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Determination of hydrazine in drinking water: Development and multivariate optimization of a rapid and simple solid phase microextraction-gas chromatography-triple quadrupole mass spectrometry protocol

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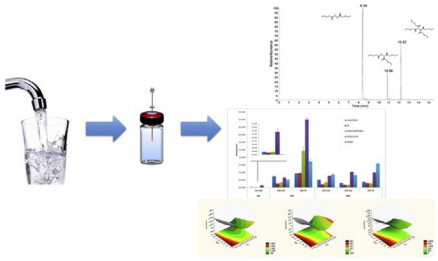
HIGHLIGHTS

- A new SPME-GC-QqQ MS approach was developed for the determination of hydrazine in drinking water at trace levels.
- Multivariate optimization was performed on derivatization reaction, mass spectrometry conditions and SPME parameters.
- SRM acquisition by GC-QqQ-MS instrument enhances the ability in analyte quantification.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the capabilities of solid phase microextraction were exploited in a fully optimized SPME-GC-QqQ-MS analytical approach for hydrazine assay. A rapid and easy method was obtained by a simple derivatization reaction with propyl chloroformate and pyridine carried out directly in water samples, followed by automated SPME analysis in the same vial without further sample handling. The affinity of the different derivatized compounds obtained towards five commercially available SPME coatings was evaluated, in order to achieve the best extraction efficiency. GC analyses were carried out using a GC-QqQ-MS instrument in selected reaction monitoring (SRM) acquisition mode which has allowed the achievement of high specificity by selecting appropriate precursor–product ion couples improving the capability in analyte identification. The multivariate approach of experimental design was crucial in order to optimize derivatization reaction, SPME process and tandem mass spectrometry parameters. Accuracy of the proposed protocol, tested at 60, 200 and 800 ng L^{-1}, provided satisfactory values (114.2%, 83.6% and 98.6%, respectively), whereas precision (RSD%) at the same concentration levels were of 10.9%, 7.9% and 7.7% respectively. Limit of detection and quantification of 4.4 and 8.3 ng L^{-1} were obtained. The reliable application of the proposed protocol to real drinking water samples confirmed its capability to be used as analytical tool for routine analyses.

1. Introduction

Hydrazine (N_2H_4) is a highly reactive base and reducing agent which has found a broad range of industrial and military

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applications. This compound has been used in rocket and spacecraft fuels as well as in agricultural chemicals and pharmaceutical intermediates, in the polymerization of urethane and manufacturing of textile dyes, as an oxygen scavenger or corrosion inhibitor in water boilers and for removal of halogens from wastewater [1–3]. Hydrazine can be found as a contaminant in drinking water especially after chlorination disinfection processes in presence of amines [4,5]. Its toxicity has been described as early as 1908 and it is known to cause irreversible cellular damage [6]. As revealed by results from in vivo studies, alkyl hydrazine derivatives are alkylating agents and the formation of methyl adducts with DNA bases may be one of the mechanisms by which hydrazine causes DNA damage and gene mutations [7,8]. Hydrazine neurotoxicity, hepatotoxicity and nephrotoxicity were confirmed in rodents [9] and also, humans' exposure to this compound can damage the liver, kidney and central nervous systems [10,11].

The vast industrial use of hydrazine implicitly lead to increasing environmental occurrence especially in groundwater in proximity of production or usage sites. The United States Environmental Protection Agency (EPA) has not classified hydrazine as a drinking water contaminant, but as a probable human carcinogen (B2) [12]. In the European Union, hydrazine classified as substance of very high concern (SVHC) with restriction on its usage by the European Chemicals Agency (ECHA). It is carcinogenic, mutagenic and toxic for reproduction (CMR) but so far still there is not a specific legislation about its occurrence in drinking water [13]. Considering the high health risk related to this compound as well as possible contamination in drinking water, it is critical to develop fast and reliable high-throughput analytical protocols capable of detection at trace levels for application to routine analysis. Determination of hydrazine has been carried out by electrochemical, spectrophotometric, potentiometric, fluorescence and chemiluminescence analysis as well as electrophoresis, at part per million and part per billion levels in environmental samples [14–27]. Both liquid- and gas-chromatographic methods with derivatization have also been used to determine hydrazine in different sample matrices. Several derivatization reagents such as naphthalene-2,3-dialdehyde [27], benzaldehyde [28], 4-chloro-5,7-dinitrobenzofurazan [29], cinnamaldehyde [30], pentafluorobenzaldehyde [31], acetone [5], ortho-phthalaldehyde [32], ethyl, octafluoropentyl and *n*-hexyl chloroformates have been used [33–35]. Most of these derivatization procedures for GC analysis required the use of liquid–liquid extraction to isolate the derivatized hydrazine from the matrices. This step often involves the use of a large sample and solvent volumes along with problems during the pre-concentration of the extracts leading to losses of volatile derivatization products. To date the lowest limits of quantification for the analysis of hydrazine in drinking water were obtained by Davis and Li [5]. In this work, hydrazine was derivatized with acetone in aqueous phase and the reaction products were extracted by liquid–liquid extraction and analyzed by GC-CI-ion trap MS. Notwithstanding the good results achieved by the aforementioned work the use of liquid–liquid extraction may constitute a bottleneck in the sample preparation process by limiting the high throughput of the overall analytical procedure.

Solid phase microextraction has shown over the years its suitability in speeding sample preparation protocols allowing simultaneous extraction and preconcentration of organic compounds from a broad range of matrices such us environmental, biological and food samples [36–39]. Moreover, it was demonstrated that the combination of alkyl chloroformate and SPME represents a convenient approach in the identification and assay of carboxylic acids and amines using automated systems with minimal sample handling [40–44]. Derivatization with alkyl chloroformate can be carried out directly in aqueous sample and the automated extraction was performed by direct immersion of the SPME fiber in the same derivatization vial to avoid the need for further sample treatment prior to GC–MS analysis.

Tandem mass spectrometry (MS/MS) is a well-known technique which is widely employed for analysis of pollutants in several matrices. In particular, using triple quadrupole mass spectrometer in selected reaction monitoring (SRM) acquisition mode improves analytical sensitivity by significantly diminishing the background while ensuring analyte identification.

This work proposes for the first time the application of solid phase microextraction to the determination of hydrazine in drinking water. The combined use of alkyl chloroformates as derivatizing reagents and SPME as sampling technique in the same protocol was chosen with the aim of obtaining an easy procedure with minimal sample handling and very low consumption of toxic solvents, which are not friendly to the environment. Moreover, the capabilities of a GC-QqQ-MS system were exploited in order to obtain very sensitive and realible assay. Using multivariate approach, a careful optimization of derivatization reaction with different alkyl chloroformates was carried out. The analytical utility of multivariate chemometric techniques was also used to investigate the tandem mass spectrometric conditions and the parameters affecting the efficiency of SPME process.

2. Materials and methods

2.1. Chemicals

Hydrazine, pyridine, sodium chloride, ethyl chloroformate (ECF), propyl chloroformate (PCF) and isobutyl chloroformate (IBCF) were obtained from Sigma–Aldrich (Milan, Italy). Labeled hydrazine $^{15}N_2H_2$, used as internal standard, was bought from C/D/N isotopes (Pointe-Claire, Quebec, Canada). The tested solid phase microextraction fibers were purchased from Supelco (Bellefonte, PA, USA) and conditioned as recommended by the manufacturer. Aqueous solutions were prepared using ultrapure water obtained from a Milli-Q plus system (Millipore, Bedford, MA)

2.2. Instrumentation and apparatus

A TSQ Quantum GC (Thermo Fischer Scientific) system constituted by a triple quadrupole mass spectrometer (QqQ) Quantum and a TRACE GC Ultra equipped with a TriPlus autosampler was used for the analysis of the samples. The capillary column used was a Thermo TR-5MS (30 m × 0.25 mm i.d., 0.25 μm film thickness). The GC oven temperature was initially held at 80 °C for 1 min, then ramped at 15 °C min^{-1}–280 °C, and held at this temperature for 5 min. The carrier gas was helium at 1 mL min^{-1} of purity 99.999% and argon at a pressure of 1.0 mTorr was used as collision gas. For SPME analyses, a Thermo PTV straight liner 1 mm (i.d.) × 2.75 mm × 105 mm was used as GC inlet liner. Analyses were performed in splitless mode (splitless time 20 min) and the injector temperature was set at 220 °C. The QqQ mass spectrometer was operated in electron ionization (EI) in selected reaction monitoring (SRM) mode. The transfer line and ionization source temperatures were set at 290 °C and 300 °C, respectively. The emission current was set at 25 μA. The scan width and scan time were set at 0.2 *m*/*z* and 0.1 s for all segments. Peak width of Q1 and Q3 were fixed at 0.7 amu.

2.3. Real samples

Ten real samples of drinking water were collected from public water supply of Rende (CS, Italy, five samples) and Cosenza (Italy, five samples) in 250-mL pre-cleaned amber glass bottles containing 25 mg of Na_2SO_3. Samples were stored in the refrigerator (4 °C)