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A review of available analytical technologies for qualitative and quantitative determination of nitramines

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This review aims to summarize the available analytical methods in the open literature for the determination of some aliphatic and cyclic nitramines. Nitramines covered in this review are the ones that can be formed from the use of amines in post-combustion CO_2 capture (PCC) plants and end up in the environment. Since the literature is quite scarce regarding the determination of nitramines in aqueous and soil samples, methods for determination of nitramines in other matrices have also been included. Since the nitramines are found in complex matrices and/or in very low concentration, an extraction step is often necessary before their determination. Liquid–liquid extraction (LLE) using dichloromethane and solid phase extraction (SPE) with an activated carbon based material have been the two most common extraction methods. Gas chromatography (GC) or reversed phase liquid chromatography (RPLC) has been used often combined with mass spectrometry (MS) in the final determination step. Presently there is no comprehensive method available that can be used for determination of all nitramines included in this review. The lowest concentration limit of quantification (cLOQ) is in the ng L^{-1} range, however, most methods appear to have a cLOQ in the μg L^{-1} range, if the cLOQ has been given.

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Environmental impact

Nitramines constitute a group of compounds that are classified as emerging environmental pollutants, being potent carcinogens. Nitramines can be formed in the atmosphere due to the release of amines from *e.g.* post combustion CO_2 capture plants. The nitramines may end up in the nature at low levels, and for the determination of these nitramines highly sensitive analytical methods are necessary. We have reviewed the available open literature on methods for the determination of nitramines that might be formed from amines used in post combustion CO_2 capture plants.

1. Introduction

This review compiles the available published analytical methods for qualitative and quantitative determination of some aliphatic (linear and cyclic) nitramines. The interest in nitramines (Fig. 1a) has increased in recent years since they are among the possible degradation products of amines used in post-combustion CO_2 capture (PCC) technology.[1–3] The human influence is the dominant cause for the observed global warming that is now reported to be more certain than ever.[4] CO_2 capture, with ultimate long-term storage, has been advanced to be a significant contributor in the global mitigation portfolio.[5,6] The amine based CO_2 capturing method is currently considered the most feasible and hence the one most likely to be first implemented on a large scale.[7] Although there is a promising technology for mitigating excess atmospheric carbon dioxide, concern has been raised since the nitramines are reported as potent carcinogens.[8] In comparison with the more well studied compound group of nitrosamines (Fig. 1b), also formed from the use of amines,[3,9] the nitramines are believed to be less carcinogenic.[8] However, due to the expected longer residence times of the nitramines in the environment, this compound group may pose a higher risk to public health and ecosystems in close vicinity of a PCC plant (<50 km)[10] than the short-lived nitrosamines which are subject to rapid photolysis.[3] Nitramines are believed to be of concern with regard to chronic exposure, whereas acute toxicity is assumed to be negligible. A number of

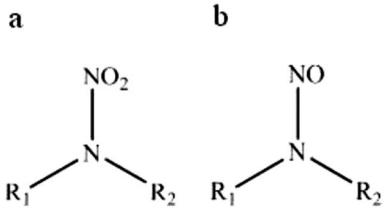

Fig. 1 Chemical structure of (a) nitramine and (b) nitrosamine. In primary nitramine/nitrosamine R1 = H and R2 = aliphatic group and in secondary nitramine/nitrosamine R1, R2 = aliphatic group.

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tests have shown that *N*-nitrodimethylamine (DMNA) and *N*-nitromethylamine (MMNA) are carcinogenic.[11,12] DMNA and MMNA are listed in the Carcinogenic Potency Database (http://toxnet.nlm.nih.gov/cpdb/), and the TD50 values for rats are 0.55 and 17.4 mg per kg per day, respectively. Due to the lack of toxicology data for nitramines, the Norwegian Institute of Public Health has suggested a combined safety threshold concentration of 4 ng of nitramines and nitrosamine per L in drinking water.[10] Other guidelines on safety threshold values are available but mostly for nitrosamines. For example the California Department of Public Health has set the notification level to 10 ng L^{-1} for *N*-nitrosodiethylamine, *N*-nitrosodimethylamine (NDMA) and *N*-nitrosodipropylamine (NDPA),[13] the Drinking Water Inspectorate for England and Wales has set the value to 9 ng L^{-1} for NDMA[14] and the Ministry of Environment of Ontario has set the value to 1 ng L^{-1} for NDMA.[15] Fjellsbø *et al.*[16] studied the eye irritation and skin sensitization/irritation/corrosion of DMNA, MMNA and 2-methyl-2-(nitroamine)-1-propanol (AMP-NO_2) and the result was that all three were irritants for the eye.

From a typical PCC plant, as illustrated in Fig. 2, two different pathways for nitramine formation exist:

1. Atmospheric degradation of amines released with the cleaned flue gas.

2. Oxidative degradation of amines inside the capture unit.

The amines typically used for CO_2 capture have low volatility (*e.g.* alkanolamines),[17] but studies have shown that small alkylamines of higher volatility are formed in the capture process[18] making concurrent atmospheric emissions with the cleaned flue gas virtually impossible to avoid.

In the atmosphere, amines may be converted to nitramines through reactions with hydroxyl radicals OH* (or NO_3/Cl/O_3)[3] and nitrating agents (NO_2) (Fig. 2). The amount of nitramine formed post-emission will therefore depend on the local mixing ratio of NO_x.[19] The hydrophilic nature of the nitramines indicates deposition with rain and fog droplets,[20] and subsequent partitioning between the terrestrial and aquatic phase.

Inside of the capture unit, nitramines may form from oxidative amine degradation in the presence of NO_x. The mechanism proposed is through formation of the nitrating agent dinitrogen tetroxide (N_2O_4).[21] The nitramines are, in contrast to the amines, not very volatile and the low volatility largely limits the direct emission from the plant.[22] The type of nitramines formed is restricted by the properties of the parent-amines. Primary and secondary amines form stable nitramines, whereas tertiary amines are degraded into secondary amines which can then react to form nitramines.[23]

2. Determination of nitramines

The number of publications in the open literature on determination of nitramines is quite scarce compared to those on nitrosamines. The analytical methodologies for determination of nitrosamines in water are quite well established and have been reviewed recently.[24] There are also a number of published standard methods for the determination of nitrosamines,[25–27] and therefore publications on determination of nitrosamines are not included in this review, unless they also cover nitramines. The nitramines included in this review and some of their chemical properties are listed in Table 1. The nitramines included in this review are nitramines that might be formed from amines used in PCC and linear aliphatic nitramines up to *n*-butyl. The mass solubility of the nitramines at pH 7 and ambient temperature ranges from 1 to 1000 g L^{-1}. But most of the nitramines have high water solubility and a low vapour pressure. Most of the primary nitramines, for example MMNA

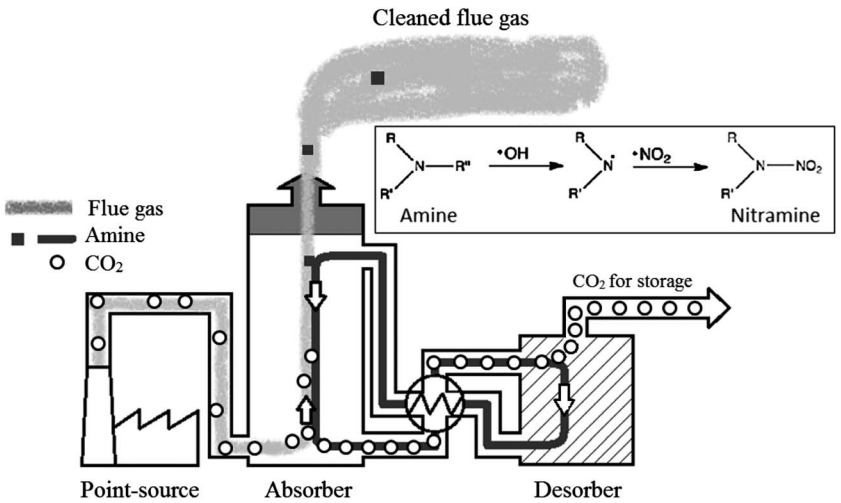


Fig. 2 Schematic illustration of the process of amine-based CO_2 capture. The flue gas (light grey) from an industrial related point-source is fed into the absorber tower in which it counter-currently contacts a stream of liquid amine solution (dark grey). The CO_2 (open circle) is captured from the flue gas by reversibly reacting with amine molecules, forming carbamate complexes. This reaction is subsequently reversed inside the desorber unit by applying heat, resulting in the production of a pure stream of CO_2 suitable for long-term storage. The amine solution is reused in the process, but small amounts may be lost along with the cleaned flue gas. In the atmosphere, rapid degradation processes initiated by the photolytically produced hydroxyl radical may result in the formation of nitramines.

Table 1 Common name, common abbreviations, CAS-no, molar mass (M), vapour pressure, log P, pK_a and chemical structure of nitramines included in the review

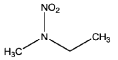
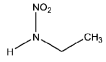
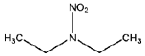
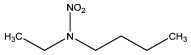
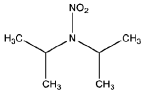
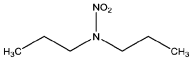
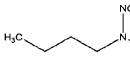
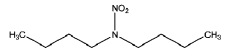
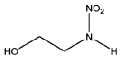
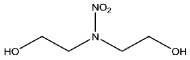
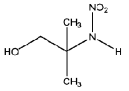
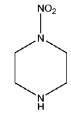
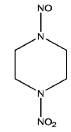
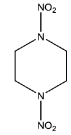
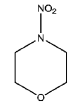
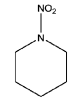
Nitramine (abbreviation)	CAS-no	M^a (g mol^{-1})	Solubility in H_2O at 25 °C, pH 7^a (g L^{-1})	Vapour pressure^a (Torr)	log P^a	p$K_a{}^a$	Structure
N-Nitromethylamine (MMNA)	598-57-2	76.05	1000	19.5	−0.598 ± 0.369	6.51 ± 0.1, −6.14 ± 0.7	
N-Nitrodimethylamine (DMNA)	4164-28-7	90.08	176	0.887	−0.447 ± 0.377	−7.12 ± 0.7	
N-Nitroethylmethylamine (EMNA)	19092-01-4	104.11	76	0.611	0.063 ± 0.377	−6.88 ± 0.7	
N-Nitroethylamine (MENA)	19091-98-6	90.08	652	8.45	−0.089 ± 0.369	6.53 ± 0.10, −6.23 ± 0.70	
N-Nitrodiethylamine (DENA)	7119-92-8	118.13	33	0.340	0.572 ± 0.377	−6.63 ± 0.7	
N-Nitrobutylethylamine (BENA)	52330-08-2	146.19	5.4	0.0481	1.591 ± 0.378	−6.63 ± 0.70	
N-Nitrodiisopropylamine (DIPNA)	4164-30-1	146.19	9.4	0.108	1.280 ± 0.407	−6.14 ± 0.70	
N-Nitrodipropylamine (DPNA)	4164-29-8	146.19	5.4	0.0481	1.591 ± 0.378	−6.67 ± 0.7	
N-Nitrobutylamine (MBNA)	3182-75-0	118.13	100	1.2	0.930 ± 0.370	6.53 ± 0.10, −6.18 ± 0.70	
N-Nitrodibutylamine (DBNA)	4164-31-2	174.24	0.98	7.34×10^{-3}	2.610 ± 0.378	−6.63 ± 0.70	
N-Nitroethanolamine (EtOHNA)	74386-82-6	106.08	1000	1.22×10^{-3}	−1.241 ± 0.433	6.24 ± 0.1, −8.04 ± 0.7	
N-Nitrodiethanolamine (diEtOHNA)	13084-48-5	150.13	171	2.86×10^{-8}	−1.732 ± 0.465	13.85 ± 0.10, −9.27 ± 0.70	
2-Methyl-2-(nitroamine)-1-propanol (AMP-NO_2)	1239666-60-4	134.13	1000	5.91×10^{-3}	−0.476 ± 0.452	6.29 ± 0.1, −7.53 ± 0.7	

Table 1 (*Contd.*)

Nitramine (abbreviation)	CAS-no	M^a (g mol^{-1})	Solubility in H_2O at 25 °C, pH 7^a (g L^{-1})	Vapour pressure^a (Torr)	log P^a	p$K_a{}^a$	Structure
N-Nitropiperazine (NIPZ)	42499-41-2	131.13	236	6.68×10^{-4}	−0.917 ± 0.495	7.58 ± 0.1	
1-Nitro-4-nitrosopiperazine (1,4-NIPZ/NPZ)	107938-05-6	160.13	13	7.49×10^{-8}	−1.143 ± 0.458	−5.61 ± 0.7	
N,N-Dinitropiperazine (1,4-NIPZ)	4164-37-8	176.13	1.5	2.37×10^{-9}	−1.561 ± 0.442	−8.80 ± 0.7	
N-Nitromorpholine (NIMOR)	4164-32-3	132.12	15	1.07×10^{-3}	−1.030 ± 0.456	−9.21 ± 0.2	
N-Nitropiperidine (NIPIP)	7119-94-0	130.15	2.5	0.0106	0.326 ± 0.369	−6.67 ± 0.2	
N-Nitropyrrolidine (NIPYR)	3760-55-2	116.12	4.1	0.0199	−0.201 ± 0.367	−6.63 ± 0.2	
N-Nitrothiazolidine	104549-75-9	134.16	3.1	1.06×10^{-4}	0.065 ± 0.596	−9.63 ± 0.2	

^{a} Values taken from SciFinder (https://scifinder.cas.org/scifinder/view/scifinder/scifinderExplore.jsf).

and *N*-nitroethanolamine (EtOHNA) are weak acids with a pK_a value around 6.2–6.5 (Table 1). Since both the estimation of possible nitramine concentrations in environmental aqueous samples and the threshold value set around the world are in the ng L^{-1} range, highly sensitive analytical methods are needed for their determination. The challenges for establishing reliable quantification methods for nitramines in environmental aqueous samples are (i) that they are present at very low concentrations (ng L^{-1}), (ii) that they are small polar/hydrophilic highly water soluble compounds and (iii) there is a lack of commercially available standards.

Nitramines that are not included in this review are nitramines used in explosives or degradation products of explosives, for example 1,3,5-trinitroperhydro-1,3,5-triazine (RDX).[28]

Table 2 summarizes the available analytical methods for determination of the nitramines listed in Table 1.

2.1 Sample preparation

The analytical chain for the analysis of a sample is divided into a number of steps: (i) planning, (ii) sample collection, (iii) sample preparation, (iv) separation, (v) detection, (vi) evaluation, (vii) interpretation and (viii) validation. The focus in this review for determination of nitramines is on step ii–v.

Sample collection (ii) is an important step regarding the determination of nitramines in environmental samples. But only a few of the articles listed in Table 2 concern nitramine determination in "real" samples, mostly different kinds of water samples. The container material used for sample collection and storage is important and should be evaluated for trace determination of nitramines, to avoid loss of nitramines due to adsorption to the container material. Some of the methods are based on EPA-method 521,[25] which is developed for determination of nitrosamines in drinking water. This method recommends to use amber glass containers for collection of water samples, to dechlorinate collected samples at the time of collection and that samples should not be stored above 6–10 °C, but not frozen.[25] Schreiber *et al.*[29] collected waste water samples in fluorinated high density polyethylene containers, but why this material was selected is not discussed. Some authors also state for how long the samples are stored before further sample preparation and analysis.[30–32] Bjerke *et al.*[33] studied both storage stability in different solvents and possible adsorption of the nitramine standards (DMNA, MMNA, EtOHNA and AMP-NO_2) on the filter used in bacterial filtration and on the wall of falcon tubes and 96-well plates. None or only very little adsorption of the nitramines was found.[33] Regarding storage, the best solvent was water at −18 °C.[33] Possible adsorption of nitramines on glass, which is commonly used for sample collection and storage, has not been published.

The sample preparation might vary depending on the subsequent separation method that will be employed. In the articles listed in Table 2 the sample preparation step is not always described and in the case of determination of nitramines in standard solutions no sample preparation is necessary, except *e.g.* dilution. For extraction of nitramines from different kinds of liquid samples (*e.g.* blood and water) either solid-phase extraction (SPE) or liquid–liquid extraction (LLE) has been used (Table 2). However, prior to the extraction sometimes some additional sample preparation steps such as adjusting of pH and/or quenching of reactions have been performed.[23,29,32–39]

In SPE the nitramines are adsorbed on a solid material and then eluted using a suitable solvent, and by using a smaller elution volume (which may also be further reduced by evaporation) compared to the sample volume applied, the nitramines are enriched. The adsorbent materials that have been used for nitramines are mainly carbon based (Table 2). Bjerke *et al.*[33] tested four different SPE materials for the extraction of DMNA, MMNA, EtOHNA and AMP-NO_2, and found an activated carbon based material to be the best adsorbent. However, some of the nitramines were so well adsorbed that only a few percent of the adsorbed amount could be eluted when different elution solvents were evaluated (See Appendix B in Bjerke *et al.*[33]). Hence improvement of the method by changing the elution strength of the solvents is needed.[33] But if nitrosamines (Fig. 1b) are also included in the analysis method another adsorbent material is recommended to be used, since studies have shown that nitrosamines might be artificially formed if the samples contain amines and nitrites, and active carbon is used as an adsorbent material.[23,40,41] Dichloromethane (DCM) has been the most commonly used elution solvent in SPE of nitramines.[23,29,31,32,34,36,42] Other solvents that have been used as the eluting solvent in SPE or as the extraction solvent in LLE are for example acetone,[30] ethyl acetate,[23,38] DCM + acetone[43] and methanol (MeOH)/tetrahydrofuran/ethylacetate + MeOH.[33]

In LLE, the extraction solvent should not be miscible with the sample solvent and the nitramines should preferably have a higher solubility in the extraction solvent than in the sample. For LLE of nitramines DCM has been the most commonly used solvent.[23,37–39,44–47] However, Bjerke *et al.*[33] showed that only 5–13% of the nitramines EtOHNA, MMNA and AMP-NO_2 were extracted by DCM from water samples, indicating that selection of the extraction solvent is important.

For both samples extracted using SPE and LLE it should also be kept in mind that if the extract is to be analyzed by reversed phase liquid chromatography (RPLC), evaporation of the organic solvent or back extraction[23] of the nitramines into water is necessary.

Since most of the samples listed in Table 2 are liquids, SPE and/or LLE have been the only extraction step necessary. But if the sample is a solid, for example soil, a suitable solid–liquid extraction method is necessary. For extraction of nitramines associated with explosives in soil samples organic solvents have been used.[48,49]

Some of the nitramines listed in Table 1 (DMNA, MMNA, *N*-nitrodiethylamine (DENA)) have also been determined in air- and aerosol samples and cartridges used for sampling have for example been Thermosorb/N, Tenax and charcoal.[9,19,50–52]

Unfortunately, only a few studies on stability of nitramines in aqueous environmental samples have been reported. Hence there is a need for investigation of stability and also possible adsorption of nitramines to sample containers. More thorough studies are also needed for evaluating adsorbent materials and elution/extraction solvents, in order to develop methods where several nitramines can be determined simultaneously at low ppt levels.

Table 2 Available analytical methods for determination of nitramines. a = cLOQ based on LOD × 3, b = Spiked recoveries, ES = elution solvent(s), SPE = solid phase extraction, DCM = dichloromethane, LLE = liquid–liquid extraction, N.A. = not available. For other abbreviations, see explanations in the abbreviation list

Nitramines	Sample	Sample preparation method	Method	Column	Mobile phase/Oven temp	Detector	cLOQ in the sample	Ref.
DMNA	Standard solutions and water samples	SPE: activated coconut charcoal, ES: acetone, V_{sample}: 500 mL, C_{factor}: 500x	GC	Supelcowax 10® 0.53 mm × 15 m × 1 μm	T_{grad}: 40–150 °C	NPD	10 ng L^{-1}	30
DMNA	Standard solutions and synthetic water samples	SPE: activated carbon, ES: DCM, IS: d_6-NDMA before SPE and d_{14}-NDPA before analysis, V_{sample}: 500 mL, C_{factor}: 1000x, according to ref. 25	GC[25]	DB-1701, 0.25 mm × 30 m × 1 μm	T_{grad}: 35–280 °C	MS (CI)	N.A.	42
DMNA	Standards and pool/ aquaria samples	SPE: activated carbon, ES: DCM, IS: d_6-NDMA before SPE and d_{14}-NDPA before analysis. V_{sample}: 500 mL, C_{factor}: 1000x, according to ref. 25	GC[25]	DB-1701, 0.25 mm × 30 m × 1.00 μm with a deactivated silica column, 0.25 mm × 5 m × 0.25 μm	T_{grad}: 34–250 °C	MS (CI)	2 ng L^{-1}	31
DMNA	Standards and municipal waste water	Reaction quenched. SPE: Ambersorb 572.[60] ES: DCM, IS: d_6-NDMA before SPE. V_{sample}: 1000 mL, C_{factor}: 1000x. modification of ref. 61	GC[61]	Supelco SPB™ 1701 capillary column 0.25 mm × 30 m × 0.25 μm	T_{grad}: 35–220 °C	MS (CI)	30 ng L^{-1} [a]	29
DMNA	Standards, water and cell cultures	EPA method 521 (ref. 25) and/or: centrifugation of cell culture. Supernatant resuspended in H_2O and extracted using LLE with DCM. V_{sample} and C_{factor}: N.A. (C_{factor} of EPA method is 500x (ref. 25))	GC[25]	Not stated	T_{grad}: 34–250 °C	MS (CI)	120ng L^{-1} [a]	36
DMNA, EMNA, DENA, DPNA, BENA, NIPYR, NIMOR, NIPIP, and DBNA	Standards	LLE of irradiated samples (water) with DCM. IS: NDEA added before LLE and 1,3-dimethyl-2-nitrobenzene added before analysis. V_{sample}: 5 mL, C_{factor}: 0.5x or 0.2x	GC	JW Scientific DB-5 ms	T_{grad}: 45–250 °C	MS (EI)	3–6 μmol L^{-1} [a], Ex DMNA: 270–540 μg L^{-1} (not specified detection limit for specific nitramines, only state that detection limit is 1–2 μM)	44
NIMOR	Standards, amine samples	LLE with DCM. IS: NPYR added before LLE. Similar method as (ref. 62 and 63) V_{sample} and C_{factor}: N.A.	GC	DB-5 capillary column		MS	N.A.	45

Table 2 (*Contd.*)

Nitramines	Sample	Sample preparation method	Method	Column	Mobile phase/Oven temp	Detector	cLOQ in the sample	Ref.
NIMOR	Standards, amine samples	Addition of Na–ascorbate. LLE with DCM. IS: NPYR added before LLE, V_{sample}: 5 mL, C_{factor}: 5*x*	GC	10% Carbowax 20M stationary phase, 2 mm × 1.8 m	T_{grad}: 120 °C and 160 °C	TEA	2.4 ng [a]	37
DMNA	Standard	N.A.	GC	1% OV-101 on Supelcoport 100–120 mesh, 0.6 cm × 170 cm	T_{grad}: 80 °C, flow: 30 mL min^{-1}	Nitrogen specific	N.A.	12
NIMOR	Amine standard bubbled with NO_2.	LLE with DCM. IS: NPYR added before LLE. Filter through cotton. V_{sample}: 5 mL, C_{factor}: N.A.	GC	10% Carbowax 20 stationary phase on chromsorb WHP 80–100 mesh packed in a glass column, 2 mm × 1.8 m	T_{grad}: 120 °C, T_{pyr}: 475 °C	TEA	N.A.	46
NIMOR	Amine standard bubbled with NO_2.	LLE with DCM. IS: NPYR added before LLE. Filter through cotton, V_{sample}: 5 mL, C_{factor}: 5*x*	GC	10% Carbowax 20 stationary phase on chromsorb WHP 80–100 mesh packed in a glass column, 2 mm × 1.8 m	T_{grad}: 120 °C, gas: helium 10 mL min^{-1}, T_{pyr}: 475 °C	TEA	N.A.	47
NIMOR	Secondary amines treated with peroxynitrite *etc.*	Reaction terminated. LLE with DCM or ethyl acetate	GC	5% FFAP on chromasorb W-HP, 3 mm × 2 m	Gas: argon 30 mL min^{-1}, T_{grad}: 120–190 °C, T_{pyr}: 700 °C	TEA	N.A.	38
		IS: NDBA or *N*-nitrosopipecolic acid added before LLE. Nitro- and nitroso-proline converted to their methyl derivatives with diazomethane. V_{sample}: 1 mL, C_{factor}: N.A.	GC	HP-1, 0.18 × 25 m × 0.18 μm film	Gas: argon 30 mL min^{-1}, T_{grad}: 50–230 °C	MS		38
DENA, DMNA, DBNA	Artificial saliva	Rubber incubated in artificial saliva, HCl and NaOH added. LLE with Extrelut and DCM	GC	10% Carbowax (20 M) on chromosorb W-AW, 2m × 1/4 inch o.d.	Gas: argon 30 mL min^{-1}, T_{grad}: 150 °C, T_{TEA}: 450 °C	TEA	N.A.	65
		IS: *N*-nitrosodiisopropylamine, added before HCl and NaOH, according to Spiegelhalder *et al.*[64]	GC	Capillary OV-101, 0.2 mm × 12 m × 0.3 μm film	T_{grad}: 30–180 °C	MS		65
DMNA, DIPNA	Standards	No sample prep.	LC	Lichrosorb SI-60, 4.6 × 250 mm	7 : 93 EtOH : isooctane	UV, 250 nm	N.A.	66

Table 2 (*Contd.*)

Nitramines	Sample	Sample preparation method	Method	Column	Mobile phase/Oven temp	Detector	cLOQ in the sample	Ref.
EtOHNA, DMNA, NIPZ	Lab-scale PCC samples	No information about sample pretreatment. Deuterated internal standard used	LC	RP-columns	MeOH, ACN, formic acid, acetate buffer	MS APCI or jet stream ESI	0.1–1 μg L^{-1}	67
EtOHNA, AMP-NO_2	Lab-scale PCC samples	No information	LC	N.A.	N.A.	MS	N.A.	68
DMNA	Standards, tap water, pool water, waste water *etc.*	With or without SPE. Some water samples quenched with ascorbic acid, some water samples filtered through cellulose nitrate filters. SPE: HLB and activated carbon. ES: DCM, V_{sample}: 1000 mL, C_{factor}: 1000*x*. Based on Krauss *et al.*[69]	LC	TSKgel G2500PWxl, 7.8 × 300 mm, 7 μm	Gradient, 25 mM phosphate buffer pH 6.7 and ACN	PCUV, 540 nm	8.8 μg L^{-1} without SPE, 12 ng L^{-1} [a] with SPE	32
DENA	Standards		LC	Zorbax-ODS, 4.6 × 150 mm	9 : 1 H_2O : ACN	UV, 254 nm	N.A.	39
DMNA, MMNA, EtOHNA, AMP-NO_2, NIPZ	Standards, air, water, *etc.*	Adjust the pH of sample to 6–6.5, SPE: activated carbon, ES: MeOH, THF, ethyl acetate/MeOH, V_{sample}: 30 mL, C_{factor}: 20*x*	LC	HSS T3, 150 × 2.1 mm, 3 μm (Waters), Atlantis T3, 150 × 2.1 mm, 3 μm (Waters)	Gradient H_2O:ACN	MS, EtOHNA: ESI−, MMNA: ESI−, DMNA: APCI +, NIPZ: ESI+, AMP-NO_2: ESI−	DMNA: 120 μg L^{-1} [a], MMNA: 6.3 μg L^{-1} [a], EtOHNA: 1.5 μg L^{-1} [a], AMP-NO_2: 0.9 μg L^{-1} [a], NIPZ: 1.5 μg L^{-1} [a]	33
DMNA	Standard solutions	No sample preparation	LC	RP-18, 250 × 4.6 mm, 5 μm	3 mM tetrabutylammonium phosphate, pH 7.0.	UV, 232 nm	N.A.	57
NIPZ, DMNA, NIMOR	Wash water lab scale PCC, standard	Quenching of H_2O_2 by addition of sodium sulphite	LC	Inertsil ODS-3, 4.6 × 250 mm, 5 μm	MeOH : H_2O or MeOH : 10 mM phosphate buffer pH 7.7	UV, 245 nm	N.A.	35
EtOHNA, diEtOHNA, 1,4-NIPZ/NPZ, 1,4-NIPZ	Wash water lab scale PCC, standards	V_{sample}/C_{factor}: no LLE or SPE	LC	Hi-Plex ligand exchange, 300 × 6.5 mm, 8 μm	H_2O	UV, 245 nm	N.A.	35
1,4-NIPZ	Standard solutions and thermolysis samples of standards	N.A.	LC	Econosphere C18, 4.6 × 250 mm, 5 μm	MeOH/THF/H_2O	UV, 229 nm	N.A.	56
DMNA, DENA, DIPNA, DPNA			LC	Lichrosorb SI-60, 4.6 × 250 mm	EtOH/isooctane or EtOH/hexane	UV, 254 nm		56
DMNA, DIPNA, NIPIP, NIPYR			GC	DB-05	T_{grad}: 50/60/80 to 180 °C	FID		56
MMNA	Standard solutions and blood samples	Proteins precipitated with MeOH	LC	RP18, 4.6 × 250 mm, 5 μm	10 mM tetrabutylammonium phosphate, pH 7.0	UV, 254 nm	N.A.	34
DMNA			GC			TEA		34

Table 2 (*Contd.*)

Nitramines	Sample	Sample preparation method	Method	Column	Mobile phase/Oven temp	Detector	cLOQ in the sample	Ref.
	Standard solutions, blood samples	Addition of NaOH and IS NDPA, SPE: Extrelut (kieselguhr). ES: DCM, V_{sample}: 20 g, C_{factor}: 20x, According to Spiegelhalder *et al.* (ref. 70)		15% Carbowax column 2 mm × 1.2 m	Helium 25 mL min^{-1} (ref. 70), T_{grad} : 175 °C (ref. 70), V_{inj}: 3–5 μL (ref. 70)		DMNA: 0.42 ng μL^{-1} [a] blood	
DMNA, MMNA	Standard solutions, cell culture samples	LLE with DCM : acetone, V_{sample}: 0.5 mL, C_{factor}: 0.5x	LC[71]	AnionSep Ice-Ion 310 Fast organic acid column, 6.5 × 150 mm	1.73 mM sulfuric acid, 35 °C	UV, 225 nm	N.A.	43
			LC[71]	Zorbax SB-C18, 0.5 × 150 mm, 5 μm	20 : 80 ACN : H_2O	MS, ESI^-		43
			GC	0.33 μm HP-5MS capillary column, 0.2 mm × 50 m	40–200 °C, helium.	MS, EI		43
EtOHNA, diEtOHNA	Standard solutions, water samples	pH adjusted to pH 2 and the day after to pH 5.5–6.0. LLE with ethyl acetate. IS: Addition of d_8-NDEtOH before LLE. V_{sample}: 500 mL, C_{factor}: 500x	LC	Agilent Hi-Plex ligand exchange, 6.5 × 300 mm, 8 μm	30 mM formic acid	MS APCI+	EtOHNA: 75 μg L^{-1} [a], diEtOHNA: 90 μg L^{-1} [a], NDEtOH: 0.6 μg L^{-1} [a]	23
NIPZ	Standard solutions, water samples	No sample prep for analysis of NPZ and NIPZ	LC	Agilent Zorbax 300-SCX 2.1 × 150 mm, 5 μm	8 : 2 10 mM Am. Form. pH 3: ACN	MS APCI+	NPZ & NIPZ: 390 μg L^{-1} [a,b] in deionized water. NIPZ: 1.2 mg L^{-1} [a] in matrix-specific	23
DMNA, NIMOR, 1,4-NIPZ, 1,4-NIPZ/NPZ	Standard solutions, water samples	SPE: activated carbon, ES: DCM,[25] IS: d_6-NDMA and d_8-NMOR added before SPE. V_{sample}: 500 mL, C_{factor}: 500x LLE with DCM. *IS*: d_6-NDMA and d_8-NMOR added before LLE. V_{sample}: 1000 mL, C_{factor}: 1000x	GC[25]	Agilent DB-1701	T_{grad}: 35–250 °C, V_{inj}: 8 μl	MS (CI)	3 μg L^{-1} [a], except 1,4-NIPZ, 1,4-NIPZ/NPZ 30 μg L^{-1} [a]	23
EtOHNA	Standard solutions, soil samples	Nitramine solution mixed with soil. Shaking and sample collection for 192 h. Sample centrifuged and filtered	LC	N.A.	N.A.	MS	N.A.	72
DMNA	Standard solutions, soil samples	As above and LLE with DCM before GC analysis. V_{sample}/C_{factor}: no information	GC	N.A.	N.A.	MS	N.A.	72

Table 2 (*Contd.*)

Nitramines	Sample	Sample preparation method	Method	Column	Mobile phase/Oven temp	Detector	cLOQ in the sample	Ref.
DMNA, DENA, DBNA	Standard solutions	None	GC	FFAP, 0.25 mm × 2 m	Temp: 120 °C	TEA	N.A.	54
			TLC	Silica gel F254	Hexane–diethylether–dichloromethane as an eluent			54
DBNA (GC)	Rat samples (microsomes, hepatocytes and urine)	Microsomes: microsomes obtained.[73] Proteins precipitated. Samples analyzed with GC and LC. Supernatant extracted with ethyl acetate before GC analysis	GC	1.5% OV-17 on chromosorb W		NPD	N.A.	75
DENA, MENA, MBNA (LC)		Hepatocytes: nitramines added to isolated hepatocytes. Samples analyzed with GC and LC	LC	LiChrosorb RP-8, 5 μm	40% ACN	N.A.		75
		Urine: urine fractionated by solvent extraction and hydrolysed by β-glucuronidase.[74] Samples analysed with GC, LC and TLC	TLC	LiChrosorb SI-100, 5 μm	Hexane : ether and hexane : ether : DCM	N.A.		75
MMNA, MBNA	Standards		TLC	Silica gel G, 10 × 20 cm, 0.3 mm	Benzene : nitromethane 2 : 1 or chloroform : nitromethane 10 : 1	UV	N.A.	53

2.2 Separation and detection

Table 2 summarises the published analytical methodologies used for qualitative and quantitative determination of nitramines. The two most common techniques used are gas chromatography (GC) and liquid chromatography (LC) in combination with different kind of detectors. However, thin layer chromatography (TLC)[53,54] has also been used in a few articles. For GC determination the analytes should have a low boiling point (bp)/vapour pressure and be thermally stable at the separation temperature, otherwise a derivatization step might be necessary. A derivatization step may, however, increase the uncertainty of the method since an extra step is added in the sample preparation procedure. From a sustainability point of view it is also advantageous to avoid derivatization since it usually results in the use of extra chemicals and more waste is produced.[55] For analytes requiring derivatization for GC, LC is an alternative technique. For determination of nitrosamines (Fig. 1b), GC is commonly used[24] since nitrosamines have a lower bp compared to the corresponding nitramine. In the standardised methods for determination of nitrosamines, for example EPA method 521,[25] GC is the recommended separation method.

2.2.1 GC. As mentioned above, GC is the separation method of choice if the analytes have low bp and are thermally stable at the temperatures needed for separation. Table 2 shows that GC has been used either as the only analysis method or in combination with LC for some of the analytes in a sample. Various GC stationary phases have been used: non-polar (5%-phenyl 95% dimethyl arylene siloxane, 5%-phenyl 95%-dimethyl polysiloxane), mid-polar (14%-cyanopropyl-phenyl 86%-dimethyl polysiloxane) and polar (polyethylene glycol). The nitramine that has been most frequently determined by GC is DMNA, but it is also the most frequently determined nitramine in general. Of the nitramines listed in Table 1 *N*-nitropiperidine (NIPIP), *N*-nitropyrrolidine (NIPYR), *N*-nitroethylmethylamine (EMNA), *N*-nitrobutylethylamine (BENA), and *N*-nitrodibutylamine (DBNA) have only been determined by GC and EtOHNA, *N*-nitropiperazine (NIPZ), AMP-NO_2, *N*-nitrodiethanolamine (diEtOHNA), *N*-nitrobutylamine (MBNA) and *N*-nitroethylamine (MENA) only by LC. Since most of the publications do not motivate the selection of the analytical method it is not apparent which method is the most suitable for the different nitramines. In some of the cases a reasonable guess is that they had an LC or GC set-up in the lab, which was used. It also appears that if they already had a suitable method for determination of the corresponding nitrosamines, the same method was used for the nitramines, since in many of the publications nitrosamines are determined together with the nitramines. Fournier *et al.*[43] used both a GC and an LC method in their study where DMNA, MMNA and NDMA were determined. A GC-MS method was applied when $^{18}O_2$, D_2O and $H_2{}^{18}O$ were used in the experiments. Oxley *et al.*[56] also used both LC and GC for the determination and state that the reason for different quantification methods depended on the properties of the different analytes studied. In the publication of Hassel *et al.*,[34] a GC method was used for determination of DMNA and MMNA, but if the sample contained [^{14}C]MMNA, the samples were fractionated by LC, and ^{14}C was determined by liquid scintillation counting. Dai *et al.*[23] used LC for the determination of EtOHNA, diEtOHNA and NIPZ, but GC for the determination of DMNA, *N*-nitromorpholine (NIMOR), and 1-nitro-4-nitrosopiperazine (1,4-NIPZ/NPZ). The use of different separation methods also required different sample preparations, see Table 2.

The various detectors used for GC determination of nitramines (Table 2) include MS, thermal energy analyzer (TEA), nitrogen–phosphorus detector (NPD) and flame ionization detector (FID). The most frequently used one is MS with either chemical ionization (CI)[23,29,31,36,42] or electron ionization (EI).[43,44]

2.2.2 LC. When LC has been chosen as the separation technique various stationary phases have also been used (Table 2). The most frequently used stationary phase is silica based C18,[33–35,39,43,56,57] which is also the most commonly used stationary phase in RPLC. However, because C18 phases from different suppliers have different properties, the retention of an analyte may be different on the various columns. None of the published methods where a C18-column has been applied has used the same type of C18-material. In a report from Bjerke *et al.*,[33] six different LC columns were tested for the separation of EtOHNA, MMNA, DMNA, AMP-NO_2 and NIPZ.[33] The two best columns with regard to efficiency and selectivity were a 2.1 × 150 mm HSS T3 column and a 2.1 × 150 mm Atlantis d-C18 column, both from Waters. Both columns are C18 based, but the retention of the five tested nitramines differs. For the HSS T3 column the elution order was NIPZ/EtOHNA – MMNA - AMP-NO_2 – DMNA using a H_2O–acetonitrile (ACN) (2–100% ACN 16 min) gradient and all compounds eluted within 4 minutes. The elution order of the nitramines on the d-C18 column was EtOHNA – MMNA – DMNA – AMP-NO_2 – NIPZ using a H_2O–ACN (0.1–99.9% ACN 8.1 min) gradient, and all compounds were eluted within 12 minutes. Their conclusion was that for all nitramines, except NIPZ, the d-C18 column was preferred, while the HSS T3 column was the best for NIPZ since the d-C18 column gave bad peak symmetry for NIPZ.[33]

Other groups have also used various columns for the determination of various nitramines in the same set of samples. Dai *et al.*[23] used several methods for determination of nitrosamines and nitramines associated with PCC. One LC method was used for the determination of nitramines/nitrosamines with alcohol as a functional group, another LC method was used for the determination of NIPZ and *N*-nitrosopiperazine (NPZ), while a GC-method (EPA method 521[25]) was used for determination of DMNA, NDMA, *N*-nitrosomethylethylamine, *N*-nitrosodiethylamine (NDEA), NDPA, *N*-nitrosomorpholine (NMOR), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosopiperidine, NIMOR, *N*-nitrosodibutylamine (NDBA), NPZ, NIPZ, 1,4-dinitrosopiperazine, 1,4-NIPZ/NPZ and *N*,*N*-dinitropiperazine (1,4-NIPZ).[23] For the LC determination of EtOHNA, diEtOHNA and *N*-nitrosodiethanolamine (NDEtOH) an Agilent Hi-Plex ligand column was used with 30 mM formic acid as the mobile phase.[23] The same group published another article half a year later where they used the same type of column for the determination of EtOHNA, diEtOHNA, 1,4-NIPZ and 1,4-NIPZ/NPZ, but this time 100% water was used as the mobile phase.[35] The reason for excluding

acid in the latter publication was not stated, but better separation was achieved on the Hi-Plex column, which is a strong cation exchange (SCX) column, when acid was excluded. Dai *et al.*[23] used another SCX column for determination of NPZ and NIPZ. The difference between the two SCX columns is the matrix used, the Hi-Plex column is styrene-divinylbenzene based, while the Zorbax SCX-column is silica based. In a later publication, Shah *et al.*[35] used an Intersil ODS-3 column to determine NIPZ, and also NIMOR and DMNA. They do not state why they choose to use different columns and methods in the two publications.

The mobile phases used with the different LC columns are shown in Table 2, and mostly isocratic elution with water and additive (acid/salt) or gradient elution with water and ACN have been used for RP separation. Lee *et al.*[32] used a size exclusion chromatography (SEC) column, but state that the separation of DMNA and the various nitrosamines was not based on the size but on hydrophobic/hydrophilic interactions with the matrix.

The conclusion is that at present there is no column material available for simultaneous LC separation of all the nitramines listed in Table 1.

In all the published LC methods, spectrometric detection, either an ultraviolet (UV)-detector or a MS (see Table 2) has been utilised. An MS is generally much more sensitive than a UV-detector, and thus MS is preferred for analysis of environmental samples where the nitramines might be present at very low concentrations. Another advantage of MS detection is that structural information and hence identification of the analytes can be obtained by analysing the fragmentation pattern of the analyte. UV absorbance spectra of DMNA and EtOHNA are shown in Fig. 3. As seen in Fig. 3 nitramines absorb light in the low UV-range, which might be a problem with gradient elution in LC, since organic solvents and other mobile phase additives often absorb light at low wavelengths. The UV wavelengths that have been used in the published LC-UV analysis (Table 2) range are between 225 nm and 254 nm.

As mentioned above, MS is a more sensitive detection method compared to UV, but it is also more expensive. Detecting nitramines by MS may be hampered by their low molar mass because of many low molar mass interfering ions from for example solvents, LC-MS systems and samples.

Both electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) have been used for ionization of nitramines (Table 2). Dai *et al.*[23] used an APCI interface with positive ionization for detection of EtOHNA, diEtOHNA and NIPZ. In a report by Bjerke *et al.*,[33] the sensitivity of both APCI and ESI in negative and positive mode was evaluated for DMNA, MMNA, EtOHNA, NIPZ and AMP-NO_2. They found that negative ionization was the best for primary nitramines (EtOHNA, AMP-NO_2, MMNA), whereas positive ionization was the best for secondary nitramines (DMNA, NIPZ). Highest sensitivity was achieved using ESI compared to APCI, but in the case of DMNA, UV-detection resulted in the highest sensitivity.[33] Fournier *et al.*[43] also used ESI for determination of DMNA and MMNA, but negative ionization was employed for both nitramines.

The choice of ionization mode has been more thoroughly studied for nitrosamines. Ripolles *et al.*[58] compared ESI and APCI for determination of eight nitrosamines and the highest sensitivity was achieved using APCI. Zhao *et al.*[59] also compared the use of ESI and APCI for determination of eight aliphatic (linear/cyclic) nitrosamines. Their conclusion was that ESI was a better alternative since the parent ion was not generated for some of the thermolabile nitrosamines in the case of APCI. Evans *et al.*[28] compared the use of ESI and APCI for determination of some explosives, whereof one was a cyclic nitramine (RDX), and the limit of detection (LOD) was better using APCI compared to ESI.

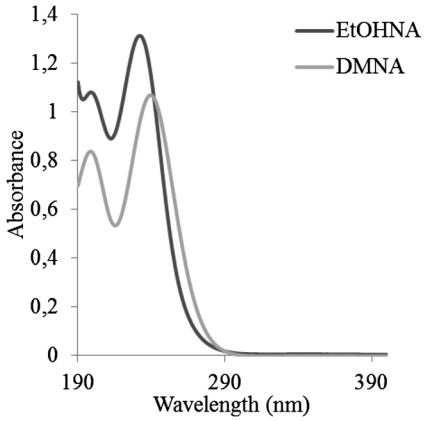


Fig. 3 Absorption spectra of EtOHNA (dark grey) and of DMNA (light grey) in aqueous solution at pH 7.

Thus regarding ionization mode and type, no general conclusion can be drawn for nitramines. The best sensitivity obtainable probably depends on a number of factors such as kind of MS and mobile phase composition. The latter has shown to have an effect on the ionization of the analytes in MS (own observations). None of the articles listed in Table 2 discusses the effect of the mobile phase composition on the sensitivity of the LC-MS methods. However, Ripolles *et al.*[58] noticed that for ESI, a H_2O/MeOH mobile phase resulted in more abundant peaks compared to a H_2O/ACN mobile phase, but this was for determination of nitrosamines. The addition of formic acid to the H_2O/MeOH mobile phase improved the signal further. When APCI was used as an ionization source, the sensitivity was better using H_2O/ACN compared to H_2O/MeOH as the mobile phase.

To date, regarding the choice of the separation method for nitramines associated with PCC, there is no method available in the open literature. A method which can be used for determination of a wide range of nitramines at low concentrations is urgently needed.

2.3 Limit of quantification, enrichment factor and selection of internal standard

The concentration limit of quantification (cLOQ) has only been reported for some of the methods listed in Table 2 and not for all of the nitramines, but in general the cLOQ is in the μg L^{-1} range. There are however, a few exceptions where the cLOQ is in the ng L^{-1} range, but only for DMNA.[29–32] Greene *et al.*,[30] Schreiber *et al.*[29] and Walse *et al.*[31] used SPE for enrichment and

GC in the separation step. With a NPD detector Greene *et al.*[30] found a cLOQ of 10 ng L^{-1}, whereas with MS detection Schreiber *et al.*[29] and Walse *et al.*[31] obtained a cLOQ of 30 ng L^{-1} and 2 ng L^{-1}, respectively. Lee *et al.*[32] also used SPE, but LC-PCUV (post column UV photolysis) for separation and detection, obtaining a cLOQ of 12 ng L^{-1}. Schreiber *et al.*[29] and Greene *et al.*[30] both obtained an extraction efficiency of 0.6, so by increasing the extraction efficiency the detection limit can be further lowered. Lee *et al.*[32] obtained a higher extraction efficiency of 0.80–0.96. The matrix of the sample can also have an interfering effect on the cLOQ and therefore it is important that the sample preparation not only enriches the nitramines but also removes interfering compounds. An example is that the cLOQ limit for NIPZ was ~390 μg L^{-1} in deionized water, but the matrix-specific cLOQ was estimated to ~1.2 mg L^{-1}.[23] NIPZ was determined without any sample preparation and this may explain the higher cLOQ, compared to that of EtOHNA and diEtOHNA.[23] The cLOQ of the nitramines is usually higher compared to the corresponding nitrosamines.[29,36,37] For example the cLOQ of diEtOHNA was 90 μg L^{-1}, which was approximately 10 times higher than that of NDEtOH.[23] The reason for this was not investigated, but the authors speculate that it was due to nitramines being more thermolabile compared to the corresponding nitrosamines.[23]

Another important factor to address in method development is improving the extraction enrichment factor, especially for samples with low concentrations of nitramines. In the four methods where the cLOQ is in the ng L^{-1} range,[29–32] the enrichment factors were 500*x* or 1000*x*, using a sample of 500 or 1000 mL, which were reduced to 0.5–1 mL. Dai *et al.*[23] obtained an enrichment factor of 500*x* or 1000*x* depending on the analyte and extraction method, but the cLOQ was in the μg L^{-1} range. The extraction efficiency varied depending on the extraction method used, from 0.25 up to 0.96–1.2.[23]

The use and selection of the internal standard (IS) is yet another important factor in the quantification. For determination of nitramines it has been most common to use nitrosamines as the IS, either a deuterium labelled nitrosamine of one of those included in the determination or a nitrosamine that is known not to be present in the samples. An IS is added to samples to compensate *e.g.* for the loss of analytes during sample preparation, control of volume of the sample and to compensate for variation in the MS detection response. Thus it is important to choose an IS that will act in a similar way as the analyte(s) of interest, otherwise there is a risk for under or over estimation of the nitramine concentration. The reason why nitrosamines have been used as an IS is probably due to the fact that in many of the methods listed in Table 2, not only nitramines were determined, but also nitrosamines, and nitrosamine standards are commercially available while that is not the case for nitramine standards. If a nitrosamine is chosen as an IS it is important to evaluate that it "behaves" similar to the nitramines in the different steps of the analysis of the sample. In some cases, *e.g.* if the extraction efficiency of the analytes of interest in the sample differ, more than one *IS* can be used. Dai *et al.*[23] for example used two different IS for the determination of DMNA, NIMOR, 1,4-NIPZ, 1,4-NIPZ/NPZ and 11 nitrosamines. A d_6-labelled NDMA was used for early eluting analytes in the GC-method and a d_8-labelled NMOR for the late eluting analytes.[23] More than one IS can also be use to compensate for different parts of the method, for example as in EPA method 521 where one IS is added before SPE and one before GC analysis.[25] Since the commercial availability of the deuterium labelled nitramine standard is very limited, another alternative is to use the so-called standard addition method as Bjerke *et al.*[33] have published. Even though the standard addition method is time consuming it compensates for matrix effects. If external calibration is used, and the calibration standards are prepared in solvents only, which appears to be the case in several of the publications, there is no compensation for possible matrix effects.

3. Concluding remarks

After reviewing the open literature regarding determination of nitramines a number of conclusions can be drawn. To date, there is no universal method published where all nitramines listed in Table 1 can be determined. The lowest reported cLOQs are obtained with GC-MS determination, but GC might not be a viable method for all nitramines due to their low volatility. Therefore, LC-MS seems to be a more promising method if you want to determine several nitramines within one analysis. Because most of the interest today is on nitramine determination in aqueous environmental samples (*e.g.* lake), LC is better suited since exchanging the water to a more volatile solvent is not necessary. For the determination of very low concentrations of nitramines, an extraction step before analysis is necessary. Either SPE or LLE can be used, but so far there is no adsorbent material or extraction solvent, respectively, available where the extraction efficiency of several nitramines is high. Regarding SPE, an alternative can be to use a mixture of adsorbents or to couple SPE columns with different adsorbents in series. Future research has to focus on the evaluation of the SPE-material and the LLE solvent, respectively, and to find an LC column material which separates a broad range of nitramines. Regarding detection, MS seems to be the alternative to use, but the ionization method and selection of the mobile phase will have an effect on the sensitivity of the method, and need to be addressed.

Since the threshold values for nitramines in environmental samples is in the ng L^{-1} range there is a need for new more sensitive analytical determination methods. The main challenge in the development of new methods is that the nitramines are small and polar, and present in very polar matrices (water).

Abbreviation list

1,4-NIPZ	*N,N*-Dinitropiperazine
1,4-NIPZ/NPZ	1-Nitro-4-nitrosopiperazine
ACN	Acetonitrile
AMP-NO_2	2-Methyl-2-(nitroamine)-1-propanol
APCI	Atmospheric chemical ionization
BENA	*N*-Nitrobutylethylamine
bp	Boiling point
C_{factor}	Concentration factor

CI	Chemical ionization
cLOQ	Concentration limit of quantification
d_{14}-NDPA	*N*-d_{14}-Nitrosodi-*n*-propylamine
d_6-NDMA	*N*-d_6-Nitrosodimethylamine
DBNA	*N*-nitrodibutylamine
DCM	Dichloromethane
DENA	*N*-Nitrodiethylamine
diEtOHNA	*N*-Nitrodiethanolamine
DIPNA	*N*-Nitrodiisopropylamine
DMNA	*N*-Nitrodimethylamine
DPNA	*N*-Nitrodipropylamine
EI	Electron ionization
EMNA	*N*-Nitroethylmethylamine
ES	Elution solvent
ESI	Electrospray ionization
EtOH	Ethanol
EtOHNA	*N*-Nitroethanolamine
FID	Flame ionization detector
GC	Gas chromatography
IS	Internal standard
LC	Liquid chromatography
LLE	Liquid–liquid extraction
LOD	Limit of detection
M	Molar mass
MBNA	*N*-Nitrobutylamine
MENA	*N*-Nitroethylamine
MeOH	Methanol
MMNA	*N*-Nitromethylamine
MS	Mass spectrometry
N.A.	Not available
NDBA	*N*-Nitrosodibutylamine
NDEA	*N*-Nitrosodiethylamine
NDEtOH	*N*-Nitrosodiethanolamine
NDPA	*N*-Nitrosodipropylamine
NIMOR	*N*-Nitromorpholine
NIPIP	*N*-Nitropiperidine
NIPYR	*N*-Nitropyrrolidine
NIPZ	*N*-Nitropiperazine
NMOR	*N*-Nitrosomorpholine
NPD	Nitrogen–Phosphours detector
NPYR	*N*-Nitrospyrrolidine
NPZ	*N*-Nitrosopiperazine
PCC	Post-combustion CO_2 capture
PCUV	Post column ultra violet
RDX	1,3,5-Trinitroperhydro-1,3,5-triazine
RPLC	Reversed phase liquid chromatography
SCX	Strong cation exchange
SEC	Size exclusion chromatography
SPE	Solid phase extraction
TEA	Thermal energy analyzer
T_{grad}	Temperature gradient
T_{pyr}	Temperature pyrolyzer
T_{TEA}	Temperature thermal energy analyzer
THF	Tetrahydrofuran
TLC	Thin layer chromatography
UV	Ultraviolet
V_{inj}	Injection volume
V_{sample}	Volume of the sample

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