

天然水中 NO_2^- 和 NO_3^- 的毛细管电泳分离测定*

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摘要 在 pH 8.2 硼酸缓冲液中, 用高效毛细管电泳分离亚硝酸根, 硝酸根, 并用内标法直接检测了矿泉水, 井水中的 NO_2^- 、 NO_3^- 。以 CTAB 为电渗流改性剂, 离子迁移时间相对标准偏差小于 1.5%; 二甲亚砷作为内标, 样品对内标的峰高比重现性较好。检测下限 NO_2^- 为 2.5×10^{-11} mol/L, NO_3^- 为 1.8×10^{-11} mol/L, 分析结果与离子色谱对照, 符合较好。

关键词 高效毛细管电泳, 硝酸根, 亚硝酸根。

高效毛细管电泳 (HPCE) 是一崭新的分离分析技术, 已由生命科学中的生物大分子 (核酸、蛋白质、多肽) 的分离分析中迅速推进到分析化学中的各个领域^[1]。它在离子型化合物, 元素的价态和形态的分析测定上, 具有试样前处理简单, 样品用量少, 分离速度快等特点。HPCE 对无机离子价态与形态的分析测定已有报道^[2], 但定量测定报道较少, 这主要是由于进样精度较难控制, 测定重现性较差。本文将毛细管电泳用于天然水中 NO_2^- 、 NO_3^- 的分离和测定。分析结果与离子色谱对照, 符合较好。

1 实验部分

1.1 仪器与试剂

自组装毛细管电泳装置。CZE1000R 型高压电源 (Spellman, USA), CV⁴ 型紫外检测器 (ISCO, USA), XWTD-204 型自动平衡记录仪 (上海大华仪表厂)。

以 0.05 mol/L 硼砂, 0.2 mol/L 硼酸为贮存液, 配制成 pH=8.2 硼酸盐缓冲溶液, 加入溴代十六烷基三甲基铵 (CTAB) (分析纯, 美菱牌, 中国医药公司生产) 为电渗流改性剂, 浓度 0.4 mmol/L。全部试剂为分析纯, 配制溶液用二次蒸馏水。

1.2 样品配制

0.1% 的二甲亚砷为电渗流标记物。

含内标标样: 取 1.0×10^{-3} mol/L NO_2^- , 9.9×10^{-4} mol/L NO_3^- 各 1 ml, 0.1% 二甲亚砷 1 ml。配成溶液 NO_2^- 5.0×10^{-3} mol/L, NO_3^- 4.9×10^{-4} mol/L, 二甲亚砷 0.05%。

含内标样品: 取某商品天然矿泉水配成含 0.05% 二甲亚砷水溶液。取笔者单位深井井水配成含 0.05% 二甲亚砷水溶液。

1.3 实验方法

石英毛细管由河北永年光导纤维厂提供, 有效长度 40 cm, 总长 60 cm 内径 50 μm 。

缓冲液置于 2 个 10 ml 烧杯内, 插入电极。毛细管的进样端加负高压, 检测端接地。恒电压操作。电压 15 kV, 电流 6 μA 。测定波长 211 nm。重力进样。

2 结果与讨论

2.1 电渗流改性剂选择

毛细管电泳分离检测无机阴离子, 在通常

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的阳极端进样，阴极端检测情况下，遇到的问题 是电渗流方向与阴离子的泳动方向相反. 对于 NO_2^- 、 NO_3^- 这类淌度大的阴离子，有可能达 不到阴极端而检测不到，用电渗流改性剂，使 得电渗流方向与无机阴离子运动方向一致，采 用阴极端进样，阳极端检测方式，从而能分析 无机阴离子.

电渗流改性剂是一种阳离子试剂，通常采 用长链季胺盐. 实验中选用溴代十六烷基三甲 基胺(CTAB)，四丁基氢氧化胺(TBA)，溴代十 六烷基吡啶(HPC). 3 种试剂在浓度相同时， 离子迁移时间、响应值、峰形、基线、管子平衡 时间各不相同. CTAB 管子平衡时间短、基线 稳、离子迁移速度快、峰形尖锐、响应值偏低； TBA 响应值较高、离子迁移时间长、分离度大、 峰形拖尾；HPC 管子平衡时间长，基线波动大.

考虑以上诸因素，选用 CTAB 作为电渗流 改性剂.

2.2 内标选择

选定的硼酸盐缓冲液中， NO_2^- ， NO_3^- 混合 液能很快分离，分离时间约 3 min. NO_2^- 峰在 前， NO_3^- 峰在后，2 离子迁移时间相差约 8 s.

实验选择几种离子型化合物作为内标物， 由于有不同程度的氧化还原性，配成 NO_2^- ， NO_3^- 混合液后，发生反应，使得 NO_2^- ， NO_3^- 离 子的迁移时间改变，峰型变化，甚至 NO_2^- 峰消 失.

二甲亚砷属中性物质，实验中一直作为测 定电渗流的标记物. 在本实验条件下迁移时间 在 6 min 左右. 它与溶液中的阴离子不发生反 应. 把它配在 NO_2^- ， NO_3^- 标准样品中，作为内 标样品. 图 1 是加内标样品的 NO_2^- 、 NO_3^- 分离 图.

内标样品的浓度实验显示，二甲亚砷的浓 度在 0.005%—0.03%时，信号太弱检测器检不 出. 本实验选用二甲亚砷浓度为 0.05%.

2.3 离子迁移时间与峰高重现性

采用重力进样，进样高度 15 cm，进样时间 5 s. 以二甲亚砷为内标的 NO_2^- ， NO_3^- 标准样品 与水样重复测定 5 次. 测定迁移时间与峰高重 现性如表 1、表 2.

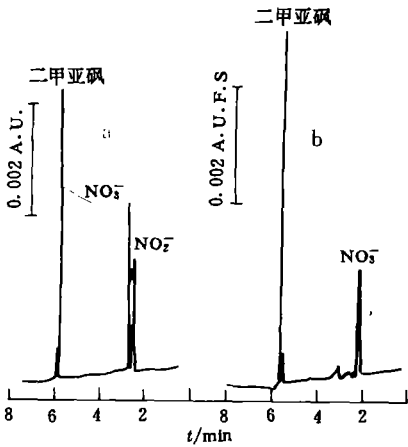


图 1 NO_2^- 和 NO_3^- 的电泳图
a. 矿泉水 b. 井水

表 1 迁移时间重现性

样 品		迁移时间/s					\bar{M}/s	RSD/%
标准样品	NO_2^-	133	135	132	134	134	134	0.53
	NO_3^-	142	142	140	142	142	142	0.40
	二甲亚砷	367	370	364	365	366	366	0.38
矿泉水	NO_2^-	138	134	132	131	132	133	1.31
	NO_3^-	143	143	142	142	143	143	0.24
	二甲亚砷	358	355	355	355	357	356	0.25
井 水	NO_3^-	142	143	143	143	143	143	143
	二甲亚砷	366	366	364	371	373	368	0.63

表 2 峰高比重现性

峰高比	样 品	比 值					\bar{M}	RSD/%
NO ₂ ⁻ /内标	标准样品	0.27	0.36	0.26	0.22	0.24	0.27	19.95
	矿泉水	0.11	0.11	0.10	0.10	0.10	0.10	5.27
NO ₃ ⁻ /内标	标准样品	0.60	0.75	0.66	0.67	0.62	0.66	8.77
	矿泉水	0.93	0.89	0.98	1.02	0.97	0.97	5.19
	井水	0.35	0.24	0.29	0.31	0.27	0.29	14.20

2.4 检测下限的测定

NO₂⁻, NO₃⁻ 在 210 nm 左右具有紫外吸收^[3]可直接检测. 在缓冲液中加入具有紫外吸收的铬酸钾也可间接检测. 2 种检测方法比较, 直接检测更简便, 柱平衡时间短, 选择性好, 灵敏度高. 直接检测下限, 对于 2 倍信噪比, 浓度检测下限 NO₂⁻ 为 1.2×10^{-5} mol/L, NO₃⁻ 为 8.6×10^{-6} mol/L, 进样量 2.1 nl, 绝对检测下限为 NO₂⁻ 2.5×10^{-11} mol, NO₃⁻ 1.8×10^{-11} mol.

2.5 分析结果对照

表 3 分析结果对照(NO₃⁻)/μg · g⁻¹

样品	HPCE	IC	相对误差
矿泉水	44	54	-18.5
井水	13	21	-38.5

表 3 是本方法与离子色谱分析结果的对照情况. 对于 10⁻⁶级水平的结果, 即 0.04%—0.001% 相对标准偏差 < 100%—50%. 符合程度满足工业分析要求的指标.

2.6 关于干扰信息讨论

在 210 nm 处检测矿泉水和井水中所得电

泳图较简单(见图 1). 对于天然水中含量较高的无机离子如 Cl⁻, SO₄²⁻, SiO₄⁴⁻ 等紫外吸收很小, 一般用间接检测的方法才能测得; 而有紫外吸收的离子如 Br⁻, I⁻ 等离子浓度相当低, 检测不到, 另外这些离子的迁移时间有较大区别, 见表 4.

表 4 离子迁移时间

无机离子	NO ₂ ⁻	NO ₃ ⁻	Br ⁻	I ⁻
迁移时间/s	134	142	100	380

电泳的分离已经消除了其他离子的干扰. 紫外吸收较强的有机离子迁移时间比无机离子长得多, 不易构成干扰.

致谢 本所晏学晨提供离子色谱数据, 谨致谢意.

参 考 文 献

1 关福玉. 分析化学, 1995, 23(10):111
2 Morin P et al. . Fresenius' Zeitschrift für Anal. Chem. , 1992, 342: 3572.
3 Jones W R, Jandik P. J. Chromatogr. 1991, 546: 445.

• 书 讯 • 《化学分析测试中的干扰消除》发行

留美博士后学者、研究员周天泽编著的该书 29.8 万字, 355 页, 已于 1996 年 7 月出版. 本书汇集了近 20 年来国内外有关文献, 首次系统地阐述了干扰的规律性, 不同测试方法、各类典型样品以及痕量分析和种态分析中的干扰消除方法. 本书适合各行业化学分析测试的从

业人员参考, 也可作为大专院校有关专业高年级和研究生的选修课教材.

本书由首都师大出版社供货, 18.00 元. 邮汇地址: 100037, 北京西三环北路 105 号; 收款者: 首都师范大学出版社发行部; 银行帐号: 北京工商银行翠微路分理处, 891296-46. 备有订单.

Study on the Residual Dynamics of Cyhalothrin in Soybean and Soil. Li Zhixiang et al. (Institute of Agro-environmental Protection, Tianjin, 300191); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 36—38

In order to make up the standards for safe use of cyhalothrin on soybean, a field experiment was conducted to study the residual dynamics of cyhalothrin in soil and leaves of soybean. The residues of cyhalothrin in green soybean, mature soybean and soil were determined by GLC. Results of two years' study showed that cyhalothrin dissipated rapidly from leaves and soil. Its half lives in leaves and soil were 6.6—7.1 and 6.7—11.6 days, respectively. The soybean field was sprayed twice with cyhalothrin at a rate of 15 g a.i./hm². At harvest, the final residues of cyhalothrin in soil was 0.008 mg/kg, the residues of cyhalothrin in green and mature soybean were all below their detectable limits (0.004 mg/kg). Cyhalothrin is a pesticide of easy dissipation ($T_{1/2} < 30$ d). It is safe if applied twice at a recommended rate (7.5 g a.i./hm²).

Key words: cyhalothrin, soybean, residue, GLC, soil.

Application of Solvent Extraction for Treatment of Wastewater from Luminous Powder (ZnS) Manufacturing Process. Zhu Wapeng and Yang Zhihua (Dept. of Environmental Engineering, Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 39—41

A solvent extraction process for zinc recovery from wastewater from luminous powder (ZnS) manufacturing process was studied. The optimum operation parameters of each unit were determined in laboratory. The zinc ion (I) in wastewater was extracted by D₂EHPA (di-(2-ethyl-hexyl)-phosphoric acid) in the state of saponification-kerosene solution and extracted back by sulfuric acid solution. The zinc recovery rate was more than 95%, nickel in wastewater was not extracted and extraction rate of copper in wastewater was less than 7%. The concentrated zinc solution could be reused in luminous powder (ZnS) manufacturing process. Concentration of zinc, copper and nickel in effluent, after treated by using lime, are lower than the National Wastewater Discharge Standards.

Key words: solvent extraction, zinc, D₂EHPA, di-(2-ethyl-hexyl)-phosphoric acid, luminous powder (ZnS).

pH Value Effect on the Reaction Mechanism of Wet FGD with Lime/Limestone. Chen Zhaoqiong et al. (Dept. of Chemical Eng., Xiangtan University, Xiangtan 411105); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 42—44

The reaction mechanism of wet FGD with Lime/Limestone was studied. The results showed that the species of ions and compounds in the solution effected significantly the reaction mechanism of wet FGD. While pH of the system < 7, main species of sulfur negative ions is HSO₃⁻ and desulphudation are forming Ca(HSO₃)₂ mainly. pH of the system > 7, then main species of sulfur negative ions is SO₃²⁻ and desulphudation are forming CaSO₃ · 1/

2H₂O or CaSO₄ · 2H₂O mainly.

Key words: pH value, FGD with lime/limestone, mechanism.

Designing and Implementation of Acidic Deposition Management Information System in Liuzhou. Guo Jinghai and He Kebin. (Dept. of Environ. Eng. Tsinghua University Beijing, 100084); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 45—47

According to analysis on environmental information regulator regime and combined with the feature of acidic deposition in Liuzhou, the structure and function of management information system of acidic deposition were analyzed systematically, system analysis, requirement analysis and software design were made in detail, on which the overall frame of system were established and five subsystem including database operating, chart, picture, database repairment and model were designed.

Key words: acid rain, acidic deposition, management information system.

Environmental Decision Support System. Peng Zhiliang et al. (South China Institute of Environmental Sciences, NEPA, Nanjing 510655); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 48—52

In this paper a new structure map for decision support systems (DSS) was presented and the concept, content and design guidelines of environmental decision support systems (EDSS) were discussed. An example based on the design guidelines above mentioned was given to illustrate the application of EDSS to regional water quality management.

Key words: environmental management, decision support system, environmental decision support system.

Determination of Nitrite and Nitrate in Water by Capillary Electrophoresis. Ren Hongxing et al. (Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, National Analytical Research Center of Electrochemistry and Spectroscopy, Changchun, 130022); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 53—55

Nitrite and nitrate in mineral water and well water have been determined by capillary electrophoresis with internal standard method at 211 nm in pH 8.2 borate buffer. Cetyltrimethylammonium bromide (CTAB) was used as electroosmotic flow modified (EOF) reagent, and the reproductivity RSDs of migration time for nitrite and nitrate anions were less than 1.5%. Dimethyl sulfoxide (0.05%) was applied as the internal standard in this detection, and the RSDs of peak high ratio of anions to dimethyl sulfoxide were around 20% for the concentration at µg/g level. Detection limits for nitrite were 2.5×10^{-11} mol, and 1.8×10^{-11} mol, respectively. The results were good agree with the results of ion chromatography.

Key words: nitrite, nitrate, internal standard method, capillary electrophoresis.

The petroleum Hydrocarbons in Economical Shellfish along the Coast of Huanghai and Bohai Seas. Shang