MASS SPECTROMETRY AS A TOOL FOR STUDY OF ORGANIC SPECIES PENETRATION THROUGH MEMBRANES

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Introduction

Mass spectrometry is a type of experimental method that enables determination of relative abundance of ions in dependence on m/z Membrane inlet (Membrane Introducing Mass Spectrometry – MIMS) supply direct connection of mass spectrometer with different types of reactors like chemical, biochemical or electrochemical cell. Differential electrochemical mass spectrometry (DEMS) is an experimental method frequently used for the study of processes important in studies of different aspects of electrode processes in general electrochemistry, electrocatalysis, electroadsorption/desorption equilibria and in fuel cell studies as well [1,2]. Typically, it has been used for mechanistic studies of adsorption and electro-oxidation of carbon oxide, methanol, formic acid etc. But there is not too many examples giving attention to greater molecules studies, mainly due to difficulties through a very complex character of MS spectrum of highly fragmenting molecules penetrating through membrane without preceding separation. On the other hand, the possibility of direct connection of a reactor with MS is a great challenge for development of a new techniques and/or evaluation methods.

Experimental

MIMS uses semipermeable membrane acting as a separator enabling selective penetration of followed molecule to the mass spectrometer – typically from working solution. Efficient hydrophobic membrane should hold a substantial part of solvent for maintenance of appropriate pressure conditions in ion source, must be selective against analyzed molecules and chemically and physically stable. From this point of view the membrane property is a critical point of the whole *set-up*. In our contribution we report the results obtained with new type of membrane introduction equipped by conductive Nafion membrane. The comparison with classical Teflon membrane separator is discussed.

For measurements it was used mass spectrometer TRIO 1000 (Finnigan MAT, Fisons Instruments, San José, USA) with software MASSLAB. The vacuum connection with the ion source of the mass spectrometer is provided by a hand controlled vacuum valve

(Balzers, type EVA 016 HX) and by the sample probe inlet valve, using the homemade stainless construction.

Used Nafion membrane (DuPont Fluoroproducts Nafion® Global Customer Service, Fayetteville, USA) was with 51μm thickness and 0,2 μm pore diameter. As referent membrane was used hydrophobic PTFE membrane (GoreTex, No. S10570, size of pore 0,02 μm, thickness 75 μm, porosity 50%). The active area of membrane was determined by the area of supporting porous steel frit Siperm^R R14, (Tridelta Siperm GmBH, Dortmund, SRN) with media size of pore 14μm and porosity 26% (diameter of frit is 10 mm) [3,4].

Two measuring modes could be used, (i) full SCAN mode of all m/z values in a chosen range of masses (SCAN mode), but less sensitive, and (ii) the single ion monitoring mode (SIM mode) which facilitates more sensitive measurement of selected ions (the maximum number of followed m/z values is limited up to 32). Some physical properties of chosen followed species are given in Table 1.

Table 1 *Some physical properties of pure species [5]*

Compound	Molar mass (g mol^{-1})	Normal boiling point (^{0}C)	Dipole moment (D)	Relative permitivity
methanol	32.04	64.6	1.7	33.0
ethanol	46.068	78.29	1.69	25.3
1-propanol	60.095	97.2	1.55	20.8
benzene	78.112	80.09	0	2.2825
toluene	92.139	110.63	0.37	2.379
p-xylene	106.17	138.3	0	2.2735
fluorobenzene	96.102	84.73	1.60	5.465
chlorobenzene	112.557	131.72	1.69	5.6995
bromobenzene	157,008	156.6	1.7	5.45

Results and discussion

All tested species chosen from three sets, the first – methanol, ethanol and 1-propanol (i) represents examples of polar, volatile species. The second – benzene, toluene and p-xylene (ii), are examples of moderately volatile but nonpolar species, whereas the last group of halogenated species (iii) are non-volatile (except fluorobenzene) and moderately polar. In all cases first, we proved the principal penetration of all mentioned compounds and the concentration dependence of major observed ion currents. As it is shown on example of the mass spectrum of fluorobenzene from NIST library of MS data [6], the signal of *m/z* = 96 is signal with highest relative abundance. With using of Nafion membrane we can observe for one unit of m/z scale shift of signal with highest relative abundance to *m/z* = 97 (see Fig. 1). Both signals belong to molecular ion M^+, where M is the molecule of fluorobenzene. The same shift of signal can be observed in the case of chlorobenzene and bromobenzene, as well as in case of aromatics, methanol and ethanol.

Only In case of 1-propanol we observe the fragmentation giving as the main ion current the *m/z* 43, whereas in standard spectrum current of *m/z* 42 is only for about 15 % of the main ion current. The less rich fragmentation is the second typical feature of observed mass spectra.

Conclusions

Tested Nafion membrane enables simplifying of mass spectra of followed species comparing to standard spectra (NIST) and spectra measured with membrane input equipped by classical Teflon membrane. This offers a new “degree of freedom” in case of usage of the membrane inlet in MIMS. Nafion membrane is permeable for all tested groups of species. Using this membrane causes shift of molecular ion signal (or main signal) and the fragmentation pattern is more simple comparing to classical electron impact ionisation. In principle the same effect was observed also in the case of simple alcohols (methanol, ethanol) [7] and aromatic compounds (benzene, toluene, xylene) [8]. This suggests the formation of protonated species via interaction with Nafion. Use of Nafion membrane in MIMS can allow the more simple evaluation of data obtained with DEMS or other membrane-based method of MIMS.

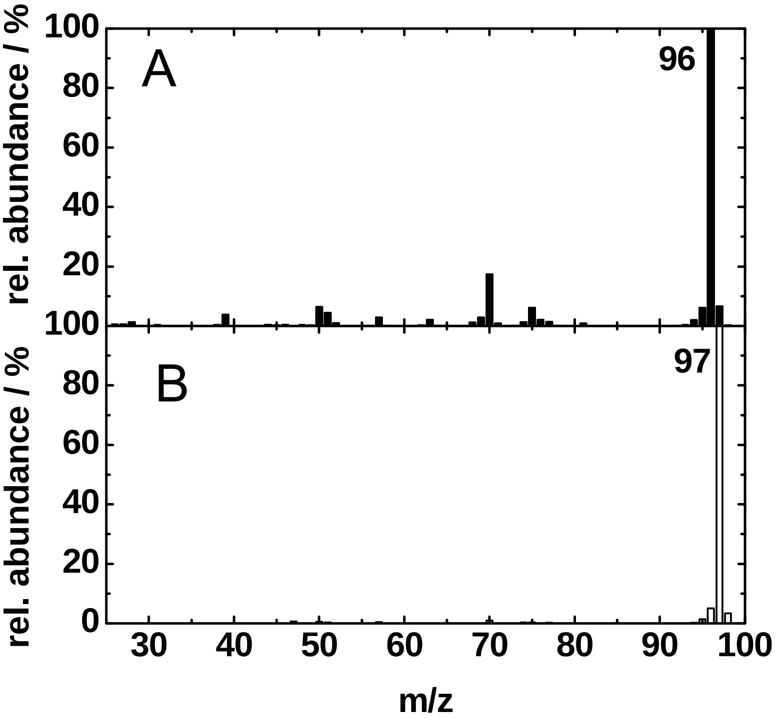

Fig. 1 *Standard mass spectrum of fluorobenzene from NIST library (A) and mass spectrum of fluorobenzene acquired with using Nafion membrane input (B).*

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References

1. B. Bittins-Cattaneo, E. Cattaneo, P. Koenigshoven., W. Vielstich in *Electroanalytical Chemistry, A Series of Advances. Vol 17* (Ed. Bard. A. J.), Marcel Dekker, New York 1991, pp. 181-220.
2. H. Baltruschat in *Interfacial Electrochemistry, Theory, Experiment, and Applications* (Ed. Wieckowski A.), Marcel Dekker, New York 2000, pp. 577-597.
3. P. Brož, E. Drbálková, P. Janderka, P. Sitko, J. Vřešťál: Chemické Listy 94 (2000) 123-128.
4. P. Janderka, E. Drbálková, J. Vřešťál: Chemické Listy 96(2) (2002) 103-110.
5. *Laboratory solvents and other liquid reagents, CRC Handbook of Chemistry and Physics,* (D. R. Lide as Editor-in-Chief), 2005 (http://www.hbcponline.com/).
6. http://webbook.nist.gov, 2005.
7. A. Marcinková: Penetration of organic species through nafion membrane to mass spectrometer, Bachelor Theses, Department of Theoretical and Physical Chemistry, Faculty of Science, Masaryk University, Brno 2005.
8. P. Janderka, P. Ostřížek, M. Gernátová: ChemZi: Proceedings of 57. Congress of chemical societies. Bratislava : Slovak Chemical Society, 2005. Tatranské Matliare 2005, page 90.