특별강연 Ⅱ

Membrane Introduction Mass Spectrometry (MIMS) for On-line, Real Time Analysis of Organic Substances

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The increasing environmental risks exert strong demands for the knowledge of environmentally significant compounds and the reduction of such compounds on the earth. The risk reduction can, in principle, be most effectively achieved by minimizing the formation of environmental pollutants, by-products in many cases, during processes in factories, power plants and other sources. This can be done by on-line, real time monitoring the formation of pollutants at the moment when they are formed, and thereby through the feed-back control of the process.

Mass spectrometer (MS) offers high sensitivity and specificity in the analysis of organic compounds. As used to analyze organic compounds below a threshold concentration, however, this technique requires a certain process enriching the target compounds out of the source stream into the sample stream entering into MS.

MIMS is based on the perm-selective property of a semipermeable membrane which interfaces between liquid or gas sample and the ion source of MS [1-3]. The selective transport of analyte molecules of interest occurs across a semipermeable membrane into MS. In the early stage of MIMS development, flat sheet membranes were used to monitor and control industrial fermentation, analyze organic compounds in water, and in many other applications. Most of the recent development of membrane interfaces has focused on the use of hollow fibers. Membranes in the form of hollow fibers offer some advantages over the flat sheet type, e.g., self-supporting ability and a larger surface area with a given module volume.

Membranes can be mounted external to the MS ion source. In the case of hollow fiber membranes, for example, the interior of the fibers can be exposed directly to the vacuum of the MS ion source. Exposure of the fiber exterior to aqueous- and vapor-phase organic compounds results in permeation of organic compounds through the fiber wall, followed by gas-phase diffusion to the MS ion source. This is called by 'flow-over' ('flow-by' or 'flow-past'), configuration. In this flow-over configuration, Helium gas can be used to sweep the permeated compounds from the membrane probe into the MS ion source.

An alternative is the 'flow-through' configuration where membranes are mounted directly in the MS ion source. As using hollow fibers, air or aqueous samples flows through the interior of the fiber, allowing organic analytes permeate through the fiber wall to the exterior of the fiber. Both types of configuration are schematically described in Fig. 1.

MIMS has been used in a wide variety of applications such as in kinetic studies, for the determination of trace organics in aqueous samples, etc. Below is given an example illustrating the usefulness of MIMS.

Chlorination of drinking water is a public health procedure which has the undesirable side effect of producing chlorinated organic compounds such as dichloroethylene, chloroamines, and organochloroamines. The formation of these compounds can be continuously on-line monitored by MIMS, and thereby their excessive production can be minimized through the feedback control of chlorination.

MIMS also offers a powerful tool for the environmental analysis of organic pollutants at a very low concentration. Organic compounds at concentrations down to low ppm or even ppb can be detected depending on the capability of the membrane interface of discriminating them. Table 1 summerizes detection limits measured for a set of compounds using a silicone rubber membrane probe in conjuction with an ion trap mass spectrometer and a triple quadrupole mass spectrometer, where the membrane is mounted in flow-through configuration.

The quantification can be performed using a calibration curve, an isotopically labeled internal standard, an external standard, and standard addition method. Among these, the last two methods are generally preferred. As using the enternal standard method, however, precaution might be taken against the response dependence on sampling temperature.

The quantitative accuracy of analysis is closely related with the linear dynamic range between the concentration of analyte in sample stream and the MS response (ion intensity). This range accessible by MIMS has been shown to cover, in general, three or more orders of magnitude in concentration, beginning at the low ppb levels. In addition, the matrix effect must be considered when analyzing samples of multi-compounds. Responses of analytes have been observed to be dependent on matrix composition at high concentration levels of analytes in a sample such as at the part-per-thousands levels.

References

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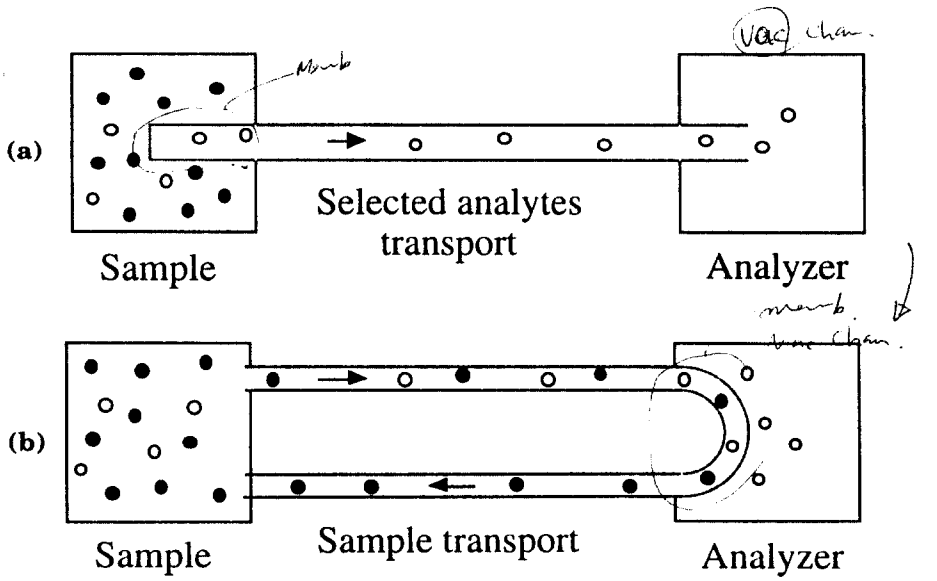

Fig. 1. The schematic description of configurations of the membrane interface in MIMS: (a) flow-over configuration, (b) flow-through configuration.

c) helium as carrier gas.

Table 1. Organic compounds of environmental significance and their detection limits (S/N = 3) using an ion trap or a triple quadrupole mass spectrometer with a 'flow-through' silicone rubber membrane probe [1].

Compound	Detection limit (ppm)
Ion Trap MS (selected ion monitoring mode)	
Benzene	0.001*
Carbon tetrachloride	0.1
Chloroform	0.11
o-Cresol	0.40
1,4-Dichlorobenzene	0.10
1,2-Dichloroethane	0.0048
Hexachloro-1,3-butadiene	0.23
Methyl ethyl ketone	0.091
Nitrobenzene	0.024
Pyridine	0.53
Tetrachloroethane	0.26
2,4,5-Trichlorophenol	0.95
Triple Quadrupole MS (multiple reaction monitoring mode)	
Benzene	0.01
Chlorobenzene	0.01
PFBOA derivative of formaldehyde	0.001*
PFBOA derivative of acetaldehyde	0.010*
Tetrahydrofuran	0.08
Dichloromethane	0.10
Acrolein	0.05*
Acrylonitrile	0.01*

* S/N ratio 2