Analytica Chimica Acta 853 (2015) 508–513

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

Determination of triacetone triperoxide using ultraviolet femtosecond multiphoton ionization time-of-flight mass spectrometry

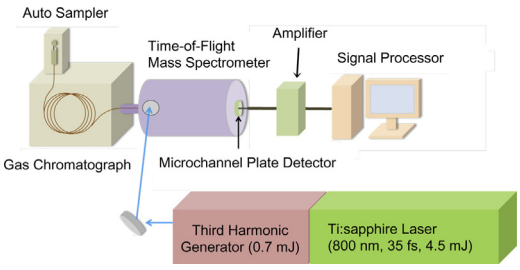
Ryota Ezoe [a], Tomoko Imasaka [b], Totaro Imasaka [a,c,*]

[a] Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
[b] Laboratory of Chemistry, Graduate School of Design, Kyushu University, 4-9-1, Shiobaru, Minami-ku, Fukuoka 815-8540, Japan
[c] Division of Optoelectronics and Photonics, Center for Future Chemistry, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

HIGHLIGHTS

- A UV ultrashort laser pulse was useful for ionization of triacetone triperoxide.
- A molecular ion was strongly enhanced in multiphoton ionization mass spectrometry.
- Triacetone triperoxide in the human blood was measured without any interferences.
- An organic compound of phorone was formed in the human blood from acetone.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 September 2014
Received in revised form 29 October 2014
Accepted 30 October 2014
Available online 1 November 2014

Keywords:
Multiphoton ionization
Mass spectrometry
Molecular ion
Triacetone triperoxide
Explosive

ABSTRACT

Triacetone triperoxide (TATP), an explosive compound, was measured using gas chromatography combined with multiphoton ionization time-of-flight mass spectrometry (GC/MPI-TOFMS). By decreasing the pulse width of a femtosecond laser from 80 to 35 fs, a molecular ion was drastically enhanced and was measured as one of the major ions in the mass spectrum. The detection limits obtained using the molecular ($M^{\bullet+}$) and fragment ($C_2H_3O^+$) ions were similar or slightly superior to those obtained using conventional mass spectrometry based on electron and chemical ionization. In order to improve the reliability, an isotope of TATP, i.e., TATP-d18, was synthesized and used as an internal standard in the trace analysis of TATP in a sample of human blood. TATP could be identified in a two-dimensional display, even though numerous interfering compounds were present in the sample. Acetone, which is frequently used as a solvent in sampling TATP, produced a chemical species with a retention time nearly identical to that of TATP and provided a $C_2H_3O^+$ fragment ion that was employed for measuring a chromatogram of TATP in conventional MS. This compound, the structure of which was assigned as phorone, was clearly differentiated from TATP based on a molecular ion observable in MPI-TOFMS.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Triacetone triperoxide (TATP), an organic peroxide, can be produced using acetone, hydrogen peroxide, and sulfuric acid as the starting materials and is a potent explosive compound [1]. Because of its properties, it has been utilized in numerous terrorist attacks. Ion mobility spectrometry has been utilized for the analysis of TATP in practical applications [2,3]. However, it suffers from a high

* Corresponding author at: Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan. Tel.: +81 92 802 2883; fax: +81 92 802 2888.
E-mail address: imasaka@cstf.kyushu-u.ac.jp (T. Imasaka).

http://dx.doi.org/10.1016/j.aca.2014.10.045
0003-2670/© 2014 Elsevier B.V. All rights reserved.

rate of errors, since the results can change depending on the conditions of the experiment and also on the contaminants present in the sample. For this reason, a hyphenated technique such as liquid chromatography/infrared spectrometry [4], gas chromatography/mass spectrometry (GC/MS) [5], or electrospray ionization/mass spectrometry [6] have been employed. Among them, GC/MS has been successfully used and is one of the most sensitive and reliable methods for its analysis. However, in conventional mass spectrometry based on electron ionization (EI), TATP does not provide a molecular ion [5]. In order to overcome this problem, a positive-ion chemical ionization (PICI) technique has been employed, because of its high selectivity. However, quasi-molecular ions such as $[M+H]^+$ and $[M+NH_4]^+$ are observed, but no molecular ion of $[M]^+$ is produced [5]. This results a more complicated mass spectrum consisting of numerous fragments and several quasi-molecular ions, thus making the assignment more difficult, especially in the trace analysis of TATP in a real sample containing numerous interfering compounds. It should be noted that acetone and related compounds are present even in cosmetics and human breath and provide fragment ions that are similar to those of TATP. Therefore, a selective and more reliable analytical method for measuring TATP in real samples would be highly desirable.

Gas chromatography combined with multiphoton ionization time-of-flight mass spectrometry (GC/MPI-TOFMS) can be used for a comprehensive analysis, allowing the simultaneous determination of numerous compounds from two-dimensional data. This technique has already been used in the analysis of polychlorinated dioxins and polycyclic aromatic hydrocarbons, in addition to several other organic compounds [7]. A vacuum-ultraviolet (VUV) light source is reported to be useful for single-photon ionization of explosives, and the wavelength dependence has been studied using a synchrotron radiation source [8]. An ultraviolet (UV) femtosecond laser has also been used for the efficient ionization of TATP and provides a molecular ion, which is difficult to produce when a long pulse of nanosecond laser is used. In a previous study, a UV femtosecond laser with a short pulse width was found to be preferred for suppressing fragmentation [9,10].

In this study, a high-power UV laser with a shorter pulse width was employed to efficiently ionize TATP in a complex matrix, human blood, which contains numerous interfering species. In order to improve the reliability of the method, an isotope of TATP, i.e., TATP-d18, was synthesized for use as an internal standard. In chemical analyses associated with criminal activities, the residue of the explosives derived from human fluids or tissues, e.g., blood, related tissue, etc., has been measured after extracting the explosive for identification [11]. Due to the redox nature of blood, TATP would be expected to rapidly disappear. To address this issue, the stability of TATP in a sample of human blood was investigated, in order to demonstrate the applicability of this method to the analysis of a real sample. On the other hand, acetone has been employed as a solvent for sampling TATP, and is also one of the chemicals for synthesizing TATP. It is therefore possible that TATP, derived from acetone, might be detected because of the redox properties of blood. In fact, a chemical species that elutes from GC with a retention time that is nearly identical to that of TATP was found in this study. In order to demonstrate superior performance of GC/MPI-TOFMS especially in the practical trace analysis of TATP, this technique was applied to the determination of TATP in human blood, which contains numerous interfering species.

2. Experimental

2.1. GC/MPI-TOFMS

The TOFMS instrument used in this study has been reported in detail elsewhere [12] and is commercially available (HGK-1, Hikari-GK, Fukuoka, Japan). An aliquot of the sample was injected into a GC system (6890GC, Agilent Technologies, CA) using an auto sampler (7683B, Agilent Technologies). Helium was used as the carrier gas, at a flow rate of 1.2 mL min^{-1}. A DB-5ms capillary column (30 m long, 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, Folsom, CA, USA) was employed for the separation of the analytes and an HP-5 capillary column (30 m long, 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, Folsom, CA, USA) for comparison with the DB-5ms column. The temperature of the GC oven was set at 50 °C for 3 min, and then increased at a rate of 8 °C min^{-1} to 130 °C, and subsequently increased at a rate of 40 °C min^{-1} to 210 °C, and then held for 5 min. The injection port was maintained at 110 °C, and the transfer line was set at 100 °C for 10 min and was then set at 210 °C. The fundamental beam of a Ti:sapphire laser (Elite, 800 nm, 35 fs, 4.5 mJ, 1 kHz; Libra, 800 nm, 80 fs, 1 mJ; Coherent Inc., CA, USA) was converted into the third harmonic emission (0.7 mJ for Elite and 0.11 mJ for Libra) for ionization of the analyte molecules. The ions induced were detected by an assembly of microchannel plates (MCP, F4655-11, Hamamatsu, Shizuoka, Japan). The signal was passed through an amplifier (Timing Amplifier 574, ORTEC) and a discriminator (Constant Fraction Discriminator 584, ORTEC) to improve the sensitivity [13]. A block diagram of the experimental apparatus is shown in Supporting information 1.

Supplementry material related to this article found, in the online version, at http://dx.doi.org/10.1016/j.aca.2014.10.045.

2.2. Sample extraction procedure

A 50-μL aliquot of human blood was placed in 24 individual vials, each of which contained 50 ng of TATP. The analyte in the sample mixture was extracted with 1 mL of dichloromethane immediately and at 1, 2, 3, 4, 5, 6, 7 days after sample preparation. A group of three vials prepared under the same conditions was used for evaluating the reproducibility of the method. After extraction and concentration of the sample, 100 μL of synthesized TATP-d18 (approximately 100 ng μL^{-1} in dichloromethane) was added to each solution for use as an internal standard. A blank solution containing no TATP was also prepared to evaluate the contamination of the GC system.

A 50-μL aliquot of human blood was added to 12 individual vials, each of which contained 100 μL of acetone. The analyte in the sample mixture was extracted using 1 mL of dichloromethane immediately and at 1, 2, 3, 4, 5, 6, 7 days after sample preparation. A pair of samples was simultaneously prepared to confirm the reproducibility of the method. After concentrating the sample, 100 μL of TATP-d18 (approximately 100 ng μL^{-1} in dichloromethane) was added to each sample solution. A sample containing no acetone was prepared for use as a blank.

2.3. Chemical regents

A standard solution of TATP dissolved in acetonitrile was purchased from Accustandard (New Haven, CT, USA). The concentration was 100 ng μL^{-1} and was sufficiently low to assure its safety. An internal standard of TATP-d18 was synthesized in our laboratory. The procedure for the syntheses followed a protocol reported in a literature [14]. Briefly, sulfuric acid was added to a mixture of acetone-d6 (2.7 μL, Wako Pure Chemical Industries, Ltd., Osaka, Japan) and 30% w/v hydrogen peroxide (4.6 μL, Wako Pure Chemical Industries, Ltd., Osaka, Japan) and the resulting solution was stored at 2 °C. After 1 h, TATP-d18 was extracted from the reaction mixture using 100 μL of dichloromethane (Wako Pure Chemical Industries, Ltd., Osaka, Japan). After concentration, 100 μL of dichloromethane was added to the sample. This isotope (TATP-d18) was used as an internal standard in the measurement

Download English Version:

https://daneshyari.com/en/article/1163692

Download Persian Version:

https://daneshyari.com/article/1163692

Daneshyari.com