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A LC–MS method allowing the analysis of HMX and RDX present at the picogram level in natural aqueous samples without a concentration step

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ABSTRACT

The introduction of chloroform into the nebulising gas of a LC/MS electrospray interface (ESI), in a perfectly controlled way, leads to the formation of intense adducts ($[M+Cl]^-$) when a mobile phase containing HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane or octogen) and RDX (1,3,5-trintro-1,3,5-triazacyclohexane or hexogen) is eluted. This LC/MS method allows the direct analysis of aqueous samples containing HMX and RDX at the pictogram level without a concentration step. The method is used to determine HMX and RDX concentrations in ground water samples from a military site.

1. Introduction

In the group of organic explosives, HMX and RDX are, among the military explosives, the most widely used (Fig. 1). Because of their toxicity (RDX is a possible human carcinogen [1]), the monitoring of the explosives released into the environment is an important topic. Those compounds can be detected in soils or in natural waters [2]. So, the use of suitable and efficient analytical methods devoted to trace analysis is therefore required.

The thermal lability of HMX and RDX (named as nitramines) preferably leads to the use of liquid chromatography (LC) instead of gas chromatography (GC) [3]. Usually, as described in the US EPA Method 8330, the analysis of aqueous samples containing explosives is carried out by LC/UV after a concentration step [4]. A sample volume equal to 1 L is necessary. This method is tedious, time-consuming and UV detection leads to a poor sensitivity ($1–10\,\mu g\,L^{-1}$).

The 2004 edition of the drinking water standards and health advisories of the US Environmental Protection Agency (US EPA) recommends a maximum of $400\,\mu g\,L^{-1}$ for HMX and a maximum of $2\,\mu g\,L^{-1}$ for RDX in drinking water for a life-time exposure [1]. The estimated quantitation limits of the EPA Method 8330, when no concentration step is achieved, are equal to $13\,\mu g\,L^{-1}$ for HMX and $14\,\mu g\,L^{-1}$ for RDX [5]. Owing to its poor sensitivity, this method is not fully fulfilled for direct analysis of aqueous samples containing traces of RDX. Thanks to its good sensitivity, mass spectrometry allows the detection of a specific ion at traces level. The development of atmospheric pressure ionisation (API) interface in mass spectrometry allows direct detection of traces of explosives by LC/MS, without a concentration step [6–8]. The complete separation of different explosives having very different physical properties (such as nitramines, nitric esters and nitroaromatics) in a same run cannot be easily realised on conventional reverse phase columns. LC separation with porous graphitic carbon (PGC) column followed by MS detection with negative adduct formation allows the analysis of nitramines, nitric esters and nitroaromatics in a single method [9,10]. Tachon et al. compare the analysis by LC/MS of explosives with an atmospheric pressure chemical ionisation (APCI) interface for forensic investigations [9]. The described LC/APCI-MS method claims good performances in terms of selectivity, sensitivity and robustness. However, the limits of detection for HMX and RDX are respectively equals to 3.6 ng and 2.2 ng. Holmgren et al. used the same method (LC separation with PGC column followed by APCI/MS) and obtained the quite similar limits of detection for HMX (0.7 ng) and RDX (3.2 ng) [10]. The main drawback of APCI interface is that it requires a high temperature (typically a minimum of 300 °C) to ensure the complete vaporisation of the mobile phase leading to partial loss of heat labile compounds. For example, the thermal decomposition values of HMX and RDX are

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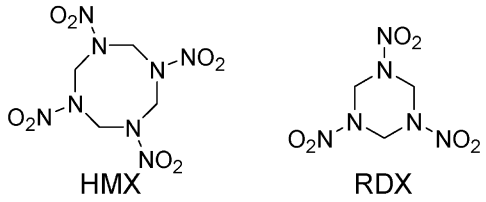

Fig. 1. Structural formulae of HMX and RDX.

respectively equals to 280 °C and 213 °C [11]. So, in APCI part of the RDX molecules decompose yielding NO_2^- species which leads to adduct formation with a second RDX molecule producing abundant $[M+NO_2]^-$ cluster ions [6]. This parameter could hamper the analysis of environmental samples containing ultratraces of such explosives.

In the case of nitramines analysis, ESI is the most suitable interface [8]. The drawback of the use of ESI instead of APCI is that nitroaromatics are more difficult to ionise. In ESI, most of the explosives are detected as adduct-species with the exception of nitroaromatics (such as trinitrotoluene, dinitrobenzene, trinitrobenzene) [12,13]. Indeed, the use of additives can enhance the analyte ionisation efficiency leading to higher mass spectrometer sensitivity. In ESI, HMX and RDX are difficult to ionise due to a lack of acidic hydrogen and because their mass spectra are composed of multiple ions [6,14]. To enhance the sensitivity and to allow a better identification of the explosives, some papers report the use of additives such as ammonium salts or organic acids [6,7,12,14,15]. In the presence of those salts, the mass spectra of HMX and RDX are composed of intensive ions of $[M+X]^-$ (X = Cl, CH_3COO, NO_3 or HCOO).

Mathis and McCord present a comprehensive method to allow the screening of a panel of high explosives (HMX, RDX, EGDN, NG and TNT) [12]. Different ammonium salts (nitrate, formate, acetate and chloride) are added to the mobile phase in order to perform multiple negative adduct formation of the different energetic compounds analysed. By adding those salts directly to the chromatographic mobile phase additional specificity and selectivity is obtained. Indeed, information relating to the relative extent of adduct formation (based on intensity ratios) in addition to adduct stability is used to provide a multiplexed detection scheme. No information on the limits of detection obtained is given.

A sensitive method for HMX quantification in environmental samples using LC/ESI-MS is reported by Pan et al. [14]. A detection limit of 0.78 pg for HMX is obtained (lowest detection limit obtained to date) by adding a small amount of acetic acid to the mobile phase and operating at relatively low heated capillary temperature.

The introduction of the additives could be done in various points of the LC/MS apparatus. Indeed, it could be introduced in the aqueous mobile phase, by a post-column system or into the gas feed of the API interface of the mass spectrometer (in the case of a volatile additive).

In this paper, a LC/MS method allowing the direct analysis of natural water samples contaminated by HMX or RDX at the pictogram level without preparation of the sample is described. The analysis of HMX and RDX is conducted because these compounds respond poorly when analysed by GC/MS. Nitroaromatics can be easily analysed by GC/MS so this work only focuses on the analysis of nitramines.

The influence of the additive introduction either in the mobile phase of the LC part or into the nebulising gas of the electrospray (ESI) interface is compared. The post-column process is not considered here because the introduction of the additive by a post-column apparatus dilutes the analyte and spreads the chromatographic peaks [16]. A system is described, allowing the introduction of a liquid additive into the nebulising gas of the electrospray ionisation (ESI) interface of a mass spectrometer, in a perfectly controlled way, leading to limits of detection for HMX and RDX at pictogram level.

2. Experimental

2.1. Chemicals

RDX and HMX standards are provided by Supelco (Saint Quentin Fallavier, France) as 1 mg mL^{-1} solutions in acetonitrile. An intermediate solution containing 1 mg L^{-1} of each compound in acetonitrile is prepared. This solution is used to prepare calibrated aqueous solutions at different concentrations. Methanol and acetonitrile are both HPLC grade and are provided by VWR (Fontenay-sous-Bois, France). HPLC grade chloroform is purchased from Sigma–Aldrich (Saint Quentin Fallavier, France). Ammonium chloride salt is from Merck (Fontenay-sous-Bois, France). Ultrapure water used for the preparation of mobile phases and standard solutions is obtained from a Millipore MilliQ-10 system. Standard solutions and samples are filtered with syringe filters before analysis (PALL Acrodisc CR 25 mm Syringe filter with 0.45 μm PTFE membrane) provided by VWR (Fontenay-sous-Bois, France).

2.2. Standard LC/MS apparatus

A VARIAN 1200L triple quadrupole mass spectrometer, equipped with an ESI interface, coupled with a VARIAN liquid chromatograph is used. In the negative mode, synthetic air is employed as nebulising gas and nitrogen is used as drying gas. The liquid chromatographic system is composed of two VARIAN 210 pumps, a vacuum membrane degasser and a VARIAN 410 MIDAS autosampler. This configuration is used when the additive is added to the mobile phase. In this case, the chromatographic separation is achieved with a VARIAN column (Pursuit C18 reversed-phase type, 25 cm × 2 mm × 5 μm) using an isocratic mobile phase made of water and methanol (50/50, v/v) at a flow-rate of 0.2 mL min^{-1}. Ammonium chloride is employed as an additive and dissolved in the aqueous mobile phase. It is introduced in the aqueous phase at low concentration ($C = 1 \times 10^{-3}$ mol L^{-1} in water) leading to an ammonium chloride concentration in the mobile phase equal to 0.5×10^{-3} mol L^{-1}. The sample injection volume is 100 μL.

2.3. Modified LC/MS apparatus

Our patented system [17], allowing the introduction of the additive into the nebulising gas of the ESI interface, needs the modification of the gas feed. A syringe-pump, a syringe and a stainless steel tee are connected to the nebulising gas supply of the ESI interface (Fig. 2). The liquid ionisable additive is introduced in the syringe and its flow rate is controlled by the syringe pump. A timer triggered by the autosampler controls the time and the length of the additive's introduction. This introduction occurs during a short time window centred around the retention time of the analyte. The additive is sprayed by the nebulising gas and is carried to the ESI needle. At the tip of the needle, the analytes – carried by the LC eluent – and the additive are ionised leading to the formation of the adduct ions (*e.g.* $[M+X]^-$ in a negative mode). Then, those ions are transferred to the analyser of the mass spectrometer. Note that in principle, any mass spectrometer equipped with an ESI interface can be used. The LC eluent is directed to the waste for the first 6 min and after 17 min of analysis via a six-port valve. The fraction of eluent between 6 min and 17 min is introduced in the ESI needle of the mass spectrometer. In this case, the chromatographic separation is achieved with a VARIAN column (Pursuit C18 reversed-phase type,