



Short communication

Triacetone triperoxide detection using low reduced-field proton transfer reaction mass spectrometer

Chengyin Shen, Jianquan Li, Haiyan Han, Hongmei Wang, Haihe Jiang, Yannan Chu*

Laboratory of Environmental Spectroscopy, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, P.O. Box 1125, Hefei, 230031 Anhui, PR China

ARTICLE INFO

Article history:

Received 6 February 2009

Received in revised form 24 April 2009

Accepted 27 April 2009

Available online 3 May 2009

Keywords:

Proton transfer reaction mass spectrometry

Triacetone triperoxide

Explosive

On-line detection

ABSTRACT

Proton transfer reaction mass spectrometry (PTR-MS) was applied to on-line detection of the explosive triacetone triperoxide (TATP) using a discharge gas of water vapor or alternative ammonia in the ion source. The dependence of ionic intensity on reduced-field in the drift tube was investigated, and the results indicate that an irregular operation using low reduced-field can enhance TATP detection due to reduced collision-induced dissociation in the drift tube. When water vapor is used as the discharge gas, the characteristic ions for TATP identification are $[\text{TATP} + \text{H}]^+$ which are detectable at a reduced-field about 50 Td. If ammonia is the discharge gas, PTR-MS exhibits a better sensitivity, the explosive TATP can be discriminated according to the adduct ions $[\text{TATP} + \text{NH}_4]^+$, and a limit of detection at ppb level can be achieved at a reduced-field around 100 Td in this PTR-MS apparatus. PTR-MS is suggested as a potential tool for on-site detection of the explosive TATP with the advantages of rapid response and high sensitivity without sample pretreatment.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Triacetone triperoxide (TATP), $\text{C}_9\text{H}_{18}\text{O}_6$ as shown in Fig. 1, is a dangerous explosive with power comparable to TNT [1]. Due to sensitivity to heat, impact and friction, TATP is extremely unstable and has no application in civil engineering or in military. However, TATP can be easily synthesized with readily available chemical precursors such as acetone, hydrogen peroxide and various acid catalysts, thus it has increasingly become an improvised explosive material frequently used in the terrorism activities including the July 2005 London transport bombings and the so-called “shoe bomber” criminals. TATP detection has attracted wide attentions and presented a challenge for public security [2].

Since TATP is thermally labile and contains no nitro groups, the analytical devices for conventional explosives are not suitable for its detection. In recent years, a variety of separation and detection techniques have been strongly investigated for TATP detection [3,4]. For instance, photoacoustic spectroscopy [5], cavity-ringdown spectroscopy [6], ion mobility spectrometry [7–10], and LC or GC separation coupled with MS detection [11–15] have been developed to analyze TATP. But the sample pretreatment and the chromatographic separation make some techniques difficult to detect TATP rapidly. Recently, selected ion flow tube mass spectrometry (SIFT-MS) [16] and desorption electrospray ionization mass spectrometry

(DESI-MS) [17,18] were applied to detect TATP in real-time. However, in their usages the compressed gases are much needed as consuming materials, and in the DESI-MS technique some chemical solvents seem to be released to an open air ambient.

Proton transfer reaction mass spectrometry (PTR-MS) is an on-line detection technique with some advantages such as fast response time, absolute concentration measurement, good limit of detection and almost no consumable. It is especially suitable to field deployment for real-time monitoring of trace volatile organic compounds (VOCs) in environmental monitoring, food inspection and medical applications [19–22]. PTR-MS uses an external discharge ion source to generate special reagent ions H_3O^+ , which do not react with the main components in air like N_2 , O_2 , and CO_2 . In contrast, it can undergo proton transfer reaction with VOCs that have proton affinities (PA) higher than that of water. In PTR-MS, an electric field E is applied along the ion reaction drift tube to induce ionic collisions with kinetic energies beyond the ion-molecular bond energies within cluster ions. Thus the product ions, forming in the proton transfer reactions of reagent ions H_3O^+ with most analytes M , are expected to appear in the form of MH^+ . The ionic collision energy in the drift tube is closely related to a reduced-field E/N , where N is the number density of gas in the drift tube. On a standard PTR-MS instrument, E/N is normally set to a regular value typically in the range of 120–160 Td (corresponding kinetic energy ~ 0.25 eV, $1 \text{ Td} = 10^{-17} \text{ V cm}^2 \text{ molecule}^{-1}$) so as to produce a protonated product for each compound.

However, for volatile compound TATP with a vapor pressure of 5.25×10^{-2} Torr at room temperature [14], it contains very weak

* Corresponding author. Tel.: +86 551 5591076; fax: +86 551 5591076.
E-mail address: ychu@aiofm.ac.cn (Y. Chu).

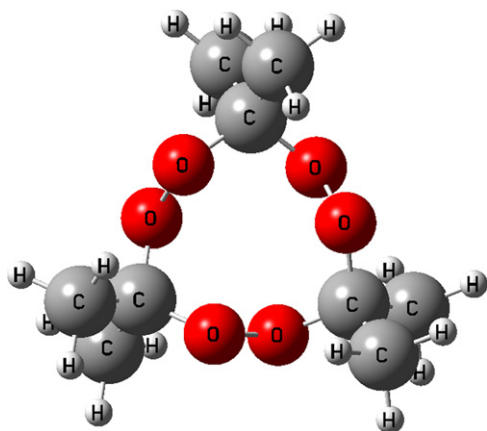


Fig. 1. Structure of triacetone triperoxide (TATP)— $C_9H_{18}O_6$.

O–O bonds [1], thereby its protonation being not easily obtainable in PTR-MS due to collision-induced dissociation in the drift tube especially when a regular E/N value is set, as often used for common VOCs determination. The purpose of this study is to find the proper reduced-field conditions for TATP identification and detection by using a discharge gas either water vapor or alternative ammonia in the ion source. This has been accomplished based on the ionic intensity dependence on the reduced-field in the drift tube. For discharge gas of water or ammonia, the strategies for TATP detection by PTR-MS are proposed. A limit of detection was estimated in the case of ammonia used as the discharge gas.

2. Experimental

TATP detection was performed with a homemade PTR-MS (Fig. 2) [23,24] and a more detailed description about the PTR-MS technique can be found elsewhere [19–22]. A hollow cathode generated either reagent ions H_3O^+ or new reagent ions NH_4^+ . They could be selected through a 3-port valve switching to a discharge gas of water vapor or ammonia. TATP vapor was introduced into the ion reaction drift tube by flowing laboratory air at a rate of 6 mL min^{-1} over the headspace of solid TATP sample at ambient temperature (297 K). The ions in the drift tube, after passing through a small differentially pumping intermediate chamber, were leaked into a vacuum chamber and were detected by a quadrupole mass spectrometer equipped with a pulse ion counting system. The standard gas of toluene was used to check the accuracy of PTR-MS determination, and the concentrations measured by PTR-MS are in agreement with the prepared concentrations in the range 10 ppb to 1.2 ppm [23].

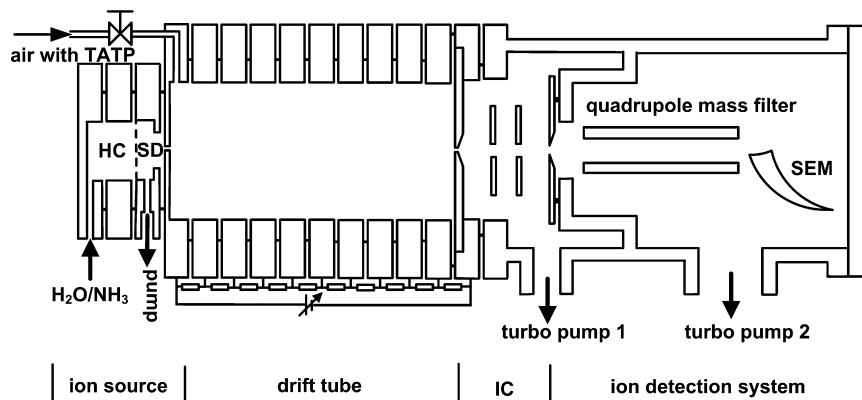


Fig. 2. Schematic diagram of the PTR-MS apparatus. GD, Glow discharge; SD, source drift region; IC, intermediate chamber; SEM, secondary electron multiplier.

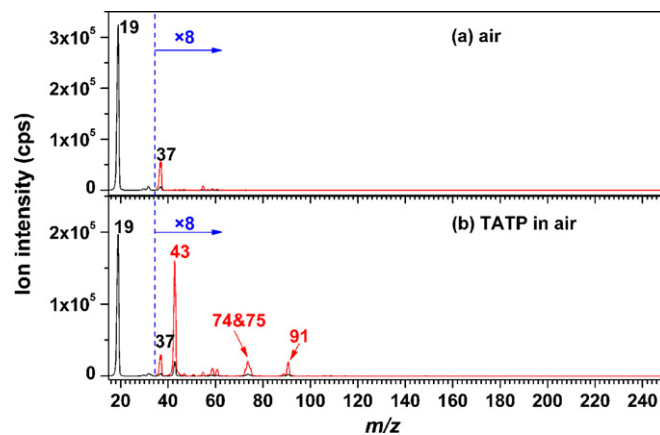


Fig. 3. Mass spectra of (a) air and (b) TATP in air detected by PTR-MS with a discharge gas of water vapor in the ion source using a regular reduced-field $E/N = 141\text{ Td}$.

The pressure in the ion reaction drift tube was kept at 1.0 Torr during the experiment, thus the reduced-field E/N could be changed by adjusting a voltage across the whole drift tube which supplied the electric field E . In the experiment, the proton transfer reaction mass spectrometer was regularly run by deliberately adding a vapor of organic chemical like toluene or acetone to the inlet flow so as to conform its normal operation conditions for the reagent ions H_3O^+ or NH_4^+ . Besides, the laboratory air was detected, and the mass spectrum was used as background to discriminate TATP ionic signals in the ensuing experiments.

The ammonia gas supplied to the ion source was directly obtained from the volatile vapor of ammonium bicarbonate in a gastight container. Small amount of TATP used in the experiment was synthesized according to a method described in the literature [1]. To remove the possible residues of acid and acetone, the TATP sample was continuously washed using water until it displays an acid neutral after the tests of PH values.

The ammonium bicarbonate is chemically pure. The chemicals used to synthesize TATP are analytical reagents. Ammonium bicarbonate and hydrogen peroxide were purchased from Sinopharm Chemical Reagent Co. Ltd. The acetone and sulfuric acid were obtained from Shanghai Zhenqi Chemical Reagent Co. Ltd. and Shanghai Linfeng Chemical Reagent Co. Ltd. respectively.

3. Results and discussion

Fig. 3 shows the mass spectra measured for laboratory air and the air with TATP vapor at a regular reduced-field $E/N = 141\text{ Td}$ using water vapor as a discharge gas in the ion source. Different from

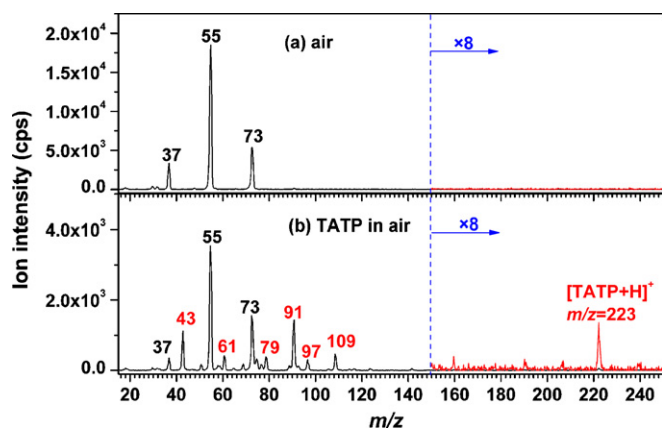


Fig. 4. Mass spectra of (a) air and (b) TATP in air detected by PTR-MS with a discharge gas of water vapor in the ion source using a low reduced-field $E/N = 50$ Td.

the SIFT-MS measurement [16], in the present PTR-MS experiment the protonated TATP at m/z 223 could not be obviously detected at such a regular reduced-field. This is because the TATP protonation is difficult due to collision-induced dissociation in the drift tube. One can note that the protonated acetone signals at m/z 59 in Fig. 3b is much weaker than that in the SIFT-MS experiment, and this probably is due to less acetone residual in our TATP sample. In addition the TATP measurement leads to the ionic peaks appeared at m/z 43, 74, 75 and 91, which are basically similar to the experimental results of TATP analysis by methane positive ion chemical ionization (PICI) mass spectrometry [15] except more abundant ions at m/z 59 in PICI owing to potential acetone residue in TATP sample. The ions at m/z 43, 74, 75 and 91 have been assigned as CH_3CO^+ , $\text{C}_3\text{H}_6\text{O}_2^+$, $\text{C}_3\text{H}_7\text{O}_2^+$ and $\text{C}_3\text{H}_7\text{O}_3^+$ respectively and their formation pathways from the $[\text{TATP} + \text{H}]^+$ fragmentation have been proposed based on the DFT calculations and MS/MS experiments [15].

To attain a characteristic peak of the protonated TATP, the reduced-field E/N in the drift tube was decreased to improve the formation of $[\text{TATP} + \text{H}]^+$ ions by reducing the collision-induced dissociation. Fig. 4 displays the mass spectra measured for air and TATP vapor at a reduced-field $E/N = 50$ Td optimized according to the intensity dependence of product ions on the E/N values. Operating at such a low reduced-field, the $[\text{TATP} + \text{H}]^+$ ions peak indeed occurs at m/z 223 although its count rate is low. In this case, the reagent ions peak of H_3O^+ is very small, and the cluster ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ ($n = 1-3$) at m/z 37, 55 and 73 are dominant. It is sure that the cluster ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ ($n = 1-3$) take part in the reactions with TATP in the drift tube (see Fig. 4a). The cluster ions formed by reaction of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ with TATP should be less strongly bound than the $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ clusters, which means that they will dissociate in the drift tube leading to formation of $[\text{TATP} + \text{H}]^+$.

In Fig. 4b, the ions at m/z 43 and 91 still exist as the product ions. The m/z 91 ions mainly involve $\text{C}_3\text{H}_7\text{O}_3^+$ with a minor contribution from $\text{H}_3\text{O}^+(\text{H}_2\text{O})_4$ in view of the relative abundance of cluster ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ in Fig. 4a. The new present ions at m/z 61, 79 and 97, with the interval of 18, may be the cluster ions involving m/z 43 ions attached by water molecules. The m/z 109 ion is also assigned as a clustering ion of m/z 91 with a water molecule. The ion at m/z 223 is an important characteristic in the TATP identification when using water vapor as the discharge gas of the ion source.

When ammonia was used as a discharge gas in the ion source, the recorded mass spectrum mainly includes reagent ions NH_4^+ at m/z 18 and product ions at m/z 43, 58, 74, 75, 91, 223 and 240. The intensity dependence of these product ions on the reduced-field E/N is shown in Fig. 5, from which a proper E/N is found to be in the range of 90–110 Td for sensitive detection of TATP according to

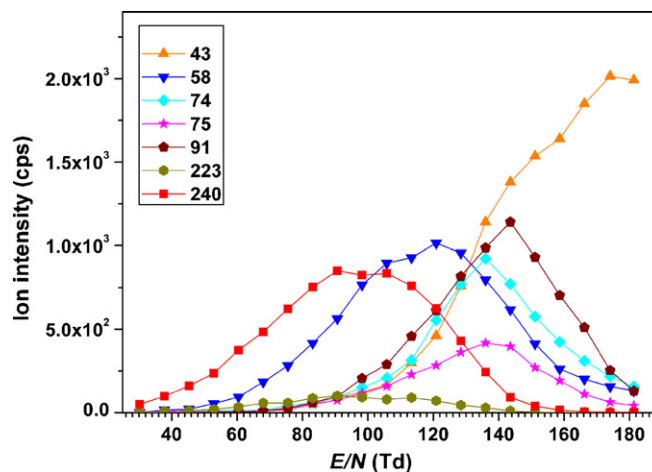


Fig. 5. Dependence of the ionic intensity on the reduced-field E/N for TATP detection by PTR-MS with a discharge gas of ammonia in the ion source.

the product ions m/z 240. Fig. 6 shows a typical mass spectrum of TATP measured at $E/N = 97$ Td, one can see that the product ions at m/z 240 and 58 are most abundant. The ionic peak at m/z 240 are arisen from the adduct ions $[\text{TATP} + \text{NH}_4]^+$. As for m/z 58 ions, to exclude a possibility originated from the residual acetone in the TATP sample, an acetone vapor was directly detected under the same experimental conditions. The results show that product ions for acetone appeared only at m/z 76 which are due to adduct ions $[\text{C}_3\text{H}_6\text{O} + \text{NH}_4]^+$. This demonstrates that the ion at m/z 58 does not result from the ionic reaction with acetone, but at present its composition and formation processes are unknown. Noteworthy is that the m/z 58 ions have also been observed in previous ammonia PICI mass spectrometry [15] and ion mobility spectrometry–mass spectrometry (IMS–MS) [8] with the reagent of ammonia, and the m/z 58 ions were tentatively attributed to acetone ions $\text{C}_3\text{H}_6\text{O}^+$ in IMS–MS [8].

From Figs. 4b and 6b, one can find that the $[\text{TATP} + \text{NH}_4]^+$ ions are more abundant compared with $[\text{TATP} + \text{H}]^+$. This indicates that TATP can be detected with a better sensitivity by using ammonia as a discharge gas in the ion source. The limit of detection can be calculated according to well-established ion-molecular reaction processes on PTR-MS [25]. It is known that the adduct ions of NH_4^+ are formed via the ternary ion-neutral reactions [26,27]. Unfortunately, the rate coefficient of the ternary ion-neutral reactions for the TATP/ NH_4^+ system is unknown; however the effective binary rate coefficient k can be estimated assuming that TATP is compa-

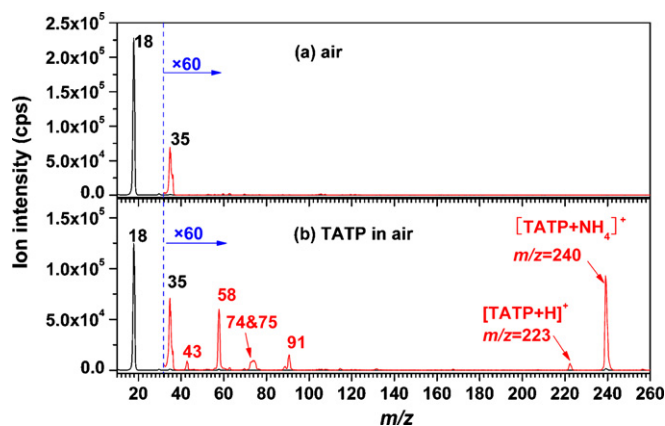


Fig. 6. Mass spectra of (a) air and (b) TATP in air detected by PTR-MS with a discharge gas of ammonia in the ion source using a low reduced-field $E/N = 97$ Td.

nable to acetone in the ionic reaction. Using the experimental data of NH_4^+ reaction with acetone [26], the value of k is calculated to be $1.72 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$ at the typical pressure 1.0 Torr in our experiment. The ion transmission ratio is 0.12 at m/z 240 relative to m/z 18 in our PTR-MS. Thus, in the present PTR-MS apparatus, the product ions at m/z 240, making up 33% of the total product ions, can be detected at a TATP concentration of about 15 ppb after a signal-to-noise ratio of 3:1 is considered [25].

4. Conclusions

When water vapor is used as a discharge gas in the ion source, the PTR-MS with a regular reduced-field in the drift tube will not produce the characteristic ions $[\text{TATP} + \text{H}]^+$ for the explosive TATP. However, a low reduced-field around 50 Td in the drift tube of PTR-MS can lead to the formation of the characteristic ions $[\text{TATP} + \text{H}]^+$, indicating that PTR-MS running at low reduced-field is a good attempt for TATP detection. The better strategy is to utilize ammonia as the discharge gas in the ion source and to operate the drift tube at a reduced-field around 100 Td. In this case PTR-MS can identify the explosive TATP according to the adduct ions $[\text{TATP} + \text{NH}_4]^+$, and a limit of detection at ppb level can be achieved with the present PTR-MS apparatus.

Our PTR-MS with the reagent ions H_3O^+ has a limit of detection around 10 ppb in common VOCs measurement [23]. In fact, a commercial PTR-MS instrument can reach a better limit of detection down to 10 ppt [19,20]. It is expected that, if such a high sensitive PTR-MS instrument is used to detect TATP, the mass spectral characteristics, particularly for the protonated TATP ion $[\text{TATP} + \text{H}]^+$ and the adduct ion $[\text{TATP} + \text{NH}_4]^+$, as revealed in this experiment by irregular operations of PTR-MS at low reduced-field, will be more remarkable, and a better limit of detection can be achieved. PTR-MS will be promising for on-site detection of the explosive TATP, and its advantages are high sensitivity and rapid response without sample pretreatment.

Acknowledgements

Financial support by the National Natural Science Foundation of China (20577049, 20707025), the Scientific Research Equipment Development Program of Chinese Academy of Sciences (Y2005015),

the National High Technology Research and Development Program of China (2007AA06Z420), the Excellent Youth Foundation of Anhui Scientific Committee (06045098), and the 11th Five-year Program of Science and Technology Development of Anhui Province (06012085B) are gratefully acknowledged.

References

- [1] F. Dubnikova, R. Kosloff, J. Almog, Y. Zeiri, R. Boese, H. Itzhaky, A. Alt, E. Keinan, *J. Am. Chem. Soc.* 127 (2005) 1146.
- [2] Y. Bhattacharjee, *Science* 320 (2008) 1416.
- [3] R. Schulte-Ladbeck, M. Vogel, U. Karst, *Anal. Bioanal. Chem.* 386 (2006) 559.
- [4] D.S. Moore, *Sens. Imaging* 8 (2007) 9.
- [5] I. Dunayevskiy, A. Tsekoun, M. Prasanna, R. Go, C.K.N. Patel, *Appl. Opt.* 46 (2007) 6397.
- [6] M.W. Todd, R.A. Provencal, T.G. Owano, B.A. Paldus, A. Kachanov, K.L. Vodopyanov, M. Hunter, S.L. Coy, J.I. Steinfeld, J.T. Arnold, *Appl. Phys. B* 75 (2002) 367.
- [7] G.A. Buttigieg, A.K. Knight, S. Denson, C. Pommier, M.B. Denton, *Forensic Sci. Int.* 135 (2003) 53.
- [8] A.J. Marr, D.M. Groves, *Int. J. Ion Mobility Spectrom.* 6 (2003) 59.
- [9] J.C. Oxley, J.L. Smith, L.J. Kirschenbaum, S. Marimanganti, S. Vadlamannati, *J. Forensic Sci.* 53 (2008) 690.
- [10] R.M. Rasanen, M. Nousiainen, K. Perakorpi, M. Sillanpaa, L. Polari, O. Anttalainen, M. Utriainen, *Anal. Chim. Acta* 623 (2008) 59.
- [11] L. Widmer, S. Watson, K. Schlatter, A. Crowson, *Analyst* 127 (2002) 1627.
- [12] X.M. Xu, A.M. van de Craats, E.M. Kok, P. de Bruyn, *J. Forensic Sci.* 49 (2004) 1230.
- [13] D. Muller, A. Levy, R. Shelef, S. Abramovich-Bar, D. Sonenfeld, T. Tamiri, *J. Forensic Sci.* 49 (2004) 935.
- [14] J.C. Oxley, J.L. Smith, K. Shinde, J. Moran, *Propell. Explos. Pyrotech.* 30 (2005) 127.
- [15] M.E. Sigman, C.D. Clark, R. Fidler, C.L. Geiger, C.A. Clausen, *Rapid Commun. Mass Spectrom.* 20 (2006) 2851.
- [16] P.F. Wilson, B.J. Prince, M.J. McEwan, *Anal. Chem.* 78 (2006) 575.
- [17] I. Cotte-Rodriguez, H. Chen, R.G. Cooks, *Chem. Commun.* (2006) 953.
- [18] I. Cotte-Rodriguez, H. Hernandez-Soto, H. Chen, R.G. Cooks, *Anal. Chem.* 80 (2008) 1512.
- [19] W. Lindinger, A. Hansel, A. Jordan, *Int. J. Mass Spectrom.* 173 (1998) 191.
- [20] J. de Gouw, C. Warneke, *Mass Spectrom. Rev.* 26 (2007) 223.
- [21] S.P. Jin, J.Q. Li, H.Y. Han, H.M. Wang, Y.N. Chu, S.K. Zhou, *Prog. Chem.* 19 (2007) 996.
- [22] R.S. Blake, P.S. Monks, A.M. Ellis, *Chem. Rev.* 109 (2009) 861.
- [23] J.Q. Li, C.Y. Shen, H.M. Wang, H.Y. Han, P.C. Zheng, G.H. Xu, H.H. Jiang, Y.N. Chu, *Chin. J. Anal. Chem.* 36 (2008) 132.
- [24] Y.J. Wang, H.Y. Han, C.Y. Shen, J.Q. Li, H.M. Wang, Y.N. Chu, *J. Pharm. Biomed. Anal.* (2009), doi:10.1016/j.jpba.2009.04.020.
- [25] A. Hansel, A. Wisthaler, *Geophys. Res. Lett.* 27 (2000) 895.
- [26] R.S. Blake, K.P. Wyche, A.M. Ellis, P.S. Monks, *Int. J. Mass Spectrom.* 254 (2006) 85.
- [27] N.G. Adams, L.M. Babcock, T.M. Mostefaoui, M.S. Kerns, *Int. J. Mass Spectrom.* 223–224 (2003) 459.