CHARACTERIZING THE PERFORMANCE OF THE BARRIER DISCHARGE IONIZATION DETECTOR FOR GAS CHROMATOGRAPHY

Maria Antoniadou[a,b], Erwin Rosenberg[a], George A. Zachariadis[b]

[a]E164 - Institute of Chemical Technologies and Analytics
[b]Aristotle University Thessaloniki, Thessaloniki, Greece

INTRODUCTION

The barrier discharge ionization detector (BID) has very recently been introduced as a new detector for gas chromatography (GC-BID). It is based on detecting the electron current formation by the ionization of the analytes eluting from the GC column in a Helium plasma [1]. The dielectric barrier discharge was initially used for industrial purposes [2] and, later, as an excitation source for analytical applications in spectroscopy [3].

The present work focuses on the performance evaluation of the commercial GC-BID instrument, as a systematic study of the analytical capabilities and figures of merit is still missing in the literature [4]. This task was addressed by analysing a large set of standard compounds from several compound classes and evaluating and comparing the results with those of the flame ionization detector (FID). Interesting differences in response behaviour were observed between the BID and the FID.

PROBLEM DESCRIPTION AND EXPERIMENTAL APPROACH

Although the GC-BID system is claimed to be usable with a large variety of analytes, only few studies verify these theoretical assumptions. Most of the studies concentrate on the detection of oxidised gaseous compounds like formic acid, acetic acid [5], CO_2, N_2O [6], where the BID is expected to challenge the FID in sensitivity, as well as a limited number of other compounds including water [7], FAME, ethyl- and pentylbenzene, C_9-C_{10} alkanes and few others [4]. For that reason a complete determination of the instrument's characteristics is important as this will indicate the type of analysis that the instrument is most suitable for.

The experiments consisted of the analysis of various compounds from the following compound classes: anilines, halogens, cyclic compounds, alkanes, aromatics, phenols, esters, alcohols. Standards were prepared in five concentrations ranging from 1 to 0.0001 µg μL^{-1} and were analysed by both GC-BID and GC-FID systems. The analytical methods in both systems were similar. (Restek RTX5-MS column, 30 m×0.25 mm, 0.25 µm film thickness, temperature gradient from 50 to 250 in 10 min; 1 µl automatically injected in split mode (20:1 split) at 250°C; detector at 300°C; 17 min total run time). Additional experiments were performed on the GC-BID instrument to test further characteristics as the dependence of the response on molecular structure. The additional standards used for this task included cyclic ketones, cycloalkanes, PAHs and alcohols, aromatics, alkanes with different solvent.

Analytical characteristics like calibration curve, sensitivity, precision, limits of detection (LOD) and quantification (LOQ) were determined from the above-mentioned measurements. Finally, the effect of the operating conditions like purge flow and discharge gas flow rate were investigated.

RESULTS AND DISCUSSION

The evaluation of GC-BID response demonstrated a generally higher sensitivity in comparison to the FID by a factor of 4.1 on average. Fig.1 shows an example for one compound class. The calibration curves typically had coefficients of determination higher than 0.999 for both detectors. The precision was investigated for measurements during the same day and the relative standard deviation (RSD%) was less than 5% for the majority of the cases. LODs ranged from 0.043 to 1.47 ng s^{-1} for the GC-BID and 0.08 - 5.1 ng s^{-1} for the GC-FID.

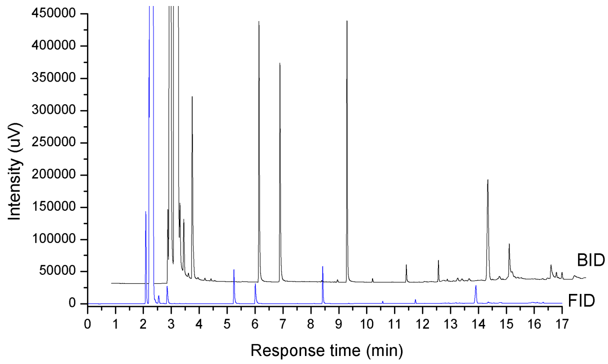

Fig. 1: Chromatogram comparison with BID and FID analysis. Upper: esters-BID, lower: esters-FID.

Fig. 2 shows the evaluation of GC-BID response for n-alkanes with carbon number C10-C17. A clear decrease of peak area response is seen with increasing carbon number. This confirms the concentration dependant behaviour of the BID detector. Also, the operating conditions like purge flow rate and discharge gas flow rate were found to significantly influence the detector response.

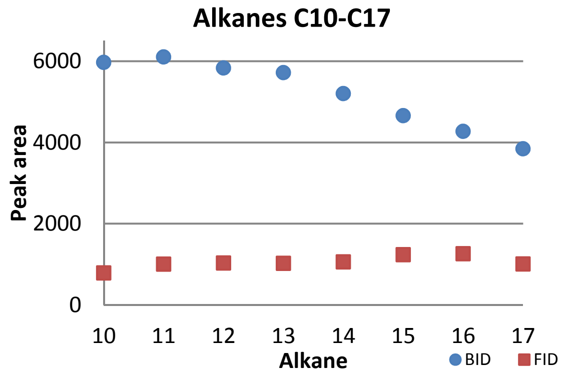

Fig. 2: BID and FID response for an alkane standard C_{10}-C_{17}.

CONCLUSION

The thorough examination of the GC-BID performance in comparison to the GC-FID allowed to better understand its operating principle and optimum operating conditions: As the generation of detector response is more likely achieved by photoionization, rather than the ionization of carbon fragments formed in the combustion of organic compounds in the FID, the response is not mass-flow but rather concentration dependent. Moreover, considerable differences in the specific response of different compound classes exist, while the BID proved to be superior to the FID in terms of sensitivity. These findings will be used to operate the BID under optimum conditions in applications requiring high sensitivity and high time resolution, as achievable by the implementation of a particular modulation technique based on the Hadamard transform.

ACKNOWLEDGMENT

Financial support of this work through the Austrian Research Promotion Agency (FFG) under Project no. 858298 ("DianaBatt") is gratefully acknowledged.

REFERENCES

[1] Shinada, K., Horiike, S., Uchiyama, S., Takechi, R., Nishimoto, T., Shimadzu Review, 2012.

[2] Kogelschatz, U., Plasma Chem. Plasma Process. 23, 1-46, 2003.

[3] Guo, C., Tang, F., Chen, J., Wang, X., Zhang, S., and Zhang, X., Anal. Bioanal. Chem. 407, 2345-2364, 2015.

[4] Franchina F. A., Maimone, M., Sciarrone, D., Purcaro, G., Tranchida, P. Q., Mondello, L., J. Chromatogr. A 1402, 102–109, 2015.

[5] Ueta, I., Nakamura, Y., Fujimura, K., Kawakubo, S., Saito, Y., Chromatographia 80, 151–156, 2017.

[6] Pascale, R., Caivano, M., Buchicchio, A., Mancini, I. M., Bianco, G., Caniani, D., J. Chromatogr. A 1480, 62-69, 2017.

[7] Frink, L. A., Armstrong, D. W., Food Chem. 205, 23–27, 2016.