International Journal of Mass Spectrometry xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Detector aging induced mass discrimination and non-linearity effects in PTR-ToF-MS

M. Müller[a], T. Mikoviny[a,b], A. Wisthaler[a,b,*]

[a] Institute of Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria
[b] NILU-Norwegian Institute for Air Research, Kjeller, Norway

ARTICLE INFO

Article history:
Received 13 November 2013
Received in revised form
10 December 2013
Accepted 10 December 2013
Available online xxx

Keywords:
PTR-TOF-MS
Quantitative chemical analysis
Micro-channel plate
Detector aging
Ion feedback

ABSTRACT

In this short technical paper we demonstrate how aging of the micro-channel plate (MCP) detector in a PTR-ToF-MS instrument induces strong mass discrimination and detection non-linearity effects. Based on exemplary data from an 11-week measurement campaign we show how detector aging led to an m/z-dependent loss in detection efficiency in the m/z 33 (−19%) to m/z 205 range (−67%). Ion signals in the upper m/z range did not increase linearly with analyte concentration (0–150 ppbv) when the MCP detector was not operated in the saturation regime. Both effects may lead to large errors in VOC quantification by PTR-ToF-MS if the instrument is not externally calibrated on a frequent basis. We also demonstrate that the current practice of minimizing ion feedback in the MCP detector will trigger the described problems. Our study may serve as a guide for diagnosing and optimizing PTR-ToF-MS detector performance.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Proton-transfer-reaction mass spectrometry (PTR-MS) is a well-established tool in analytical chemistry for on-line and real-time detection of volatile organic compounds (VOC). It is based on non-dissociative proton transfer reactions from gas-phase hydronium ions (H_3O^+) to organic analyte molecules A. An ion drift tube is used to establish well-defined pseudo-first order ion-molecule reaction conditions. Mass spectrometrically detected abundances of protonated analyte molecules AH^+ scale linearly with neutral analyte densities [A] in the sampling matrix, which typically consists of air. The PTR-MS method is being applied for VOC detection in atmospheric science ([1]; and references therein), in health research ([2]; and references therein), in food science and technology ([3]; and references therein) and in other emerging fields of application (e.g. homeland security, indoor air quality, industrial process gas monitoring).

Conventional PTR-MS instruments use quadrupole mass spectrometers (QMS) with a secondary electron multiplier/pulse counting system for ion detection. Recently, high mass resolution time-of-flight mass spectrometers (ToF-MS) have been implemented to improve both the speed and specificity of the mass spectrometric analysis and to increase the detection efficiency for high mass-to-charge (m/z) signals [4,5].

PTR-MS instruments are usually calibrated using certified VOC gas mixtures, i.e. pressurized nitrogen cylinders that contain stable and accurately known amounts of selected VOC. To derive the instrumental response curve or sensitivity of the instrument (in cps/ppbv), count rates (in counts per second, cps) of analyte ions (AH^+) are measured as a function of the applied mixing ratio (in parts per billion by volume, ppbv) generated by dynamic dilution of the VOC gas mixture. Often it is, however, not feasible to produce or acquire gas standards that contain all analytes of interest. In addition, it is not possible to store reactive or sticky organic gases in a pressurized gas cylinder and more complicated calibration methods need to be applied (e.g. use of diffusion tubes, permeation tubes, photolytic sources).

If no external calibration method is available, the analyte concentration [A] can be calculated from the pseudo-first order kinetic equation which leads to the following well-known expression [6]:

$$[A] = \frac{1}{kt}\frac{[AH^+]}{[H_3O^+]} \quad (1)$$

in which k is the proton transfer reaction rate coefficient, t is the ion residence time in the drift tube and $[AH^+]$ and $[H_3O^+]$ are ion densities in the drift tube. Exothermic proton transfer reactions occur at the collisional rate which can be calculated from ion–molecule collision theories ([7]; and references therein). The

* Corresponding author at: NILU - Norwegian Institute for Air Research, P.O. Box 100, 2027 Kjeller, Norway. Tel.: +47 6389 8000.
E-mail addresses: armin.wisthaler@nilu.no, armin.wisthaler@uibk.ac.at (A. Wisthaler).

1387-3806/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ijms.2013.12.008

ion residence time can be calculated from the known mobility of H_3O^+ ions in air. The ratio of ion densities $[AH^+]/[H_3O^+]$ in the drift tube ideally corresponds to the ratio of the respective count rates measured at the detector.

Often it is, however, not considered that, in both the PTR-QMS and the PTR-ToF-MS instrument, AH^+ and H_3O^+ ions are not detected with the same efficiency, which leads to an error in the calculation of analyte concentrations. A relative difference in the detection efficiency of ions with different m/z-values is correctly referred to as "mass discrimination". The term "transmission", which refers to the ratio of the number of ions reaching the detector and the number of ions entering the m/z-analyzer, should not be used in this context. Mass discrimination occurs during the extraction of ions from the drift tube into the MS, in the MS itself (QMS only) and at the detector. Here we only discuss potential mass discrimination effects introduced by the use of the micro-channel plate (MCP) detector in the PTR-ToF-MS instrument. This type of detector and its operation characteristics are new to most PTR-ToF-MS users. We thus provide some basic introductory material before presenting our study on the performance of the MCP in our PTR-ToF-MS instrument.

An MCP is an array of several millions of linear capillary-type electron multipliers oriented parallel to each other. The channel axes are biased at a small angle (<10°) to the impact surface where an ion hits the wall of a channel with sufficient energy to cause a primary electron emission. Primary electrons are then accelerated by a voltage applied across the MCP. Secondary electrons are emitted, starting an electron avalanche within the MCP channels which ultimately amplifies the initial ion signal by several orders of magnitude. To increase the detector gain, two or three MCPs are usually mounted in series, assembled in chevron or Z-stack configuration [8].

The MCP gain was found to depend upon detector age as well as energy, angle and m/z value of the impacting ion [9–11,17]. Krems et al. [12] found that the MCP efficiency for different positive ion species in the range from m/z 14 to m/z 132 scales to a single curve when plotted as a function of the impact energy divided by $m/z^{0.5}$. Geno and Macfarlane [18] found a linear relationship for the secondary electron emission in the mass range between m/z 86 and m/z 1059 and an exponential correlation for higher m/z values. Axelsson et al. [13] developed an empirical method to correct for mass discrimination effects in matrix-assisted laser desorption/ionization TOF-MS. To minimize ion-energy dependent mass discrimination, ions are usually accelerated through a several kV potential difference before impacting the MCP surface. This so-called ion post-acceleration makes sure that all incident ions in the m/z-range of interest have the required minimum velocity to effectively generate an electron cascade.

Based on its operation principle, an MCP detector should always be used in a high gain mode (or saturation mode; both terms are herein used interchangeably) to avoid mass discrimination effects when single ions are counted as it is done in PTR-ToF-MS instruments. This is to make sure that the electron avalanche is always in saturation and not dependent upon the m/z-value of the impacting ion. One problem with high gain operation is the so-called ion feedback [14,16] which refers to the formation of positive ions from impurities or the residual vacuum in the exit region of the MCP channels. These ions eventually move back through the channels initiating a second electron avalanche and producing a satellite ion peak in the ToF mass spectrum. The use of an MCP stack assembly reduces ion feedback effects, but for the chevron assembly (as used in the PTR-ToF-MS) it is still not negligible. To minimize ion feedback artifacts, PTR-ToF-MS users often do not operate their MCPs in full saturation mode which may introduce strong mass discrimination effects. Similar effects arise when the MCP gain changes over time, both during start-up operation and due to aging over an extended period of operation. Here, we summarize the experiences and tests made during a multi-week measurement campaign exemplifying the errors that may be introduced in quantitative PTR-ToF-MS analyses due to detector-aging induced mass discrimination and non-linearity effects.

2. Materials and methods

2.1. PTR-ToF-MS

A commercial PTR-TOF 8000 instrument (Ionicon Analytik, Innsbruck, Austria) was deployed during an 11-week (with interruptions) measurement campaign at an atmosphere simulation chamber facility. The drift tube was operated at 2.4 mbar pressure, 75 °C temperature and 400 V drift voltage. The PTR-TOF 8000 instrument includes an orthogonal acceleration reflectron time-of-flight mass spectrometer (G-TOF; Tofwerk AG, Thun, Switzerland) which uses a two-stage MCP detector in chevron configuration with a channel length/diameter of 46:1, a bias angle of 8° and an open area ratio of 66% (PHOTONIS Inc., Sturbridge, MA, USA). Applied total MCP voltages (U_{MCP}) were 2240 V and 2460 V. U_{MCP} was only applied during daytime operation (~11 h); during night the voltage was turned off. The post acceleration voltage was set to 5200 V (i.e. close to the maximum settable value of 5300 V) to minimize ion-energy dependent mass discrimination in the m/z range of interest (m/z 21–205). Signal processing in the PTR-TOF 8000 instrument includes an Ionwerks XCD amplifier-discriminator (Ionwerks Inc., Houston, TX, USA) and a high performance time-to-digital converter (HPTDC8-PCI, Cronologic GmbH & Co. KG, Frankfurt, Germany) with 0.1 ns time resolution.

PTR-ToF-MS data were recorded using the TOFDAQ v1.83 data acquisition software (Tofwerk AG, Thun, Switzerland). Mass spectra were recorded up to m/z 350 at 20–60 s integration time. The PTR-TOF Data Analyzer software [15] was used for data analysis.

A dynamically diluted (typically 0–150 ppbv) gas standard (Apel-Riemer Environmental Inc., CO, USA) was used for multi-point instrument calibration which was carried out on a monthly basis. The certified gas standard contained ~1 ppmv of formaldehyde, methanol, acetonitrile, acetaldehyde, acrolein, acetone, isoprene, methyl ethyl ketone, benzene, toluene, hexanal, p-xylene, 1,3,5-trimethylbenzene, 1,2,4,5-tetramethylbenzene, α-pinene, p-dichlorobenzene, decanal, 1,2,4-trichlorobenzene, 1,3,5-triisopropylbenzene, respectively. The accuracy of the gas standard was ±5%.

For external mass axis calibration, a small amount of limonene (in N_2) was continuously added to the PTR-ToF-MS inlet sampling flow from a home-built permeation source to generate a constant mixing ratio of ~1 ppbv in the sampling matrix.

3. Results

3.1. Mass discrimination effects

Limonene, which was used in our study for external mass axis calibration, forms two major ion signals in PTR-MS instruments, a fragment ion at m/z 81 ($C_6H_9^+$) and the protonated parent ion at m/z 137 ($C_{10}H_{17}^+$). Based on our experience with PTR-QMS instruments, stable drift tube operation parameters result in a stable and highly reproducible m/z 81 to m/z 137 ratio in the recorded mass spectra. Any changes in the observed m/z 81 to m/z 137 ratio of a stably operated instrument can thus be used as an on-line diagnostic tool to trace mass discrimination effects in the mass analyzer and/or the detector.

Fig. 1 illustrates the m/z 81 to m/z 137 ratio as observed during 11 weeks of PTR-ToF-MS operation in a laboratory environment. After

Please cite this article in press as: M. Müller, et al., Int. J. Mass Spectrom. (2014), http://dx.doi.org/10.1016/j.ijms.2013.12.008

Download English Version:

https://daneshyari.com/en/article/7605118

Download Persian Version:

https://daneshyari.com/article/7605118

Daneshyari.com