions from at least two compounds. Between the mass-to-charge regions of 50 - 80, the fragments primarily arise from cyclohexene and hexane, while toluene produces ion signals between 90 and 95 m/z. No detectable signal can be attributed to the molecular ion of hexane because of fragmentation. The peaks at m/z 81 and 83 could correspond to the molecular ion of cyclohexene and it is possible that hexane may also contribute to these fragments. While the peak of m/z 91 is present at detectable levels and corresponds to (pseudo) molecular ions of toluene. Therefore, while toluene could be measured with reasonable certainty, the other two compounds (cyclohexene and hexane) in this test mixture could only be quantified with considerable difficulty.

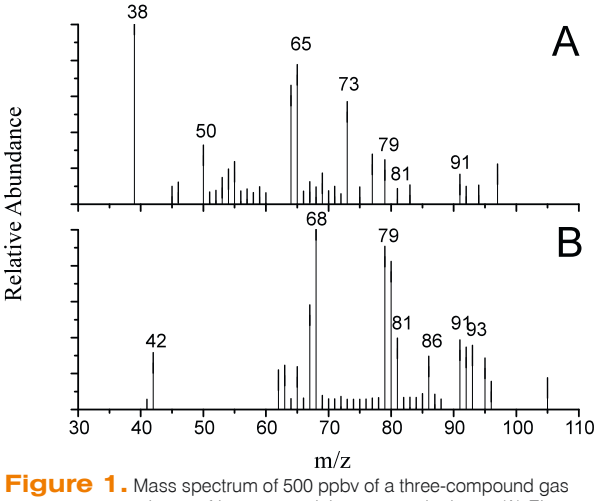

Figure 1. Mass spectrum of 500 ppbv of a three-compound gas mixture of hexane, cyclohexene, and toluene (A) EI mass spectrum of the mixture, (B) CH_3CN chemical ionization mass spectrum.

Fig. 1B shows the mass spectrum of the same mixture of three compounds (at the same concentrations) using CH_3CN as the chemical reagent. The mass spectra show less fragmentation for cyclohexane and cyclohexene. The ion signals are concentrated in a few major fragments rather than a series of low intensity ions as seen in Fig. 1A. Pseudo molecular ions for each compound in the mixture are evident (m/z 81 for cyclohexene, m/z 86 for hexane, and m/z 91 and 93 for toluene). Each molecular ion is accompanied by isotopic variant peaks (to the right) and H atom loss peaks (to the left), and less other fragmentation is also observed. Some overlapping fragments are still observed between m/z 60-80, which were also present in the EI spectrum. Fig. 1B demonstrates the ability of CH_3CN to produce a characteristic ion signal for alkanes and alkenes and also to enhance the signal of the aromatics that can in turn be used to identify each.

The expectations of applying CH_3CN as CI reagent for the detection of short-chain aliphatic hydrocarbon compounds are that the reagent ion $(CH_3CN)^+$ may help to produce a molecular ion, M^+, a protonated molecular ion, $[M+H]^+$, or an adduct species $[M+CH_2CN]^+$ as the base peak for the test compounds [23]. Unfortunately, the mass spectra of the test compounds were dominated by the appearance of a few specific fragments with high enough intensity that would allow for more reliable identification rather than a series of low intensity ions. The formation of a relatively weak molecular ion, M^+, and the protonated molecular ion, $[M+H]^+$, was only observed for the aromatic compound. The adduct species, $[M+CH_2CN]^+$, was never observed for any hydrocarbon compound in this work.

Possible explanations for not observing the adduct formation are: (1) the test compounds were relatively short chain hydrocarbons (all less than 12 carbons), while Traldi *et al.* [23] applied the reagent to long chain compounds (20 carbons and more); and (2) technical information obtained some time after doing this work indicated that CH_3CN may have degraded the seals in the valve/vacuum interface system of the used ion trap, leading to poor performance of CH_3CN as a CI reagent. We have not repeated these experiments with a chemically compatible valve system to date to verify whether the latter was in fact a problem.

Although extensive fragmentation is produced by electron ionization, the fragmentation patterns are useful for identifying target compounds by comparing mass spectra to those in the literature databases. This advantage becomes a significant obstacle with a MIMS experiment since MIMS lacks a physical separation step. When CH_3CN CI is used, larger pseudo molecular ions peaks for some of the compounds were observed and this permits the MIMS technique to identify and quantify more easily. Some of these compounds do not show a strong unique fragment ion in EI mode.

3.1. Detection limits and Quantitation

Fig. 2 shows the calibration curves of two selected compounds (for simplicity) in the concentration range of 100 to 1000 ppbv (parts-per-billion by volume in N_2). The signals are the sum of selected fragments m/z 91+93 for toluene and m/z 71+72 for pentane. The data demonstrate the linearity of the response of the MIMS system, correlation coefficients $R^2 \sim 0.97$ and 0.98 for toluene and pentane respectively.

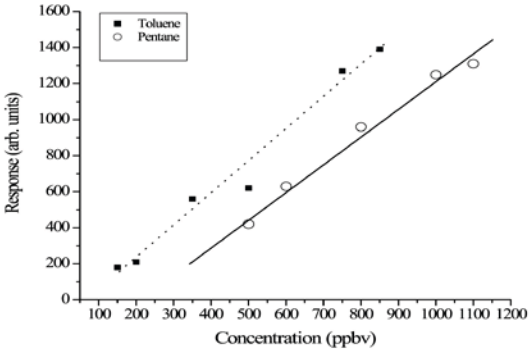

Figure 2. Calibration curves for toluene and pentane using CH_3CN as the CI reagent.

The limits of detection for the selected hydrocarbons measured individually or in pairs by the MIMS system using CH_3CN as the CI reagent varied significantly, depending on the chemical nature of the compounds (Table 1). The test compounds were chosen to represent the different types of non-polar hydrocarbons: alkanes, alkenes, and aromatics. For relatively low vapor pressure aromatics (p-xylene, and toluene) the detection limits were below 200 ppbv. For higher vapor pressure compounds (pentane, hexane, cyclohexane, and cyclohexene) the detection limits were found to be higher. This can be primarily attributed to the low solubility and diffusivity of the higher vapor pressure compounds in the Silastic membrane. The detection limits were calculated from the calibration curves as the concentration corresponding to a signal as 3σ the blank.

3.2. Analytical Application

The relatively low pressure of alkanes and alkenes, combined with low solubility and diffusivity in the membrane, makes the detection and analysis of non-polar alkanes and alkenes in air a challenging problem. By using CH_3CN as the CI reagent, this concentrates the ion fragmentation of these compounds into a series of intense peaks that may be suitable for improving the sensitivity and the ability of the MIMS for direct mixture analysis [4,14,15,19,20,24].

Considering the proposed CI reagent produces high detection limits for the test compounds, it is believed that coupling CH_3CN CI with a preconcentration step [7,25-28] or with a mathematical based multicomponent quantitation method such as a nonlinear asymmetric error function-based least mean square method (NALMS), which can identify and quantify individual compounds in sample mixtures based on the ability of computer generated software to analyze and separate complex multicomponent EI spectra into the individual constituents, could be useful in increasing the selectivity of MIMS when measuring non-polar hydrocarbons in air samples.

4. Conclusion

This work demonstrates that CH_3CN can be used as a CI reagent in MIMS to identify non-polar hydrocarbons in gas mixture samples. Although the proposed chemical ionization reagent does not achieve state of the art detection limits for alkanes and alkenes, CH_3CN CI is able to reduce the complexity of the mass spectra by producing molecular ion fragments, which can be used for quantitative purposes. The sensitivity could be improved if the MIMS method incorporated a preconcentration method, in which case the system could be useful for environmental field studies.

Acknowledgments

The authors are grateful to Professor Dean B. Atkinson at Chemistry Department at Portland State University (Oregon, USA) for his help doing this work and his valuable help in the discussion. Also the authors would like to acknowledge the financial support of the Faculty of Graduate Studies at the Tafila Technical University and Dr. Gunther Steinfeld at the Institute of Inorganic and Analytical Chemistry at Freiburg University (Germany).

Table 1. Detection limits of selected non-polar hydrocarbons using CH_3CN as a chemical ionization reagent.

Name of compound	Molar Mass (g mol^{-1})	Monitored Fragments	Detection limit (ppbv)
p-Xylene	106	*m/z* 106+105	150
Toluene	92	*m/z* 93+91	100
Cyclohexane	84	*m/z* 83+84	700
Cyclohexene	82	*m/z* 81	820
Hexane	86	*m/z* 86	900
Pentane	72	*m/z* 72+71	450

References

[1] R.A. Ketola, T. Kotiaho, M.E. Cisper, T.M. Allen, J. Mass Spectrom. 37(5), 457 (2002)
[2] R.C. Johnson, R.G. Cooks, T.M. Allen, M.E. Cisper, P.H. Hemberger, Mass Spectrom. Rev. 19(1), 1 (2000)
[3] R.G. Cooks, T. Kotiaho, In: J.J. Breen, M.J. Dellarco (Ed.), Pollution Prevention in Industrial Processes (American Chemical Society, Washington D.C., 1992) 126
[4] L.S. Riter, Z. Takats, L. Charles, R.G. Cooks, Rapid Commun. Mass Spectrom. 15(17), 1520 (2001)
[5] R.M. Alberici, R. Sparrapan, W.F. Jardim, M.N. Eberlin, Environ. Sci. Technol. 41, 373 (2000)
[6] K. Sharara, J. Mansouri, A.G. Fane, P.T. Crisp, P. Calderon, M. Guilhaus, Water Sci. Technol. 41, 373 (2000)
[7] M.A. Mendes, R.S. Pimpim, T. Kotiaho, M.N. Eberlin, Anal. Chem. 68(19), 3502 (1996)
[8] L.S. Riter, Z. Takats, R.G. Cooks, Analyst 126(11), 1980 (2001)
[9] M.E. Cisper, P.H. Hemberger, Rapid Commun. Mass Spectrom. 11, 1454 (1997)
[10] M.E. Cisper, C.G. Gill, L.E. Townsend, P.H. Hemberger, Anal. Chem. 67(8), 413 (1995)
[11] R. Haddad, N.F. Hoehr, M.A. Mendes, M.N. Eberlin, Analyst 126(8), 1212 (2001)

[12] F.R. Lauritsen, J. Rose, Analyst 125(9), 1577 (2000)
[13] J.S. Brodbelt, J.N. Louris, R.G. Cooks, Anal. Chem. 59(9), 1278 (1987)
[14] V.T. Virkki, R.A. Ketola, M. Ojala, T. Kotiaho, V. Komppa, A. Grove, S. Facchetti, Anal. Chem. 67(8), 1421 (1995)
[15] R.A. Ketola, M. Ojala, V. Komppa, T. Kotiaho, J. Juujarvi, J. Heikkonen, Rapid Commun. Mass Spectrom. 13(8), 654 (1999)
[16] J. Brodbelt, R. Cooks, J. Tou, G. Kallos, M. Dryzga, Anal. Chem. 59(3), 454 (1987)
[17] S.M. Gordon, P.J. Callahan, D.V. Kenny, J.D. Pleil, Rapid Commun. Mass Spectrom. 10(9), 1038 (1996)
[18] F. Wedian, D.B. Atkinson, Environ. Sci. Technol. 36, 4152 (2002)
[19] S.K. Ohorodnik, R.E. Shaffer, J.H. Callahan, S.L. Rose-Pehrsson, Anal. Chem. 69(22), 4721 (1997)
[20] F.R. Lauritsen, T.K. Choudhury, L.E. Dejarme, R.G. Cooks, Anal. Chim. Acta 266(1), 1 (1992)
[21] M.E. Cisper, A.W. Garrett, D. Cameron, P.H. Hemberger, Anal. Chem. 68(13), 2097 (1996)
[22] F. Wedian, D.B. Atkinson, Environ. Sci. Technol. 37, 4425 (2003)
[23] G. Moneti, G. Pieraccini, F.R. Dani, S. Catinella, P. Traldi, Rapid Commun. Mass Spectrom. 10, 167 (1996)
[24] P.S.H. Wong, R.G. Cooks, M.E. Cisper, P.H. Hemberger, Environ. Sci. Technol. 29(5), 215A (1995)
[25] R.A. Ketola, C. Gron, F.R. Lauritsen, Rapid Commun. Mass Spectrom. 12(12), 773 (1998)
[26] G.L. Kok, M.E. Cisper, P.H. Hemberger, J. Am. Mass Spectrom. 7, 1172 (1996)
[27] M. Leth, F.R. Lauritsen, Rapid Commun. Mass Spectrom. 9(7), 591 (1995)
[28] F.R. Lauritsen, R.A. Ketola, Anal. Chem. 69(23), 4917 (1997)