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# 水中偏二甲肼及其转化产物检测方法研究进展

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**摘要:** 水中偏二甲肼(UDMH)及其转化产物的快速检测对于其污染控制具有重要意义。本文梳理了色谱法(包括气相色谱、高效液相色谱和离子色谱)和非色谱法(包括电化学法、分光光度法、化学发光法)对水中UDMH的检测研究进展,并简要介绍了色谱法在水中UDMH转化产物检测方面的应用研究,指出了不同检测方法在检测浓度范围、样品前处理、抗干扰能力等方面的优缺点,认为色谱前处理装置的高效自动化设计、多种分离和检测技术联用是解决水中UDMH和其转化产物检测难题的未来发展方向。

**关键词:** 偏二甲肼(UDMH);转化产物;色谱法;光谱法

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## 1 引言

偏二甲肼(UDMH)常被用作火箭、导弹的液体推进燃料<sup>[1-2]</sup>,且在植物生长调节、化学合成、制药等方面应用广泛<sup>[3-4]</sup>。但UDMH的毒性较高,具有强致癌性<sup>[5-8]</sup>。俄罗斯规定农业用水中UDMH的极值为 $0.5 \mu\text{g}\cdot\text{L}^{-1}$ ,家庭用水中UDMH的允许水平为 $0.06 \mu\text{g}\cdot\text{L}^{-1}$ <sup>[9]</sup>。我国GB 14374-1993规定航天推进剂废水中UDMH的最高允许排放浓度为 $0.5 \text{mg}\cdot\text{L}^{-1}$ <sup>[10]</sup>。研究表明,未经处理的UDMH遗留在水体中将对人类生存产生严重威胁,而且UDMH氧化后还会产生系列有毒物质,如亚硝基二甲胺(NDMA)、四甲基四氮烯(TMT)、N,N-二甲基甲酰胺(DMF)、偏脞(FDMH)、1-甲基-1H-1,2,4-三唑(MT)、二甲胺、甲醛等,数量达上百种<sup>[11-14]</sup>。

水体中UDMH及其转化产物的检测是其污染控制的重要方面,气相色谱(GC)、高效液相色谱(HPLC)、离子色谱(IC)、电化学法、分光光度法、化学发光法等已广泛应用于该检测领域,经过几十年的发展,其检测范围、检测限、检测种类等都得到了较大提

升。本文从色谱法和非色谱法两个方面,系统梳理了水中UDMH检测研究进展,简要介绍了色谱法在水中UDMH转化产物检测中的研究现状,展望了水中UDMH及其转化产物检测研究的发展方向,以期对相关检测技术的后续研究提供参考。

## 2 水中UDMH检测

### 2.1 色谱法检测水中UDMH

#### 2.1.1 气相色谱(GC)法检测水中UDMH

GC检测灵敏度高、分析速度快、运行成本低,溶剂用量少,受到广大分析工作者的青睐<sup>[15]</sup>,也成为水中UDMH及其转化产物检测的重要手段。但GC法用于水中UDMH检测时面临两个问题,一是水的热膨胀率较大,容易导致GC溢出;二是UDMH具有较强的吸附性和反应活性,与色谱柱相互作用会影响检测结果的准确度和重复性,产生拖尾峰、缩短柱寿命等问题<sup>[16]</sup>。因此,利用GC法分析水中UDMH含量时要排除水基质和UDMH自身对检测过程带来的影响,通常的做法是在UDMH水样进入色谱柱之前对其进行衍生和萃取处理。丙酮、糠醛、水杨醛、2-硝基苯甲醛都曾作为GC法分析UDMH的衍生剂,但是UDMH与上述物质反应时存在衍生时间长、产物不稳定、干扰物影响等问题<sup>[17-21]</sup>。Cathum S等<sup>[22]</sup>研究了几种芳香醛作UDMH衍生剂的效果,发现以4-硝基苯甲醛、4-氯

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GAO Xin, YANG Yu-xue, LU Xin, et al. Progress Progress on Detection Methods of UDMH and Its Transformation Products in Water[J]. Chinese Journal of Energetic Materials (Hanneng Cailiao), 2022, 30(6):611-621.

苯甲醛和4-氰苯甲醛作衍生剂时检测效果较好,但由于衍生得到的腙类产物对光敏感,在检测过程中需采取避光措施。二氯甲烷常被用作GC法测定水中UDMH的萃取溶剂,萃取时加入适量NaCl可有效提高萃取率。衍生和萃取的顺序对检测结果也有一定影响,Cathum S等<sup>[22]</sup>发现若先用二氯甲烷萃取水中UDMH再分别用4-硝基苯甲醛、4-氯苯甲醛和4-氰苯甲醛进行衍生,除4-氰苯甲醛以外,其他两种物质衍生后UDMH的加标回收率明显降低(如表1所示),由此认为UDMH的衍生反应需在萃取之前完成,从而获得最大检测灵敏度。除衍生萃取的前处理方法外,张伟<sup>[23]</sup>等在GC法检测水中UDMH时采用顶空进样,根据气液平衡原理,当UDMH气液达到平衡时直接吸取气体组分,可定量分析0.05~5.0  $\mu\text{g}\cdot\text{L}^{-1}$ 线性范围内的UDMH,检出限为0.0187  $\mu\text{g}\cdot\text{L}^{-1}$ 。

表1 衍生和萃取顺序对水中UDMH回收率的影响<sup>[22]</sup>

Table 1 Effect of derivatization and extraction sequence on recovery of UDMH from water<sup>[22]</sup>

Derivatization agent	% Recovery ( $n=3$ )	
	Derivatization performed after extraction	Derivatization performed before extraction
4-Cyanobenzaldehyde	13.0 $\pm$ 1.7	89.0 $\pm$ 6.6
4-Nitrobenzaldehyde	16.3 $\pm$ 0.6	38.3 $\pm$ 1.2
4-Chlorobenzaldehyde	25.0 $\pm$ 2.0	18.3 $\pm$ 0.6

GC法用于水中UDMH检测时,由于衍生、萃取等前处理速度及仪器自身型号规格的限制,一般适用于实验室内水样的化验分析。

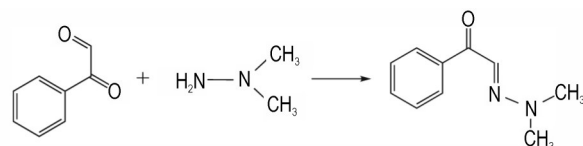
### 2.1.2 高效液相色谱(HPLC)法检测水中UDMH

HPLC法在分析鉴别化合物时不受其挥发性、热稳定性等的限制<sup>[24-25]</sup>,与GC法相比,更适用于水基质中UDMH的直接进样分析。采用HPLC-电化学检测<sup>[26-27]</sup>、HPLC-MS检测<sup>[9]</sup>、HPLC-UV检测<sup>[28-29]</sup>等方法分析水中UDMH的研究都已见报道。与GC法情况类似,HPLC法在现场分析的实时性及便携性方面受到一定限制,一般适用于实验室内含UDMH水样的分析。

UDMH水溶液在波长200 nm附近会产生一宽频特征吸收峰<sup>[30]</sup>,但是水和常见的HPLC用流动相试剂,如甲醇、乙醇、乙腈等,都会在此区域产生干扰吸收,因此HPLC法不能采用UV检测器直接测定UDMH。为了解决此问题,Abdou等<sup>[28]</sup>先用水杨醛将UDMH衍生化,再利用UV检测器测定其衍生化产物在254 nm

处的特征峰,间接分析UDMH的含量,由此避免了水和流动相产生干扰吸收的问题,但是此法对检测低水平( $\mu\text{g}\cdot\text{L}^{-1}$ )的脒不够灵敏。而Kester P E课题组<sup>[27]</sup>同样以水杨醛作衍生剂,采用电化学检测器将水中UDMH的检出限提高至0.20  $\mu\text{g}\cdot\text{L}^{-1}$ 。预浓缩处理技术可以有效提升HPLC检测水中UDMH的能力,Smirnov R S等<sup>[29]</sup>采用固相萃取预浓缩技术,对乙二醛衍生化的UDMH进行处理,使水中UDMH的检测范围拓展至0.01~20  $\mu\text{g}\cdot\text{L}^{-1}$ 。邬春涛等<sup>[31]</sup>利用填充吸附微萃取富集浓缩技术来处理甲醛衍生化的UDMH水样,有效减少了检测中有机溶剂的使用量,检测时间缩短至几分钟。

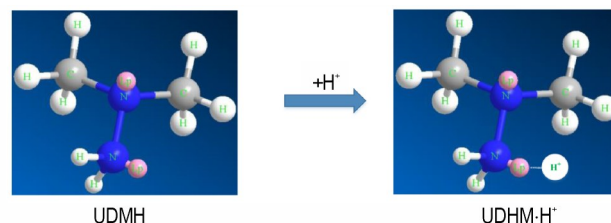
乙二醛做衍生剂时得到的衍生产物分子量较小,会影响MS检测UDMH的灵敏度。针对该问题,Osipenko S V等<sup>[9]</sup>采用苯乙二醛作衍生剂,衍生过程如Scheme 1所示,得到了分子量较大的衍生产物,提高了MS的响应灵敏度,衍生产物还携带易于识别的苯环官能团,采用该法测定时,不进行浓缩预处理即可快速测定天然水体中0.03~1  $\mu\text{g}\cdot\text{L}^{-1}$ 的UDMH。Denisov<sup>[32]</sup>和韩莹<sup>[33]</sup>等的研究中选择4-硝基苯甲醛作UDMH的衍生剂,得到的衍生产物同样可起到提高MS检测灵敏度的效果。



Scheme 1 Derivatization of phenylglyoxal with UDMH<sup>[9]</sup>

### 2.1.3 IC法检测水中UDMH

随着IC分离柱的快速发展,IC检测从一种传统上用于分析无机阴阳离子的分析技术逐渐拓展至水溶性、可电离小分子物质的分析领域<sup>[34-35]</sup>。酸性环境下,UDMH会质子化而生成阳离子物质UDMH $\cdot\text{H}^+$ ,过程如Scheme 2所示。基于这一特性,采用阳离子交换柱的IC法已应用于实验室内水中UDMH的分析检测研究。



Scheme 2 Protonation of UDMH<sup>[36]</sup>

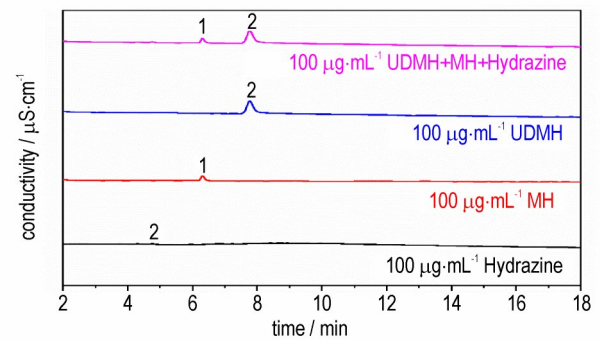
孙素莉等<sup>[37]</sup>用IC法分析水中UDMH时,以 $20\text{ mmol}\cdot\text{L}^{-1}$ 甲烷磺酸溶液为淋洗液将UDMH质子化,而后在CS12A(250 mm×4 mm)阳离子交换柱上进行分离,采用电导检测(CD)能够对 $25\sim 1000\text{ mg}\cdot\text{L}^{-1}$ 范围内的UDMH进行测量,检出限可低至 $0.05\text{ mg}\cdot\text{L}^{-1}$ 。周峰等<sup>[36]</sup>也研究了IC-CD分析测定水中UDMH的方法,优化确定淋洗液组成为 $0.75\text{ mmol}\cdot\text{L}^{-1}$ 的2,6-吡啶二羧酸和 $1.5\text{ mmol}\cdot\text{L}^{-1}$ 的硝酸混合液,实现了 $0.5\sim 1000\text{ mg}\cdot\text{L}^{-1}$ 浓度范围内水中UDMH的快速检测,满足GB 14374-1993规定的UDMH检测需求。与其他方法相比,IC-CD法能够实现水中较宽浓度范围内UDMH的检测分析,在分析高浓度UDMH水样时无需多次加水稀释,可避免由此造成的操作误差。但IC-CD法的稳定性易受样品中其他电活性杂质的干扰<sup>[38-39]</sup>,与UDMH组成(含-N-NH<sub>2</sub>和-CH<sub>3</sub>基团)相似的甲基胂(含-N-NH<sub>2</sub>和-CH<sub>3</sub>基团)、胂(含-N-NH<sub>2</sub>基团)对测定结果的准确性也可能产生影响。周峰等<sup>[36]</sup>就此进行了相关研究,结果表明(如图1所示),低于 $100\text{ }\mu\text{g}\cdot\text{L}^{-1}$ 的碱金属离子(如Li<sup>+</sup>、Na<sup>+</sup>、K<sup>+</sup>、Ca<sup>2+</sup>、Mg<sup>2+</sup>)不会干扰此法对UDMH的检测,甲基胂和胂的存在也不会影响IC柱内UDMH的分离以及后续CD测定的准确性。

## 2.2 非色谱法检测水中UDMH

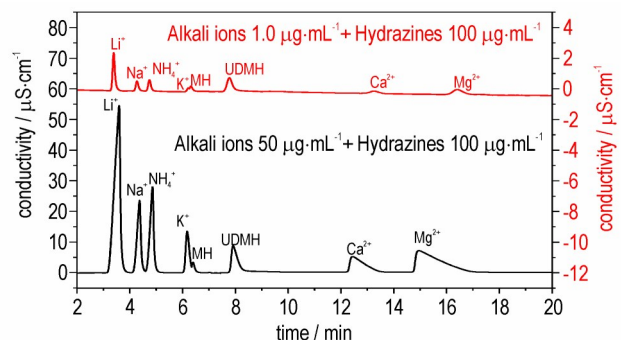
### 2.2.1 电化学法检测水中UDMH

与色谱检测相比,电化学检测设备简单、成本低,无需复杂的前处理,应用于水中UDMH现场快速分析时具有天然优势。电化学检测UDMH的原理如下:在电催化活性电极作用下,UDMH氧化过程的化学信号被转化为相应的电信号,根据电信号强弱可以反推得到一定范围内UDMH的浓度。

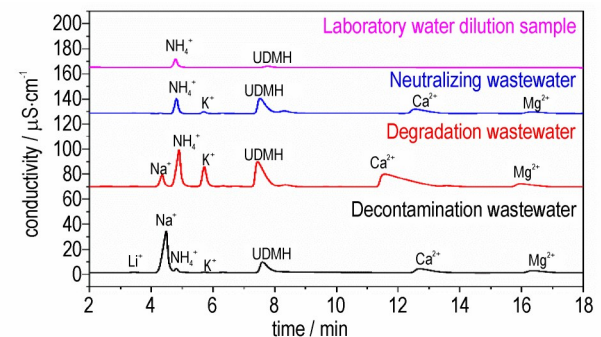
电化学分析过程中,活性电极的电子传输特性、比表面积、对目标检测物质的选择特异性等都会影响检测效果。普鲁士蓝(PB)分子中高自旋三价铁和低自旋二价铁的存在使其成为一种良好的导电活性物质<sup>[40]</sup>,基于这一特性,任向红等制备了PB修饰的碳糊电极(PB/CPE)<sup>[41]</sup>和PB/碳纳米管(TNTs)/CPE电极<sup>[42-43]</sup>。研究发现两种电极在检测水中UDMH时响应良好,尤其是PB/TNTs/CPE电极,引入比表面积较大的TNTs可为PB提供更多附着点位的同时还能进一步提高反应过程中的电子转移效率,其对UDMH的检测限可至 $2.6\times 10^{-2}\text{ mg}\cdot\text{L}^{-1}$ ,线性检测范围为 $0.3\sim 100\text{ mg}\cdot\text{L}^{-1}$ 。碳材料具有超高的导电性及较为活泼的电催化活性,用其修饰电化学检测电极可有效增强电子传导过程。



a. the analysis of UDMH, methyl hydrazine (MH) and hydrazine in IC-CD



b. the interference of separation and detection between hydrazines and alkali metal ions



c. different types of actual wastewater ions chromatograms

图1 金属离子和胂对IC-CD法测定水中UDMH的影响<sup>[36]</sup>

Fig.1 Influence of cations and hydrazines on the determination of UDMH in water by IC-CD method<sup>[36]</sup>

刘祥莹教授课题组用多壁碳纳米管<sup>[44]</sup>和氧化石墨烯/Nafion<sup>[45]</sup>分别修饰玻碳电极来检测水中UDMH,结果表明二者均能较大程度提升电极对水中UDMH的分析能力,检测限可达 $4.38\times 10^{-2}\text{ mg}\cdot\text{L}^{-1}$ 。

利用电化学电极检测水中UDMH时,常见的阴阳离子,如K<sup>+</sup>、Na<sup>+</sup>、Ca<sup>2+</sup>、Fe<sup>2+</sup>、Cu<sup>2+</sup>、Cl<sup>-</sup>、NO<sub>3</sub><sup>-</sup>、CO<sub>3</sub><sup>2-</sup>、SO<sub>4</sub><sup>2-</sup>等,超过一定限度后会影响电极的电子传输特性,进而影响检测精度,测定前需预先去除上述电活性物质的干扰。此外,甲基胂、无水胂、苯胺等物质和UDMH含有相似的结构基团,从而会干扰电极对目标



物质UDMH的选择识别能力,相应增加检测误差,因此提高电极对UDMH的特异性选择能力应是未来电化学电极检测的重点研究方向。

### 2.2.2 分光光度法检测水中UDMH

UDMH本身在近紫外光和可见光区域无特征吸收光谱,因此利用分光光度法分析水中UDMH时需要先对其进行衍生化处理来获得在此光谱区间的吸收产物<sup>[46-47]</sup>。美国职业安全与卫生研究所(NIOSH)提出使用磷钼酸分光光度法测定水中微量UDMH<sup>[48]</sup>,中国GB/T 14376-1993建立了氨基亚铁氰化钠分光光度法来分析水中UDMH含量<sup>[49]</sup>。前者的衍生过程需在95℃下进行60 min,后者的衍生过程需在30℃下进行60 min,反应时间较长,并且测定过程都需使用有害化学试剂。俄罗斯联邦<sup>[50]</sup>提出4-硝基苯甲醛衍生化分光光度法分析水中UDMH浓度,衍生过程在沸腾水浴中进行,反应时间仅需5 min,对UDMH的检出限为5 μg·L<sup>-1</sup>。Kosyakova D S等<sup>[47]</sup>针对环境中UDMH可能与胂、甲基胂并存的情况,以5-硝基-2-呋喃甲醛作衍生剂,建立了一种选择性分光光度法来同时测定这三种物质,在优化的反应条件下(pH=5、衍生剂浓度2 mmol·L<sup>-1</sup>、反应温度60℃、反应时间40 min),UDMH、胂与甲基胂的检出限分别可达1.5 μg·L<sup>-1</sup>、5 μg·L<sup>-1</sup>和3 μg·L<sup>-1</sup>。

分散在液相中的Au纳米粒子会因局域表面等离子体共振(LSPR)效应而使溶液显示独特的颜色,并具有特定的UV-Vis吸收特征<sup>[51-53]</sup>。基于这一原理,Zarei A R等<sup>[54]</sup>在UDMH水溶液中加入Au<sup>3+</sup>,UDMH还原溶液中的Au<sup>3+</sup>,反应产生的Au纳米粒子量与UDMH浓度正相关,再用分光光度法测定Au纳米粒子在λ<sub>max</sub>=550 nm处的LSPR吸收光谱强度,如图2所示(测

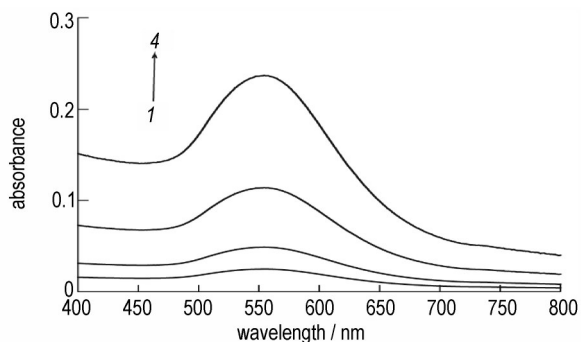


图2 不同浓度UDMH(μg·mL<sup>-1</sup>)作用下Au NPs的紫外-可见吸收光谱:(1)1.0,(2)2.0,(3)5.0,(4)10<sup>[54]</sup>

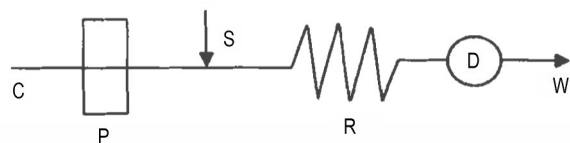
Fig.2 UV-Vis absorption spectra of Au NPs formed in the presence of different concentrations of UDMH, μg·mL<sup>-1</sup>: (1) 1.0, (2) 2.0, (3) 5.0, (4) 10<sup>[54]</sup>

定条件:80 μg·mL<sup>-1</sup> Au(III);15 mM 十六烷基三甲基氯化铵;pH值8.0;反应时间5 min),从而间接推算出水中UDMH浓度。该测定过程需要大约5 min,对水中UDMH的线性检测范围为0.20~10 mg·L<sup>-1</sup>,检出限为0.2 mg·L<sup>-1</sup>。

分光光度法所需仪器设备简单、成本低、易操作,但无法实现水中UDMH的实时分析,更适合实验室分析使用。

### 2.2.3 鲁米诺化学发光法检测水中UDMH

UDMH氧化过程会释放出一定能量,该能量可以激发鲁米诺,使其由基态跃迁至激发态。当鲁米诺由激发态返回至基态时会辐射出最大波长为425 nm的蓝光,测定蓝光的强弱可以间接检测UDMH的浓度<sup>[55-57]</sup>。鲁米诺化学发光体系由氧化剂和鲁米诺共同组成,检测过程中氧化剂将UDMH氧化,鲁米诺则作为发光剂。鲁米诺化学发光反应的速度很快,捕捉发光强度峰值的时间非常短,利用该法进行分析时需确保溶液中UDMH与氧化剂能够快速有效混合,为此常将鲁米诺化学发光法与流动注射技术联合使用。流动注射技术(工作原理如图3所示)集进样、反应、监测等过程控制于一体,可提升检测灵敏度和重现性,缩短测定时间<sup>[58]</sup>。目前,高锰酸钾-鲁米诺<sup>[56]</sup>、高碘酸钾-鲁米诺<sup>[57]</sup>、溴酸钾-鲁米诺<sup>[59]</sup>等发光体系联合流动注射技术都已在水中UDMH的检测中得到研究,线性检测范围为1.0×10<sup>-4</sup>~1.0×10<sup>-1</sup> mg·L<sup>-1</sup>。



C: carrier flow; P: liquid driving device; S: sample injection; R: reaction pipeline; D: detector; W: waste liquid

图3 流动注射工作原理<sup>[60]</sup>

Fig.3 Working principle of flow injection<sup>[60]</sup>

鲁米诺化学发光法检测水中UDMH的效果通常受溶液pH、鲁米诺浓度、氧化剂浓度、流动注射器参数等影响,并且检测需要的鲁米诺溶液需要提前7 d配制,保存时间较短<sup>[56]</sup>,使该法在现场实时分析方面受到一定限制。鲁米诺化学发光法、电化学检测法和分光光度法的检测原理各不相同,但三者和分析水中UDMH时都易受甲基胂、胂等与UDMH结构性质类似化合物的干扰,因此研究具有特异性选择的类“分子探针识别器”对于提高上述方法的抗干扰能力尤为关键。此外,与鲁米诺化学发光法、分光光度法相比,电

化学法具有方便携带、操作简便等优势,在水中UDMH现场快速检测应用方面更具发展前景,但该方法不具备对较低含量( $\mu\text{g}\cdot\text{L}^{-1}$ )UDMH的检测能力,在水中不同浓度UDMH检测需求中需与鲁米诺化学发光法、分光光度法相互补充。

### 3 水中UDMH转化产物检测

#### 3.1 GC法检测水中UDMH转化产物

与水中UDMH测定不同,GC法分析水中UDMH转化产物时一般无需衍生化处理,但同样需要去除水的基质效应。液液萃取、固相微萃取(SPME)、顶空SPME、真空顶空SPME等去除水基质的方式联合GC-MS检测已在一种或多种UDMH转化产物的分析中得到应用。张光友等<sup>[61]</sup>利用NDMA和水的沸点差异且NDMA在水中溶解度小的特性,采用蒸馏+二氯甲烷萃取、无水 $\text{Na}_2\text{SO}_4$ 干燥后常温氮气吹扫的方式进行,离子监测模式下GC-MS对NDMA的检出限为 $2\mu\text{g}$ ,回收率达89.9%~96.3%。Buryak A K等<sup>[62]</sup>用GC-MS分析了高锰酸钾和过氧化氢降解水中UDMH的效果,采用二氯甲烷萃取,无水 $\text{Na}_2\text{SO}_4$ 干燥进行样品前处理,程序升温模式下GC-MS可同时测定12种转化产物。Ul'yanovskii等<sup>[63]</sup>用乙腈萃取水中UDMH转化产物,在HP-INNOWAX极性固定相上分离后,串联质谱(MS-MS)检测器可同时分析8种转化产物,检出限( $0.3\sim 2.3\text{ ng}\cdot\text{mL}^{-1}$ )比同样条件下GC/MS法提高了1~2个数量级。

萃取操作是为了去除GC测定时水的基质效应,但人工萃取方式会一定程度上增加分析误差。SPME是一种集采样、萃取、浓缩和进样于一体的萃取新技术,自动化程度高,可减少人为操作导致的分析误差,已被广泛用作各种复杂体系中低含量组分检测的前处理手段<sup>[64-68]</sup>,也为微量甚至痕量UDMH转化产物的分析检测提供了有力帮助。Bulat Kenessov等<sup>[69]</sup>利用顶空SPME分析水中UDMH的转化产物甲醛二甲基脒(FADMH)时,先在 $30\text{ }^\circ\text{C}$ 下抽提1分钟进行柱前处理,样品经GC分离后,MS和氮磷检测器对FADMH的检出限分别可达 $1.5\mu\text{g}\cdot\text{L}^{-1}$ 和 $0.5\mu\text{g}\cdot\text{L}^{-1}$ 。Bakaikina N V等<sup>[70]</sup>也采用顶空SPME进行柱前处理,正电离模式下GC-MS/MS可同时测定13种转化物质,最低检测限在 $0.14\mu\text{g}\cdot\text{L}^{-1}$ 以下,进一步扩展了UDMH转化产物的检测种类,降低了其检测限。但在Bakaikina N V等的研究中,顶空SPME需要在 $50\text{ }^\circ\text{C}$ 下进行60 min才可得

到最佳萃取效果,前处理所需时间较长。据报道,降低压力可以减少气相传质阻力,促进物质从水或固体样品到气相、再到SPME涂层的传质过程<sup>[71-72]</sup>。基于此,Orazbayeva D等<sup>[73]</sup>在顶空SPME的基础上引入真空手段,发现在萃取温度和时间相同的条件下,真空顶空SPME(Vac-HSSPME)对水中UDMH几种转化产物(对二氮杂苯-吡嗪PAn、1-甲基-1H-吡嗪MPA、亚硝基二甲胺NDMA、N,N-二甲基甲酰胺DMF、1-甲基-1H-1,2,4-三唑MTA、偏脒FDMH、1-甲基-咪唑MIA、甲酰胺FA和1H-吡嗪PAI)的提取能力显著优于普通的顶空SPME(HSSPME),如图4所示。当采用Vac-HSSPME处理时,在萃取温度为 $40\text{ }^\circ\text{C}$ 、 $50\text{ }^\circ\text{C}$ 和 $70\text{ }^\circ\text{C}$ 时,大多数转化产物在30 min后即可达到最大响应值,而采用普通的HSSPME处理、温度为 $70\text{ }^\circ\text{C}$ 时,萃取60 min还未能获得最大响应值,相较之下,Vac-HSSPME可极大缩短样品前处理时间。

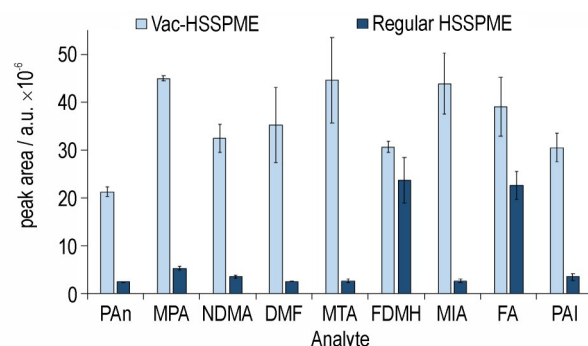


图4 真空辅助和常规HSSPME提取水样中UDMH转化产物对比(提取温度 $50\text{ }^\circ\text{C}$ ,采样时间30 min)<sup>[73]</sup>

Fig.4 Comparison of vacuum-assisted and regular HSSPME for the extraction of UDMH transformation products from water samples (extraction temperature  $50\text{ }^\circ\text{C}$ , sampling time 30 min)<sup>[73]</sup>

GC联合UV、MS等检测器已能分析多种水中UDMH转化产物,但在其众多转化产物中,有些产物具有热不稳定性或非挥发性,很难用GC法进行分析<sup>[74]</sup>,因此,需要借助HPLC等其他手段实现。

#### 3.2 HPLC法检测水中UDMH转化产物

HPLC法分析水中UDMH转化产物不受水质基质的限制,但不同转化产物的有效分离成为制约其检测效果的关键。夏本立<sup>[75]</sup>和高鑫<sup>[76]</sup>等利用HPLC-UV法测定水中UDMH单一转化产物时,为了使目标分析物能从复杂的多组分体系中分离,采取优化流动相中甲醇和水的比例、控制流速等手段,在 $\lambda=230\text{ nm}$ 和 $\lambda=235\text{ nm}$ 处分别对NDMA和FDMH进行了定量分析。Ul'yanovskii N V课题组<sup>[39]</sup>为了解决水中UDMH不

同转化产物的有效分离问题,以多孔石墨化碳为色谱柱固定相,通过混合保留机制成功分离了MT、NDMA、DMF、甲醛和乙醛二甲胺等转化产物,并采用MS进行了检测,解决了这5种转化产物弱保留的难题。高分辨率轨道阱质谱具有灵敏度和质量精度高的

双重优势,已广泛用于多目标化合物的快速筛查领域<sup>[77-80]</sup>。Ul'yanovskii N V等<sup>[74]</sup>以HPLC联合高分辨率轨道阱质谱检测器同时测定了多种质荷比( $m/z$ )较小(150以下)的转化产物,如图5所示,为低分子量转化产物的快速筛查提供了手段。

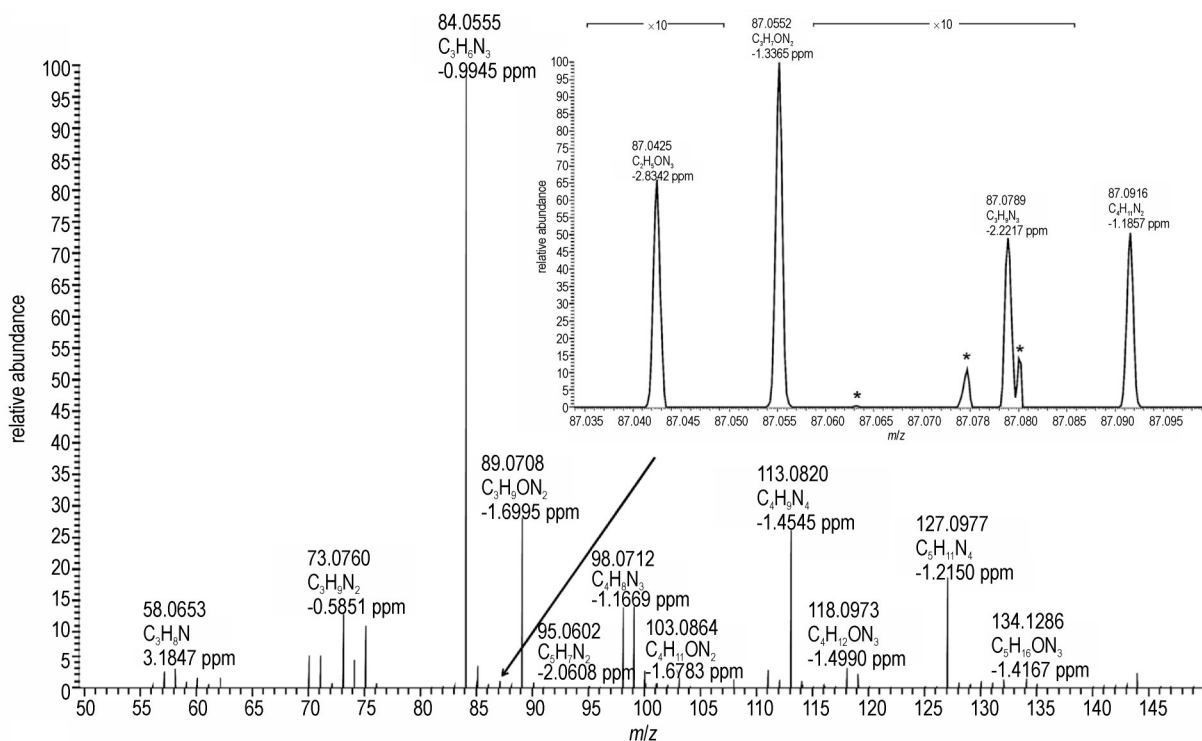


图5 UDMH与 $H_2O_2$ 氧化的最终产物(反应时间45天)的质谱(同位素峰以星号标注)<sup>[74]</sup>

Fig.5 Mass spectrum of the final products (reaction time 45 days) of UDMH oxidation with  $H_2O_2$  (Isotope peaks are denoted by asterisks)<sup>[74]</sup>

### 3.3 IC法检测水中UDMH转化产物

UDMH和其部分碱性转化产物可以通过酸性淋洗液质子化后,在阳离子交换柱上进行分离检测。但是一些转化产物,如NDMA、DMF、MT等,在酸性淋洗液作为流动相时不会出现明显的质子化,无法用离子交换色谱对其进行分析。离子对色谱可以通过不同保留机制同时分离带电和不带电化合物,是一种选择性更强的分析方法。基于此,Smolenkov A D课题组<sup>[24]</sup>探讨了离子对色谱分析水中UDMH及其转化产物的能力,采用梯度洗脱模式使多种不同特性的转化产物有效分离,如图6所示,不易离子化的NDMA和MT也能被检测到。离子对色谱法与离子交换色谱法形成互补,进一步拓展了IC法检测UDMH转化产物的种类,但是离子对试剂的使用导致该法的噪声较高,检测限比离子交换色谱的稍差<sup>[24]</sup>。

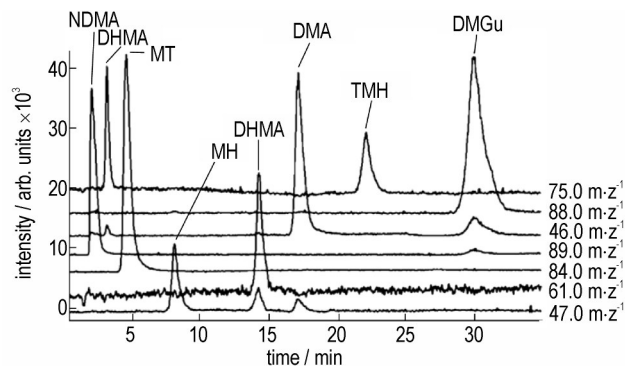


图6 利用离子对色谱和梯度洗脱模式分离UDMH及其转化产物<sup>[24]</sup>

Fig.6 Separation of UDMH and its products of transformation using ion-pair chromatography and gradient elution mode<sup>[24]</sup>

## 4 结论和展望

水中UDMH及其转化产物的检测是实现其污染



控制的先决手段,经过几十年的发展,其检测能力得到了较大提升。色谱法和非色谱法各具优势、互为补充,对水中UDMH的检测范围可低至几 $\mu\text{g}\cdot\text{L}^{-1}$ 、高至几千 $\text{mg}\cdot\text{L}^{-1}$ ;水中UDMH转化产物的检测则主要集中于色谱法,已实现对一种或多种转化产物的同时测定。尽管如此,现有技术对水中UDMH及其转化产物的分析检测能力距离实际检测需要仍存在一定差距。主要体现在:

(1)水中UDMH的浓度涵盖范围较广,当前检测手段尚无法满足较宽浓度范围的快速检测需求。

在UDMH污染发生的不同场所、不同阶段,水体中UDMH的浓度范围较大,检测需求从几 $\mu\text{g}\cdot\text{L}^{-1}$ 到几千 $\text{mg}\cdot\text{L}^{-1}$ 甚至 $\text{g}\cdot\text{L}^{-1}$ 量级。目前,基于一种检测手段无法实现上述较宽范围的检测需求。

(2)水中UDMH的转化产物种类繁多,实现同时快速测定多种转化产物还有一定差距。

对性质结构相近的UDMH转化产物分析测定时,其关键是使各组分有效分离。目前色谱检测柱前分离虽已实现自动化在线模式,但限于当前技术发展水平,在分离种类、重现性等方面仍有待进一步提升。对性质差异较大的UDMH转化产物进行检测时,经色谱分离后检测器是关键。目前很难在一种检测器上实现多种性质差异较大转化产物的同时测定。

针对水中UDMH及其转化产物检测现状,未来可着重从以下两个方面进行研究探索。

(1)基于高效自动化前处理的GC或HPLC色谱串联质谱快速检测水中UDMH。

GC或HPLC色谱串联质谱法因较高的测量精度而更具发展前景,未来可针对GC、HPLC对水基质中UDMH检测时的进样要求,重点研究开发一种高效自动化的前处理装置,以满足水中较宽浓度范围UDMH的快速检测需求。

(2)基于多种分离和检测技术联合使用的水中UDMH转化产物分析。

水中UDMH转化产物种类较多,性质差异大小不一,要实现对众多转化产物的多残留分析、高回收率、高重现性、低检出限,开发基于多种分离和检测技术联合使用的检测方法应作为未来重点研究方向。

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## Progress Progress on Detection Methods of UDMH and Its Transformation Products in Water

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**Abstract:** Rapid detection of unsymmetrical dimethylhydrazine (UDMH) and its transformation products in water is of great significance for its pollution control. This paper reviews the research progress of chromatographic methods (including gas chromatography, high performance liquid chromatography, and ion chromatography) and non-chromatographic methods (including the electrochemical method, spectrophotometry and chemiluminescence) in the detection of UDMH in water. Then, application of chromatography in the detection of UDMH conversion products in water was briefly introduced. The advantages and disadvantages of different detection methods in the detection concentration range, sample pretreatment and anti-interference ability, etc., were pointed out. It was suggested that the design of efficient automatic chromatographic pretreatment device and the combination of various separation and detection technologies would be the future development direction to solve the detection problem of UDMH and its transformation products in water.

**Key words:** unsymmetrical dimethylhydrazine(UDMH); transformation products; chromatographic method; spectrographic method

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