Characteristics of Charge Exchange Chemical Ionization (CI) in an Atmospheric Pressure Gas Chromatography (APGC) Source and Applied Uses

Steven Lai1, Rhys Jones2, David Douce3, John Dunstan4, Douglas Stevens5

1. Waters Corporation, Beverly, MA 01915 2. Waters Corporation, Manchester, UK 3. M23 9LZ 3. Waters Corporation, Milford, MA 01757

INTRODUCTION

Charge exchange CI was among the ionization techniques studied and reviewed and used in Gas Chromatography-1 Mass Spectrometry in the 1970’s, however, with the introduction and acceptance of the EI ion source, it was subsequently relegated to a niche role for the determination of certain classes of compounds. The APGC source as described here offers a solution to the challenges of charge exchange CI, minimizing the requirements for a low vacuum system, thereby offering the advantage of applying the technique in a wider range of applications. Unlike the EI source, the APGC source allows the use of multiple charge exchange ions, offering the ability to generate multiple product ions from a single analyte. It is also noted to be free from polymerization interference.

METHODS

APGC analysis was performed on a variety of samples and standards. Samples for the determination of particular biomarkers were obtained from the US EPA 8270 mixture. Samples were analyzed as follows: (I) Direct Sample Introduction: under EI conditions, the samples were introduced directly into the source chamber via the corona pin, the resulting ions were then measured using EI spectrometry. (II) Charge Exchange and (III) Protonation. Note that the molecular ion formed under charge exchange conditions, M+.

RESULTS AND DISCUSSION

During the qualification of the instrument a thorough investigation of the relationship between cone gas, auxiliary gas flow (50L/Hr), and anode current in addition to the cone gas and auxiliary gas flow rates. These observations show that reduced auxiliary gas flow maintains optimal instrument performance (Figure 3). These observations also show that reduced auxiliary gas flow maintains optimal instrument performance (Figure 3). These observations also show that reduced auxiliary gas flow maintains optimal instrument performance (Figure 3). These observations also show that reduced auxiliary gas flow maintains optimal instrument performance (Figure 3). These observations also show that reduced auxiliary gas flow maintains optimal instrument performance (Figure 3). These observations also show that reduced auxiliary gas flow maintains optimal instrument performance (Figure 3). These observations also show that reduced auxiliary gas flow maintains optimal instrument performance (Figure 3). These observations also show that reduced auxiliary gas flow maintains optimal instrument performance (Figure 3).

CONCLUSIONS

• Systematic investigation of optimum charge exchange conditions for the APGC source led to the determination of optimal instrument settings which were input into the instrument prototypes.

• By combining charge exchange ionization with MS/MS mode operation, it was possible to acquire accurate mass measured intact molecular ion and fragmentation data within a relatively short time. The ability to measure accurate mass MS/MS data from the APGC source conditions was demonstrated to be very analogous to that from a tandem quadrupole (Xevo TQ-MS). The similarity in fragment ions from the EI and APGC/CID systems further supported the MS/MS results.

• Petroleum biomarker analysis performed using EI GC/MS and atmospheric pressure charge exchange CI GC/MS/MS demonstrated to be very similar to the same MS/MS transitions for the determination of cyclic hydrocarbons.

• Sensitive detection of TCDD was demonstrated using charge exchange with APGC operated in MS/MS mode by applying the same transitions as used with EI GC/MS.

References


Figure 3. A cut away view of the APGC ionization/reactor chamber showing coordinate of components during APGC operation. Auxiliary gas flow path is indicated by blue arrows. A black arrow indicates the direction of adjustment for the corona pin position. Optimum corona pin position and corona pin current in addition to the cone gas and auxiliary gas flow rates.

Figure 4. Response of charge exchange ionization with respect to cone gas, auxiliary gas and corona pin current in addition to the cone gas and auxiliary gas flow rates.

Figure 5. Three dimensional contour plots showing relationship between cone gas and auxiliary gas settings with corresponding corona pin current (I) Charge Exchange and (II) Protonation. Note the improved separation of the final four target analytes. The table below shows the variation of cone gas and auxiliary gas flow with corresponding corona pin current.

Figure 6. Heat map of selected analytes from a standard US EPA 8270 mixture. APGC (CI) shows the optimum (green) cone gas settings for each analyte.

Figure 7. Bar chart of high energy EI data from APGC analysis on an US EPA 8270 snapshot to MS/MS library spectrum for eicosapentaenoic acid (EPA) and 20:4n6 (DHA, 14:0).

Figure 8. AECI/MS/MS data from relevant sourced ionization chamber showing similarity of EI data to MS/MS library data. The table below shows that from a marine source signal and was analyzed in the standards and conditions. The APGC system supports evidence of the identification of a marine source input.

Figure 9. AECI/MS/MS data from relevant sourced ionization chamber showing similarity of EI data to MS/MS library data. The table below shows that from a marine source signal and was analyzed in the standards and conditions. The APGC system supports evidence of the identification of a marine source input.

Figure 10. APGC (CI) and EI GC/MS/MS data from tandem quadrupole (Xevo TQ-MS). This is a North Sea sample analyzed in 2011. The similarity in fragment ions from the EI and APGC/CID systems further supported the MS/MS results.

Figure 11. APGC (CI) GC/MS/MS data from tandem quadrupole (Xevo TQ-MS). This is a North Sea sample analyzed in 2011. The similarity in fragment ions from the EI and APGC/CID systems further supported the MS/MS results.

Figure 12. Tandem MS/MS results for APGC MRM acquisition (transition) in APGC GC/MS and atmospheric pressure charge exchange CI GC/MS/MS data from tandem quadrupole (Xevo TQ-MS).

TO DOWNLOAD A COPY OF THIS POSTER, VISIT WWW.WATERS.COM/POSTERS

©2013 Waters Corporation