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碱性过硫酸盐消解-紫外二阶导数光谱法测定地热水中总溶解氮

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摘要: 地热水的过度开发利用导致地热水中总溶解氮含量过高，造成水质恶化，同时伴随地热水中总溶解氮中不同形态氮的相互转化，对人类健康和经济发展造成严重影响。因此，地热水中总溶解氮的测定，对研究总溶解氮的生物地球化学循环和地热水的合理开发利用具有重要意义。针对地热水具有化学成分复杂多变、干扰组分多的特点，本文建立了碱性过硫酸盐消解-紫外二阶导数光谱法测定地热水中总溶解氮的方法，其中总溶解氮以硝酸根-氮的形式定量测定，其二阶导数光谱图可消除大部分干扰因素。通过研究硝酸根-氮紫外二阶导数光谱图，确定波长 266.6nm 对应的二阶导数值为特征吸光度。通过单因素水平实验和双因素方差分析实验优化消解反应中的消解参数，表明在一定条件范围内，稀释方案是影响总溶解氮测定最重要的因素，推荐选择消解温度为 120℃，消解时间为 20min，碱性过硫酸钾溶液体积为 5.0mL；选择样品体积为 10.0mL，在样品消解前稀释。共存离子干扰实验表明，高含量溴离子对总溶解氮的测定有正干扰。在 0.20～5.0mg/L 线性范围内，建立硝酸根 (以氮计) 标准溶液校准曲线，其决定系数 R^2=0.9996。本方法加标回收率在 94.0%～103.5% 之间，相对偏差在 0.83%～3.36% 之间，准确度和可靠性高，干扰因素可控，需要样品量小，仪器成本低，可满足地热水中总溶解氮的快速、简单、准确批量检测需求。

关键词: 碱性过硫酸盐；紫外二阶导数光谱法；消解；地热水；总溶解氮

要点:

(1) 硝酸根-氮的紫外二阶导数光谱图在波长 226.6nm 处峰型好，其特征吸收值与浓度成正比。

(2) 稀释方案是消解反应中影响总溶解氮测定最重要的因素。

(3) 高含量溴离子对总溶解氮的测定产生正干扰。

中图分类号: O657.3　　**文献标识码:** A

总溶解氮 (TDN) 是水中所有溶解性的含氮化合物的总量, 包括溶解无机氮 (DIN) 和溶解有机氮 (DON), 其中溶解无机氮还包括硝酸盐氮、氨氮、亚硝酸盐氮等[1]。总溶解氮主要来源于农业施肥、爆炸物、生活污水、大气沉降及动植物和微生物代谢活动等, 是评价水质恶化的重要指标, 衡量水质被污染及自净状况[1-2]。过量的总溶解氮随水体自然移动, 对水质和人类健康造成重大威胁[3]。地热水作为宝贵的液态矿产资源, 可用于温泉、发电、生产饮用矿泉水、养殖等[4-5], 近年来被广泛开发利用[6-7]。然而, 由于人们的过度开采, 导致了地热水中总溶解氮含量过高, 地热水水质严重恶化[8]。过高的总溶解氮会导致地热水水体富营养化, 影响养殖生物环境及其他方面; 同时饮用过量的亚硝酸氮/硝酸氮和

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氨氮超标的地热矿泉水, 对人体分别具有高致癌风险及对淋巴细胞、味觉、嗅觉毒害作用[8-9], 而总溶解氮中氨氮、亚硝酸氮、硝酸氮又可以相互转化, 其危害作用不容忽视。为解决地热水中总溶解氮污染问题, 精确、快速检测其中总溶解氮的含量十分必要, 对于充分研究总溶解氮的生物地球化学循环和地热水的合理开发利用具有重要意义。

溶解无机氮的检测方法有很多, 而溶解有机氮的结构、成分复杂, 其检测方法尚不明确。总溶解氮主要通过消解前处理, 使各个形态的氮转化为硝酸盐氮, 再进行定量测定。常见的消解方法有紫外氧化法[10-11]、高温燃烧法[12-14]、碱性过硫酸盐消解法[15-17]等。紫外氧化法存在氧化不完全、回收率较低和变异性大等问题; 高温燃烧法的转化效率高, 但需要特定的仪器且价格较高。样品中总溶解氮转化为硝酸盐氮后, 可采用离子色谱法[18-20]、镉柱还原法[21-23]、紫外可见分光光度法[24-26]等方法测定。离子色谱法无需其他试剂, 绿色环保, 但分析时间长, 效率低。镉柱还原法是将硝酸盐用镉柱还原为亚硝酸盐, 还原率较高, 但镉的毒性较大, 污染环境。紫外可见分光光度法具有适用范围宽、灵敏度高等优点, 但存在样品中多组分混合物重叠吸收、定性和定量分析准确度低等问题。

碱性过硫酸盐消解法是一种被广泛应用的湿法化学消解方法, 具有使用设备简单、氧化效率高等优点, 过硫酸盐被热分解成毒性较小的硫酸盐, 消解后样品中总溶解氮全部转化为硝酸盐氮。但在实际应用中, 消解时间、消解温度、过硫酸盐用量等均影响总溶解氮的测定, 一些研究[16, 27]表明消解时间长达 40～60min, 严重降低了测定效率。与其他水体相比, 地热水具有化学成分复杂多变、盐度大的特点, 采用行业标准《水质 总氮的测定 碱性过硫酸钾消解紫外分光光度法》(HJ 636—2012) 测定总溶解氮时, 干扰组分多, 准确度低。而紫外二阶导数光谱法[28-30]是解决干扰因素多的最佳方法, 其紫外二阶导数光谱图峰型好, 灵敏度和分辨率高; 而关于碱性过硫酸盐消解法和紫外二阶导数光谱法联用测定总溶解氮的报道较少[27]。基于此, 本文采用碱性过硫酸盐消解-紫外二阶导数光谱法联用测定地热水中总溶解氮, 其二阶导数光谱图可消除大部分干扰因素, 是测定地热水中总溶解氮的理想方法, 其中总溶解氮以硝酸根-氮的形式定量测定。实验主要研究了紫外二阶导数光谱图确定定量测定硝酸根-氮含量的特征吸光度, 通过单因素水平实验和双因素方差分析实验, 优化碱性过硫酸钾消解反应中的消解时间、稀释方案等参数。考察了地热水中高含量共存离子的干扰情况和标准曲线的拟合度及线性范围后, 通过实际样品加标回收实验以及与行业标准方法进行对比, 对方法的可靠性和准确性进行了验证。

1　实验部分

1.1　仪器和主要试剂

实验主要使用仪器为紫外可见分光光度计 (UV2550 型, 日本岛津公司), 波长范围为 190～800nm; 石英比色皿光程 10mm; 高压蒸汽灭菌器 (最高温度不低于 120℃); 具塞磨口玻璃比色管容量 25mL 等。

硝酸钾标准储备溶液: BWZ7192—2016, 浓度 1000mg/L, 以氮计。

水中总氮标准储备溶液: GBW(E)083307, 浓度 1000mg/L, 以氮计。

水中氨氮标准储备溶液: GBW(E)083304, 浓度 1000mg/L, 以氮计。

水中尿素氮标准储备溶液: GBW(E)085011, 浓度 1000mg/L, 以氮计。

硝酸钾标准使用溶液 (浓度 10.0mg/L, 以氮计): 由硝酸钾标准储备溶液逐级稀释而成。

碱性过硫酸钾溶液 (40.0g/L): 称取 40.0g 过硫酸钾和 15.0g 氢氧化钠于超纯水中, 定容至 1.0L。

过硫酸钾、氢氧化钠、浓盐酸、氯化钠、硫酸钠、碳酸氢钠等试剂皆为优级纯。10% 盐酸溶液。实验用水为超纯水, 电阻率为 18.2MΩ·cm。

1.2　实验方法

精确移取 0、0.20、0.50、1.00、2.00、3.00、5.00 硝酸钾标准使用溶液 (10.0mg/L, 以氮计) 于 25mL 玻璃比色管中, 用超纯水定容体积至 10mL。上述溶液中硝酸根 (以氮计) 的浓度分别为 0.00、0.20、0.50、1.00、2.00、3.00、5.00mg/L, 再分别加入 5.00mL 碱性过硫酸钾溶液 (40.0g/L), 塞紧管塞, 用塑料膜和皮筋扎紧管塞, 置于高压蒸汽灭菌器中进行消解反应, 温度升至 120℃ 后保持 20min, 冷却至室温后, 加入 1.0mL 10% 的盐酸溶液, 用超纯水定容体积至 25mL, 摇匀后上机测定。

本实验采用紫外二阶导数光谱法, 总溶解氮以硝酸根-氮的形式定量测定。以空白溶液作参比, 采用 10mm 石英比色皿, 波长扫描范围为 190～270nm, 选定并记录硝酸根 (以氮计) 在波长 226.6nm 处二阶导数吸收值。以标准溶液吸光度为横坐标, 硝酸根

(以氮计) 含量为纵坐标绘制校准曲线，使用校准曲线对所有样品进行定量分析。样品溶液取样量为 10.00mL，实验方法同硝酸根 (以氮计) 标准系列，同时做空白对照实验。如样品中总溶解氮含量过高，超出标准曲线最大值，可将样品溶液稀释后重新测定。

2　结果与讨论

2.1　紫外二阶导数光谱分析及波长的确定

地热水样品普遍矿化度较大，样品中各物质成分复杂，存在胶体、悬浮物及有机物，通过紫外可见分光光度法分析总溶解氮含量时特征峰值不明显，干扰因素多，相互重叠，且双波长紫外分光光度法也无法完全这些消除干扰。而紫外二阶导数光谱法则是解决这些问题的有效方法，具有放大微弱吸收峰、提高灵敏度和分辨率、消除噪声干扰等能力。

紫外二阶导数光谱法中，波长的作用有提高灵敏度和分辨率、减少背景干扰等。图 1 为硝酸根-氮标准溶液和地热水样品溶液的紫外光谱图、一阶和二阶导数光谱图。其紫外光谱图峰型杂乱且不对称，特征吸收峰不明显，干扰物质多；一阶导数光谱出现负峰，进行二阶导数处理后，其二阶导数光谱图分辨率高，大部分干扰因素消除，图像更为灵敏，在波长 226.6nm 处存在特征吸收值，且不受其他成分的干扰。本实验中硝酸根-氮二阶导数光谱图波形及出峰时间与王静敏等[28]、陈晓伟等[29]、Ferree 等[27]研究获得的规律大致相同，进一步说明了方法的可靠性。图 2 为不同浓度的硝酸根-氮标准溶液的二阶导数光谱图，在波长 226.6nm 处峰型好，稳定性高，其特征吸收值与硝酸根-氮浓度成正比。因此，确定波长 226.6nm 对应的二阶导数值为定量测定硝酸根-氮含量的特征吸光度。

2.2　碱性过硫酸钾消解反应参数的优化

碱性过硫酸钾消解反应中，消解参数的选择对于准确定量测定地热水中总溶解氮至关重要。消解反应中，其中消解温度、消解时间、碱性过硫酸钾溶液体积、样品体积与稀释方案是 5 个最为关键的因素。本实验中，逐级稀释配制总溶解氮 (TDN)、溶解无机氮 (DIN)-氨氮和溶解有机氮 (DON)-尿素质控样品，其浓度分别为 15.0、10.0、21.0mg/L，利用上述质控样品进行消解时间、消解温度、碱性过硫酸钾溶液体积的单因素水平实验，结果如图 3 所示。

Ferree 等[27]指出消解时间为 60min 时，总溶解氮的回收率高于消解时间 30min 的回收率。由图 3a 可以看出，本实验结果与刘振超等[17]改进测定水质总氮方法中对消解时间的讨论结果大致相同。在消解时间为 0～60min 范围内，消解时间为 0 时，所有质控样品中硝酸根-氮回收值为 0，说明样品不经过高温高压反应，各种形式的氮无法转换成硝酸盐-氮。当消解时间＜10min 时，各质控样品回收值都偏低，且相对偏差大；当消解时间≥20min 后，三种质控样品的回收值皆趋近理论值。如图 3b 所示，消解温度为 105℃ 时，总氮和无机氮质控样品回收值偏大，其原因可能是温度过低，碱性过硫酸钾氧化不完全，干扰总氮的测定；当温度达到 110℃ 后，三种质控样品的回收值与理论值没有显著差异。碱性过硫酸钾溶液体积对消解反应的影响如图 3c 所示，碱性过硫酸钾溶液体积为 1.0～4.0mL 时，三种质控样品的回收值皆有低于理论值的情况；当体积为 5.0～6.0mL 时，其回收值皆接近理论值。综合考虑质控及实际样品，实验推荐消解温度为 120℃，消解时间为 20min，碱性过硫酸钾溶液体积为 5.0mL。

对样品体积与稀释方案进行双因素方差分析实验，结果如图 4 所示。消解后稀释的样品，各质控样

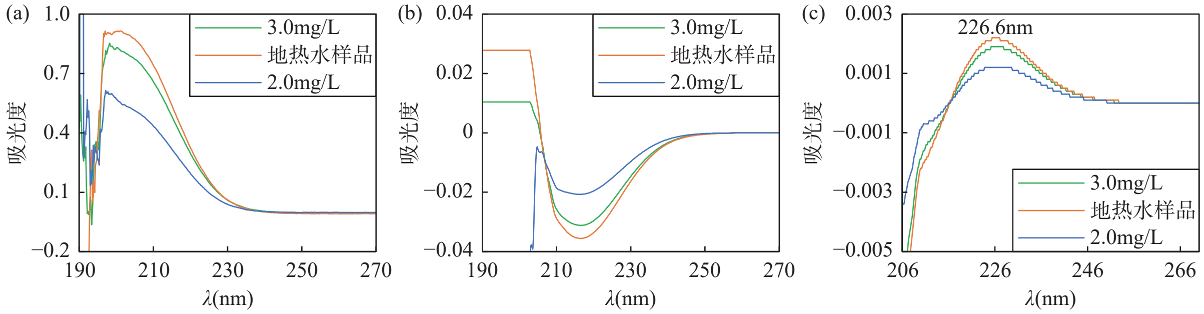

图1　硝酸根-氮标准溶液和地热水样品溶液的紫外光谱图 (a)、一阶 (b) 和二阶导数光谱图 (c)

Fig. 1　UV spectra (a), first derivative spectra (b) and second derivative spectra (c) of nitrate-nitrogen standard solution and geothermal water sample solution.

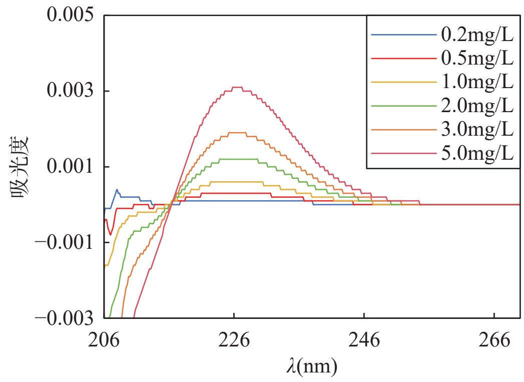

图2　不同浓度的硝酸根-氮标准溶液的二阶导数光谱图

Fig. 2　Second derivative spectra of nitrate-nitrogen standard solutions with different concentrations.

品的回收值显著低于理论值; 而样品体积对测定结果影响不大。稀释方案是影响总溶解氮测定最重要的因素, 与 Ferree 等[27]的实验结果相同。考虑样品稀释的倍率及相对误差, 实验选择样品体积为 10.0mL, 在样品消解前稀释。

2.3　共存离子的干扰与消除

地热水矿化度较高, 基体成分复杂, 样品消解后采用紫外二阶导数光谱法测定总溶解氮 (TDN) 时, 可能有其他共存离子产生干扰。地热水中高含量离子主要以钠离子 (Na$^+$)、氯离子 (Cl$^-$)、硫酸根离子 (SO$_4^{2-}$)、碳酸氢根离子 (HCO$_3^-$)、溴离子 (Br$^-$)、碘离子 (I$^-$) 和氟离子 (F$^-$) 为主。结合实际样品中各离子的浓度范围, 实验配制了 6 组分别含有 2000mg/L 氯化钠、2000mg/L 硫酸钠、800mg/L 碳酸氢钠、10mg/L 溴离子、10mg/L 碘离子、10mg/L 氟离子的总溶解氮质控样品 (3.0mg/L), 通过比较这 6 组质控样品中总溶解氮的测定值, 以评估各共存离子对总溶解氮测定的影响, 结果如图 5 所示。6 组总溶解氮质控样品中, 含有 10mg/L 溴离子的质控样品回收值偏高, 其他离子对总溶解氮分析的干扰不明显。在分析溴含量高的样品时, 可以将样品先过银型预处理柱或者其他方法去除溴离子后, 再进行定量分析。

2.4　校准曲线及线性范围

在 0.20 ~ 5.0mg/L 线性范围内, 配制硝酸根 (以氮计) 标准系列溶液浓度分别为 0.00、0.20、0.50、1.00、2.00、3.00、5.00mg/L, 按照本文 1.2 节实验方法进行测定, 绘制校准曲线。校准曲线线性回归方程为 y=1599.1x+0.0267, 其中 x 为标准溶液紫外二阶导数光谱图在波长 266.6nm 处吸光度, y 为标准溶液硝酸根 (以氮计) 浓度 (mg/L), 决定系数 R^2=0.9996, 线性拟合度满意, 符合实验分析的要求。

地热水中总溶解氮含量目前没有确定范围, 取决于不同的用途及地质条件、污染因素等。参考《地表水环境质量标准》(GB 3838—2002) 规定, Ⅰ类水、Ⅱ类水、Ⅲ类水、Ⅳ类水、Ⅴ类水中总溶解氮限值 (mg/L) 分别为≤0.20、≤0.5、≤1.0、≤1.5、≤2.0。因此, 0.20 ~ 5.0mg/L 线性范围可满足总溶解氮的分析测定要求, 部分因污染因素而导致总溶解氮含量特别高的样品可稀释后测定。

2.5　实际样品测定及加标回收

为了验证采用本文方法测定地热水中总溶解氮 (TDN) 的可靠性, 分别选取甘肃兰州、山西晋中、四川甘孜藏族自治州、河南安阳 4 个地区地热水样品, 按照上述方法测定样品中的总溶解氮, 同时加入

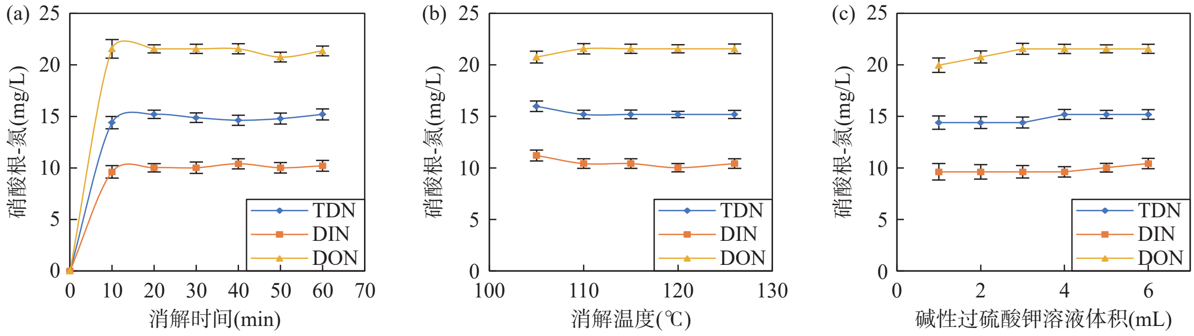

图3　消解时间 (a)、消解温度 (b) 和碱性过硫酸钾溶液体积 (c) 对总溶解氮 (TDN)、溶解无机氮 (DIN) 和溶解有机氮 (DON) 质控样品测定结果的影响

Fig. 3　Effects of digestion time (a), digestion temperature (b) and volume of alkaline potassium persulfate solution (c) on the determination of total dissolved nitrogen (TDN), dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON) in quality control samples.

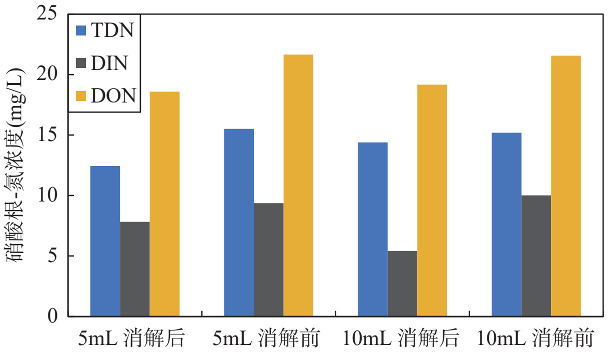

图4　样品体积与稀释方案对总溶解氮 (TDN)、溶解无机氮 (DIN) 和溶解有机氮 (DON) 质控样品测定结果的影响

Fig. 4　Effects of sample volume and dilution scheme on analytical results of total dissolved nitrogen (TDN), dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON) quality control samples.

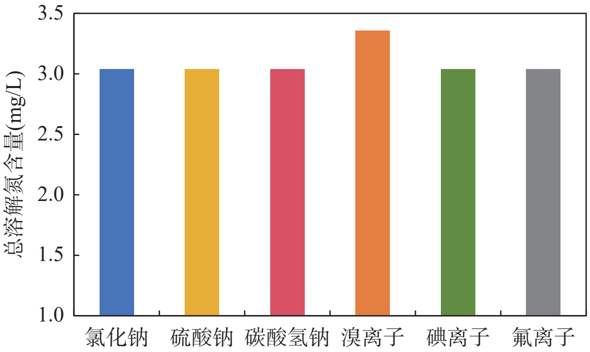

图5　共存离子对总溶解氮测定结果的影响

Fig. 5　Effects of coexisting ions on the determination of total dissolved nitrogen.

不同含量的总氮标准溶液，其回收结果列于表 1。扣除本底值后，各样品总溶解氮的加标回收率皆在 94.0% ~ 103.5% 之间，相对偏差在 0.83% ~ 3.36% 之间，说明本文方法的检测结果准确可靠。

2.6　方法对比

目前暂时缺乏地热水标准样品，因此本实验根据地热水中各离子的大致浓度范围，自配 2 个含有不同浓度总溶解氮的地热水标准样品(编号 S1 和 S2)，样品中常规离子大致浓度为：钾 (20mg/L)、钠 (2000mg/L)、钙 (200mg/L)、镁 (100mg/L)、氯离子 (2500mg/L)、硫酸根 (1300mg/L)、重碳酸根 (500mg/L)，总溶解氮浓度为 1.60mg/L 和 4.50mg/L。分别采用本文方法和行业标准方法《水质 总氮的测定 碱性过硫酸钾消解紫外分光光度法》(HJ 636—2012) 进行 6 次平行测定，计算的相对标准偏差 (RSD)、与理论值偏差、两种方法测定结果相对偏差列于表 2。由于自配样品的化学成分相对简单，不含有胶体、有机物等干扰成分，两种方法的测定结果比较一致，相对偏差分别为 1.83% 和 2.18%，但是本文方法测定值的 RSD 及其与理论值的偏差皆优于行业标准方法。

3　结论

建立了碱性过硫酸盐消解-紫外二阶导数光谱法测定地热水中总溶解氮的方法，总溶解氮以硝酸根-氮的形式定量分析。通过研究硝酸根-氮紫外二阶导数光谱图确定特征吸光度，其特征吸光度与硝酸根-氮浓度呈现良好的线性关系。通过单因素水平实验和双因素方差分析实验，优化消解反应中的条

表 1　实际样品的测定及加标回收率

Table 1　Determination of actual samples and spike recoveries.

样品编号	总溶解氮含量 (mg/L)				相对偏差 (%)	回收率 (%)
	本底值	加标量	理论测定值	实际测定值		
1#	0.33	0.50	0.83	0.81	2.41	96.0
		1.00	1.33	1.37	3.01	104.0
		2.00	2.33	2.40	3.00	103.5
2#	1.45	0.50	1.95	1.92	1.54	94.0
		1.00	2.45	2.40	2.04	95.0
		2.00	3.45	3.52	2.03	103.5
3#	0.49	0.50	0.99	0.97	2.02	96.0
		1.00	1.49	1.44	3.36	95.0
		2.00	2.49	2.42	2.81	96.5
4#	1.92	0.50	2.42	2.40	0.83	96.0
		1.00	2.92	2.86	2.05	94.0
		2.00	3.92	3.83	2.30	95.5

表 2　方法对比实验 (*n*=6)

Table 2　Comparison of analytical results obtained by different methods (*n*=6).

样品编号	总溶解氮含量理论值 (mg/L)	本文方法			行业标准方法（碱性过硫酸钾消解紫外分光光度法）			本文方法与行业标准方法的相对偏差 (%)
		测定值 (mg/L)	RSD (%)	与理论值的相对偏差 (%)	测定值 (mg/L)	RSD (%)	与理论值的相对偏差 (%)	
S1	1.60	1.62	1.85	1.25	1.65	2.89	3.12	1.83
S2	4.50	4.54	1.69	0.89	4.64	3.57	3.11	2.18

件参数，降低了基体干扰，提高了分析效率和准确性。消除共存离子干扰后，采用本文方法建立标准曲线，测定实际样品中总溶解氮含量，同时与行业标准方法进行对比实验，其重现性好，准确性高。

本文方法具有强抗干扰能力的特点，可解决地热水样品化学组成复杂、干扰因素多的问题，需要的样品量小，仪器成本低，为地热水中总溶解氮的测定提供了一种高效、适用的分析方法。该方法也适用于分析地表水、生活饮用水等其他水样中的硝酸根和总溶解氮含量，后续工作可以进一步探索研究。

Total Dissolved Nitrogen in Geothermal Water by Ultraviolet Second Derivative Spectrometry with Alkaline Persulfate Digestion

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HIGHLIGHTS

(1) The ultraviolet second derivative spectrum of nitrate-nitrogen showed a good peak shape at a wavelength of 226.6nm, and its characteristic absorption value was directly proportional to the concentration.

(2) Dilution scheme was the most important factor affecting the determination of total dissolved nitrogen in the digestion reaction.

(3) High content of bromide ions had a positive interference on the determination of total dissolved nitrogen.

ABSTRACT: In view of variable chemical composition and numerous interfering components, the method for the determination of total dissolved nitrogen in geothermal water by alkaline persulfate digestion-ultraviolet second derivative spectrometry was developed. The total dissolved nitrogen was quantitatively determined in the form of nitrate-nitrogen. The second derivative value corresponding to wavelength 266.6nm was determined as the characteristic absorbance. The parameters in digestion reaction were optimized by single-factor level experiments and a two-factor ANOVA experiment. The digestion temperature, digestion time and solution volume of alkaline potassium persulfate were recommended to be 120℃, 20min and 5.0mL, respectively. The sample volume was 10.0mL, and dilution was performed prior to sample digestion. High content of bromide ions had a positive interference on the determination of total dissolved nitrogen. In the linear range of 0.20−5.0mg/L, the calibration curve of nitrate-nitrogen was established with its coefficient of determination R^2=0.9996. The actual samples were determined with the recovery rate (94.0%−103.5%) and the relative deviation (0.83%−3.36%). Compared with the industry standard method, the experimental results were satisfactory. This method has high accuracy and reliability, controllable interference factors, small sample amount, low instrument cost, and can meet the rapid, simple and accurate batch detection of total dissolved nitrogen in geothermal water. The BRIEF REPORT is available for this paper at http://www.ykcs.ac.cn/en/article/doi/10.15898/j.ykcs.202411210239.

KEY WORDS: alkaline persulfate; ultraviolet second derivative spectrometry; digestion; geothermal water; total dissolved nitrogen

BRIEF REPORT

Significance: The excessive exploitation and utilization of geothermal water has led to an excessively high total dissolved nitrogen content in geothermal water, causing water quality deterioration[8]. At the same time, it is accompanied by the mutual transformation of different forms of nitrogen in the total dissolved nitrogen, which has a serious impact on human health and economic development[8-9]. To solve the problem of total dissolved nitrogen pollution in geothermal water, it is essential to accurately and rapidly determine the content of total dissolved nitrogen. Total dissolved nitrogen is converted into nitrate-nitrogen through digestion reactions, and then quantitatively determined. The alkaline persulfate digestion method[15-17] is a widely used digestion method, which has the advantages of simple equipment and high oxidation efficiency. Geothermal water has a high mineralization degree and complex composition, with the presence of colloids, organic matter, etc. When using traditional methods[24-26] to determine total dissolved nitrogen, there are many interfering components and low accuracy. With these problems in mind, the method of alkaline persulfate digestion-ultraviolet second derivative spectrometry was used to determine total dissolved nitrogen in geothermal water. Its second derivative spectrogram can eliminate most of the interfering factors.

Methods: (1) Experimental method. Prepare a standard series solution of nitrate-nitrogen (0−5.0mg/L) in a 25mL glass colorimetric tube, make up to 10mL, add 5.00mL of alkaline potassium persulfate solution (40.0g/L), tighten tube plugs, and place it in a high-pressure steam sterilizer (120℃, 20min). After cooling, add 1.0mL of 10% hydrochloric acid solution, dilute to 25mL, and shake well. The blank solution was used as a reference, and a 10mm quartz cuvette was used with a wavelength scanning range of 190−270nm, and the second derivative absorption value of nitrate-nitrogen at a wavelength of 226.6nm was selected and recorded. The calibration curve was drawn with the absorbance of the standard solution as the abscissa and the content of nitrate-nitrogen as the ordinate. The sample volume was 10.00mL, and the experimental method was the same as that of the nitrate-nitrogen standard series, and a blank control experiment was also performed.

(2) Wavelength and digestion parameters. ① In the ultraviolet second derivative spectrometry, the wavelength plays a role in improving resolution and reducing background interference. Fig.1 shows the ultraviolet spectra, first derivative spectra, and second derivative spectra of the nitrate-nitrogen standard solution and the geothermal water sample solution. Fig.2 shows the second derivative spectra of nitrate-nitrogen standard solutions of different concentrations. ② The selection of digestion parameters is crucial for accurately determining the total dissolved nitrogen in geothermal water. Quality control samples of total dissolved nitrogen, dissolved inorganic nitrogen, and dissolved organic nitrogen were prepared, with concentrations of 15.0, 10.0, and 21.0mg/L, respectively. Single-factor level experiments were conducted on digestion time, digestion temperature, and the volume of alkaline potassium persulfate solution using these quality control samples (Fig.3). A two-factor ANOVA experiment was carried out on sample volume and dilution scheme (Fig.4).

(3) Coexisting ions. The geothermal water has a high mineralization degree and a complex matrix composition. Six groups of quality control samples of total dissolved nitrogen (3.0mg/L) were prepared, each containing 2000mg/L sodium chloride, 2000mg/L sodium sulfate, 800mg/L sodium bicarbonate, 10mg/L bromide ions, 10mg/L

iodide ions, and 10mg/L fluoride ions, respectively. The determination contents of total dissolved nitrogen in these six groups of quality control samples were compared to evaluate the influence of coexisting ions on the determination results of total dissolved nitrogen (Fig.5).

Data and Results: Through the study of the ultraviolet second derivative spectra of nitrate-nitrogen, it was determined that the second derivative value at a wavelength of 266.6nm was the characteristic absorbance, and the characteristic absorbance had a good linear relationship with the nitrate-nitrogen concentration. Through single-factor level experiments and a two-factor variance analysis experiment, the parameters in the digestion reaction were optimized. It was found that within a certain range of conditions, the dilution scheme was the most important factor affecting the determination of total dissolved nitrogen. Recommendations for the selection of the digestion temperature, digestion time, and volume of alkaline potassium persulfate solution are 120℃, 20min, and 5.0mL, respectively; the sample volume should be 10.0mL, and the dilution stage should be before sample digestion. In the coexisting ion interference experiment, it was found that high content of bromide ions had a positive interference on the determination of total dissolved nitrogen. Within the linear range of 0.20−5.0mg/L, a calibration curve of nitrate-nitrogen standard solutions was established, with its coefficient of determination R^2=0.9996. The actual samples were measured and spike recovery tests were conducted (Table 1). The recovery rates were between 94.0% and 103.5%, and the relative deviations were between 0.83% and 3.36%.

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