流动注射化学发光法测定氨氮的研究

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摘要 根据氨与次氯酸盐反应使次氯酸盐-Luminol 化学发光强度降低，建立了测定氨的流动注射化学发光法．试验了各种条件对发光强度的影响，考查了方法的精密度和准确度．在优化条件下，方法的线性范围为 0.02—0.5mg/L，变异系数小于 5.2%，相对误差小于 ±8.0%．分析速度为 120次/h．用于天然水氨气分析获得满意结果．

关键词：氨氮；鲁米诺；化学发光法；流动注射分析．

水质分析中氨氮的测定，国内外常用的和近期报道的都为比色法和电极法[1-5]．本文根据氨与次氯酸盐反应生成氯胺而使次氯酸盐-鲁米诺化学发光强度降低，提出了氨的流动注射化学发光分析法，用该方法测定了合成样和天然水中氨氮，结果满意．

一、实 验

1. 仪器与试剂

FICT-8604 化学发光分析仪（江苏电分析仪器厂）；XWT-S 台式记录仪（上海自动化仪表三厂）；NaClO 溶液：自制并以碘量法标定．实验中所用不同浓度的 NaClO 均以相应 pH 缓冲液配制；Luminol(E. Merck) 溶液(5.0×10^{-3}mol/L)：用 0.01mol/L KOH 配制，其他浓度均以相应 pH 缓冲液配制；铵标准溶液：用氯化铵(分析纯)配制．氨氮浓度，贮存液 1.0mg/mL，工作液 0.010mg/mL；缓冲溶液：0.05mol/L Na_2CO_3 与 0.1mol/L $NaHCO_3$ 按不同比例混合，酸度计校正 pH 值．

2. 实验方法

用内径 1mm 的聚乙烯管按图 1 连接，并按图中参数进行实验．采样时间 10s，进样时间 20s，进样频率 120 次/h．Luminol 浓度 1.0×10^{-3}mol/L，NaClO 浓度 4.0×10^{-5}mol/L，缓冲溶液 pH 为 10.8．测量时用

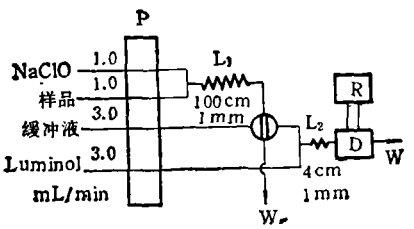

图 1 流动注射化学发光分析系统

P 蠕动泵 D 化学发光仪检测器 R 记录仪 L_1、L_2 反应管 W 废液

空白发光强度与样品发光强度的差值定量．

二、结果与讨论

1. 介质 pH 值的选择

文献[6]对氨与次氯酸的反应进行过研究．结果表明，在 pH7.5～12.0 范围内，氨与次氯酸定量反应生成氯胺．笔者试验了硼砂-Na_2CO_3、$NaHCO_3$-Na_2CO_3 等缓冲溶液介质中 NaClO 与 Luminol 的化学发光行为，表明使用不同组成的缓冲溶液，其发光强度差异很大，其中以在 $NaHCO_3$-Na_2CO_3 缓冲溶液中发光强度最大且重现性好．本文以 $NaHCO_3$-Na_2CO_3 为缓冲溶液，测量了不同 pH 值时的化学发光强度，结果如图 2 所示．由图可知，在 pH 为 10.8 时发光强度最大．故选择 pH 为 10.8 的缓冲溶液进行实验．

2. 载液流速的选择

以 pH 为 10.8 的缓冲溶液为载液，控制

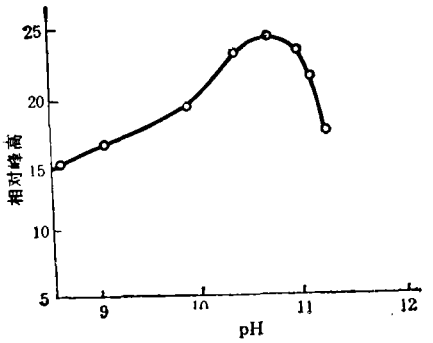

图 2　酸度对发光强度的影响

载液与 Luminol 流速相等，测量 4.0×10^{-5} mol/L NaClO 与 1.0×10^{-3}mol/L Luminol 在不同载液流速下的化学发光强度，实验结果如图 3。当载液流速大于 2.7ml/min 时发光强度最大且稳定，故在实验中选载液、Luminol 的流速均为 3.0ml/min。

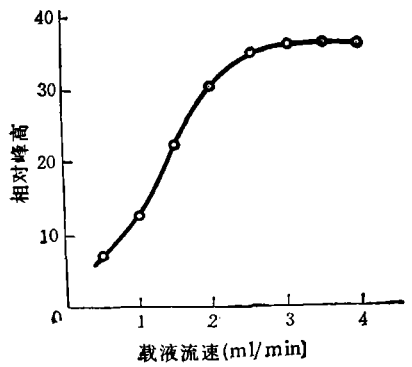

图 3　载液流速对发光强度的影响

3. 管道长度的选择

需要通过实验确定的反应管道长度有 L_1 和 L_2。L_2 为 NaClO 与 Luminol 的反应管道，应越短越好，本文设计 $L_2=4$cm。L_1 为 NaClO 与氨的反应管道，它对测量的灵敏度影响很大。笔者测量并绘制了不同 L_1 时的标准曲线，结果如图 4。由图 4 看出，随着 L_1 长度增大，测量的灵敏度增加，当 L_1 大于 100cm 时，标准曲线的斜率基本一致。实验时选择 $L_1=100$cm。

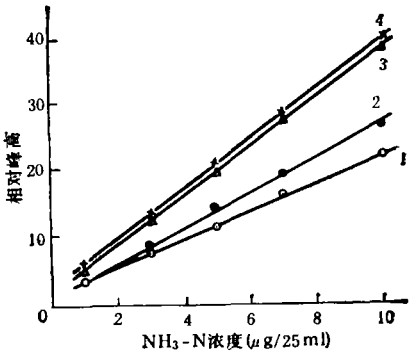

图 4　管道长度 L_1 对发光强度的影响
Lm 1.0×10^{-3}mol/L　NaClO 4.0×10^{-5}mol/L
1. 20cm　2. 60cm　3. 100cm　4. 150cm

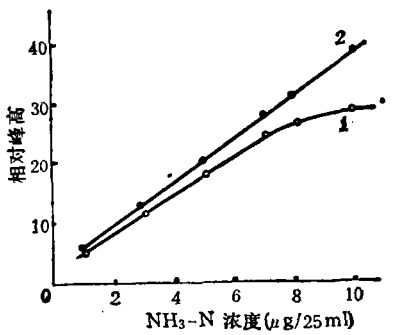

图 5　NaClO 浓度对发光强度的影响
固定 Lm 1.0×10^{-3}mol/L　1. NaClO 2.0×10^{-5}mol/L
2. $NaClO_3$　4.0×10^{-5}mol

4. NaClO 浓度的影响

实验表明，在一定范围内，当 NaClO 浓度固定时，随着 Luminol 浓度增加，化学发光强度增大。图 5 为固定 Luminol 浓度 1.0×10^{-3}mol/L 时，NaClO浓度分别为 2.0×10^{-5}和 4.0×10^{-5}mol/L 绘制的标准曲线。由图 5 看出，NaClO的浓度不同，标准曲线的线性范围和测定限不同。氨氮的测定下限约为 NaClO 浓度的 5%，上限约为 NaClO 浓度的 90%。在选定的最佳条件下，用 4.0×10^{-5}mol/LNaClO 实验，NH_3-N 浓度在 0.02—0.5 mg/L 范围内呈线性关系，线性回归方程为 $\Delta H=1.42+93.7c$（c 为 mgNH_3-N/L），相关系数 $r=0.988$，剩余标准差 $s=2.14$。

5. 干扰及消除

表 1 合成水样分析结果

合成水样组成 (mg/L)	NH_3-N 加入量 (mg/L)	测定结果 ($n=3$)		回收率 (%)	相对误差 (%)
		平均值 (mg/L)	变异系数(%)		
NaCl(400), KNO_3(100)	0.0500	0.0480	5.2	96	−4.0
Ca^{2+}、Mg^{2+}(100) Fe^{3+}、Pb^{2+}、Cu^{2+}(1)	0.200	0.184	3.1	92	−8.0
F^-、S^{2-}(2)	0.400	0.416	2.4	104	+4.0

表 2 水样 NH_3-N 分析结果 ($n=3$, mg/L)

水 样	测定值	标准加入量	加标后测定值	回收率(%)
环城湖水 1#	0.506	0.400	0.848	86
2#	0.465	0.400	0.845	95
徒骇河水	0.900	0.400	1.28	94
校内井水	0.064	0.040	0.107	92

用氨浓度为 0.010mmol/L的溶液按实验方法对可能产生干扰的离子作了试验，相对误差在 ±5% 以内可允许的离子或化合物浓度 (mmol/L) 为 NaCl、KCl(100), $MgCl_2$、$CaCl_2$(10), Ni^{2+}、Mn^{2+}、Fe^{3+}、Fe^{2+}(0.005), Cu^{2+}(0.001)。当水样中有还原性物质存在或共存离子的浓度超出允许浓度以及水样浑浊、有颜色时可用膜分离[7]或预蒸馏[1]消除干扰。

三、样品分析

按文献[1]预蒸馏处理，测定了合成样和天然水中的氨氮含量，结果如表 1、2。

四、小 结

本文提出的测定氨氮的流动注射化学发光法，灵敏度高，操作简便，分析速度快。应用国产流动注射化学发光分析仪测定了天然水中氨氮，结果满意。

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matic compounds in the ambient air has been developed. This device is composed of GC-FID, a six-way valve and a vacuum pump, which is controlled by a microprocessor in GC. Air samples were analyzed qualitatively and quantitatively by the device for three weeks, and 16 kinds of aromatic compounds such as benzene, methylbenzene etc and the changing trends of their concentrations were observed in Huhehot.

Key Words: automatic and continuous determination, aromatic compounds, ambient air.

Determination of Methyl Nitrite and Methyl Nitrate in Exhaust Gas from the Engine Fuelled with Methanol. Zhao Ruilan (Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing): *Chin. J. Environ. Sci.*, **11**(4), 1990, pp.53—57

A GC analytical method for determination of methyl nitrite and methyl nitrate concentrations in exhauset gas from the engine fuelled with methanol has been established. The minimal concentrations of MeONO and $MeONO_2$ determined by this method are 20ppb and 50ppb respectively. The prepared MeONO and $MeONO_2$ were identified with mass-spectrometry and stability of the samples of these substances were observed with gas chromatography. The concentrations of the pollutants exhausted from Santana *M100* engine were determined in 5—250 ppm for MeONO and less than 50ppb for $MeONO_2$.

Key Words: determination, methyl nitrite, methyl nitrate, exhaust gas, methanol.

Study on Determination of Nitrochlorobenzenes in Water by Headspace-GC. Han Changmian (Hubei Environmental Monitoring Station, Wuhan): *Chin. J. Environ. Sci.*, **11**(4), 1990, pp. 58—61

This paper first reports the development of Head-GC method in determination of nitrochlorabenzenes, the boiling points of which range between 235°C and 245°C. The method is simple and quick in operation, and also can totally avoid the interference of high-boiling-point compounds such as BHC, DDT and troubles of emulsification of extractive involved in extraction procedure. It has less harm and risk to human body and the environment. Wide Linear range (from 1 μg/L to 14 mg/L) can be easily obtained just by varying the headspace sampling volume (from 5 μL to 1 mL). The minimum detection limits for (o-, m- & p-) nitrochlorobenzenes could attain below 0.1 μg/L. The relative standard deviation is less than 5.6 percent.

Key Words: nitrochlorobenzene, headspace-GC.

Chemiluminescence Determination of Ammoniacal Nitrogen Using Flow Injection Analysis. Liu Daojie, Liu Renmin (Dept. of Chemistry, Liaocheng Teachers College, Shandong): *Chin. J. Environ. Sci.*, **11**(4), 1990, pp.62—64

A flow injection system for determination of ammonia based on the chemiluminescence reaction between hypochlorite and luminol has been developed. Ammonia reacts with hypochlorite to form monochloramine in basic solution which decreases the observed chemiluminescence intensity. The method has the advantages of high sensitivity, high speed and automation. The linear range of determination is 0.02—0.5 mg/L, the variation coefficient is within 5.2% and the relative error less than ±8%. The method has been applied to determination of ammoniacal nitrogen in natural water with the recovery of 86—95%.

Key Words: chemiluminescence determination ammoniacal nitrogen, flow injection.

Measurement of Air Exchanging Rate in Rooms Using Diluted Tracer Gas. Wang Jingshu, Yu Xiufen, Shi Aiwei (China Institute for Radiation Protection, Taiyuan): *Chin. J. Environ. Sci.*, **11**(4), 1990, pp.65—69

In this paper, an attempt has been made in measuring air exchanging rates in the rooms of some different buildings near Dayawan Nuclear Power Station in October of 1988. The diluted tracer gas (SF_6) technique was used. SF_6 concentration $C(t)$ at time t in the measured building is described as

$$C(t) = C_0 e^{-\lambda t} \text{ or } \ln C(t) = \ln C - \lambda t$$

The exchanging rate Q is equal to $v \cdot \lambda$ in which v is the volume of room or building and λ is air exchanging frequency per hour. In the measurement, SF_6 concentrations were analyzed by using a portable gas chromatagraph. The λ values were taken from $0.6h^{-1}$ to $2.8h^{-1}$ in accordance with different types of rooms.

Key Words: measurement, air exchanging rate, room.

Design of the Modules and the Data Base in A Regional Environmental Information System (REMIS). Long Peixiang et al. (Department of Environmental Engineering, Tsinghua Univers-