N263 溶剂萃取分析环境样品中微量放射性钍

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摘要　本文用阴离子交换剂 N263 作为钍的萃取剂,使待测样品中的钍与铀、镭、铁、稀土等杂质元素分离,并对萃取与反萃取,干扰离子,回收率等因素进行了研究。拟定了硝酸体系萃取,盐酸反萃取,偶氮胂 III 比色测定的分析方法,同时测定了土壤、植物、煤及水样中钍含量.

关键词　钍分析;环境样品;萃取.

随着环境保护发展,对环境样品中微量钍的分析提出了更高要求,本文主要探讨了环境样品中微量钍的分析方法,对钍的含量在 0.0001% 以上样品采用 N263 季胺型液体阴离子萃取剂,使待测样品中铀、稀土等杂质元素进行分离,用 3 mol/L 盐酸反萃取,0.1% 偶氮胂 III 比色测定。本文研究了萃取与反萃取的条件影响,拟定了微量钍的分析步骤。本方法操作简便、快速、成本低,萃取剂可重复使用,适用于环境样品中痕量水平的分析。

一、实　验　步　骤

(一)仪器与试剂

仪器:722 光栅分光光度计

主要试剂:1.N263 季胺型萃取剂(氯化甲基三烷基胺);2.标准钍溶液,10 μg/ml,硝酸介质;3.铀试剂 III,0.1% 水溶液;4.抗坏血酸,5% 水溶液;5.草酸,5% 水溶液;6.盐酸,分析纯;7.硝酸,分析纯;8.环己烷,分析纯。

(二)条件实验

1.工作曲线和标准曲线的制作

(1)标准曲线　取标准钍 1、5、10、15、20 μg 分别加入 25 ml 容量瓶中,直接加入 5% 草酸 1 ml,10% 抗坏血酸 2 滴,0.1% 偶氮胂 III 1 ml,用 3 mol/L 盐酸稀至刻度,摇匀后在 722 光栅分光光度计上,以试剂空白作对比,660nm 波长处 1cm 比色槽比色。(2)工作曲线取　1、5、10、15、20 μg 标准钍分别加入 60 ml 分液漏斗中,加入 15 ml 3.5 mol/L 硝酸,15 ml 5% N263,环己烷溶液萃取 2 min,弃去水相,再用 15 ml 3 mol/L 盐酸反萃 2 min,缓慢摇动,分层后水相转入 25 ml 容量瓶中,其它条件同上,以试剂空白作对比,在 660 nm 波长比色。工作
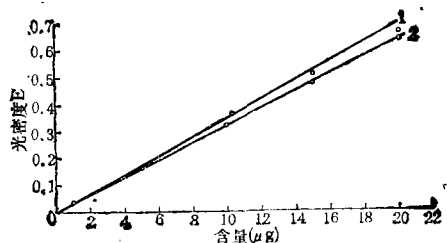

图 1　标准曲线和工作曲线的比较
1.标准曲线 $Y = 0.0079 + 0.032X$　2.工作曲线
$$Y = 0.0055 + 0.0312X$$

曲线和标准曲线比较见图 1。

2.萃取酸度

钍在硝酸介质中形成 $[Th(NO_3)_6]^{2-}$ 阴离子络合物,硝酸浓度在 3—7 mol/L 时能被阴离子萃取剂萃取,萃取率高。选择 2—8 mol/L 不同硝酸浓度萃取,结果表明在 3—7 mol/L 时对钍萃取率高(见表 1)。为降低成本,减少后处理酸度,选择了 3.5 mol/L 硝酸作为萃取浓度。

3.反萃酸度

钍在盐酸介质中进行反萃取不被阴离子萃取剂络合,铀、稀土等元素且被络合萃入有机相。利用这一特性,用盐酸反萃取,杂质离子不被反萃入水相,不同浓度盐酸反萃见表 2,表 2 表明,1—7 mol/L 盐酸反萃取对钍反萃率高,选择 3 mol/L 盐酸作为反萃取酸度。

4.共存离子干扰影响

环境样品中钍一般与铀、镭、稀土共存,反萃时仅有 1% 铀存在于水相,在环境样品中铀、镭、稀土为 r 级水平,比色时一般不干扰钍的分光光度测定。加杂质离子对钍的回收率影响见表 3。

表1　不同 HNO₃ 浓度对钍萃取率的影响

HNO₃ (mol/L)	1	2	3	4	5	6	7	8	9	10
加钍量 (μg)	10	10	10	10	10	10	10	10	10	10
萃取率 (%)	51.2	84.1	94.3	96.3	96.4	95.5	95.4	94.0	87.1	70.2

表2　不同 HCl 浓度对钍反萃率的影响

HCl (mol/L)	1	2	3	4	5	6	7	8	9	10
加钍量 (μg)	10	10	10	10	10	10	10	10	10	10
反萃率 (%)	96.1	96.2	96.2	95.6	95.4	95.4	94.3	72.2	70.0	64.3

表3　加杂质离子对钍回收率的影响

加入离子	加入量 (μg)	钍加入量 (μg)	钍回收率 (%)
铀	10	10	97.2
	20	10	97.4
	30	10	96.7
镭 226	5	10	97.3
	10	10	97.0
	15	10	97.1

（三）样品的分析步骤

准确称取经 100 目筛选样品放入刚玉坩埚内，加入 5 g 过氧化钠，1 g 氢氧化钠，在 600℃ 马福炉内灼烧 10 min，样品熔融至流体状，冷却后用 200 ml 热水浸取，并加热至沸，取下澄清，过滤，用 1% 氢氧化钠清洗坩埚 3 次，沉淀物用 4 mol/L 热硝酸逐滴加入溶解，并直接滤入 60 ml 分液漏斗中，加 15 ml 5% N₂₃₅ 环己烷溶液萃取 2 min，静止分相后，弃去水相，用 3.5 mol/L 硝酸溶液清洗有机相一次，弃去水相，再用 3 mol/L 盐酸 15 ml 反萃取 2 min，反萃液转入 25 ml 容量瓶中，加 2 滴 5% 抗坏血酸，1 ml 5% 草酸，加 0.1% 钍试剂 III 1ml，用 3 mol/L 盐酸稀释至刻度，摇匀，以空白试剂作对比，在 722 光栅分光光度计上，660 nm 波长处比色，由工作曲线上查到相应钍含量。

（四）计算方法

1.固体样品　　$c = \dfrac{N}{W \cdot A}$

式中，c 为样品中钍含量 （μg/g）；N 为由标准曲线查到的钍含量（μg）；W 为分析用样品重量（g）；

A 为化学回收率（%）。

2.植物样品　　$c = \dfrac{N \cdot G}{W_1 \cdot A}$

式中，c 为样品中钍含量 （μg/g）；G 为灰鲜重比（g 灰/kg 鲜重）；W_1 为分析用灰重量（g）。

3.水样　　$c = \dfrac{N}{V \cdot A}$

式中，c 为水样中钍含量 （μg/L）；V 为分析用水样体积 （L）。

二、结果与讨论

应用本方法分析了土壤、煤、植物、粉煤灰、天然水中放射性钍含量。 植物分析需进行样品预处理，将取植物样品连根洗净、晾干、炭化、灰化后称样 2g （视样品含量），其它步骤相同。天然水样取样 4 L，加 50 mg 3 价铁，用氢氧化钠调节 pH ＝ 9，形成沉淀物后再按上述操作步骤进行。二种不同分析方法结果见表4。

表4　环境样品中微量钍的含量

样品 (μg/g)	样品数 (个)	N₂₃₅ 萃取	P₃₅₀ 萃取
土壤	10	11.0±0.8	10.7±0.7
煤	20	12.3±0.7	11.9±0.5
粉煤灰	20	15.4±1.0	15.0±1.1
大米 μg/kg	5	1.1±0.07	1.2±0.6
青菜 μg/kg	5	1.3±0.1	1.4±0.2
长江水 μg/L	5	0.12±0.06	0.11±0.07

表5是本分析方法回收率，在已知钍含量样品中加入一定量标准钍，按操作步骤进行。从表5看，

实验结果见图1. 图1表明,被测气体愈浓,则其变色柱长度愈长. 正如式 (3) 予示的结果, L 与 c 成正比关系.

(3) 变色柱长度与进样体积的关系

流速固定 (50 ml/min) 条件下,我们考察了进样体积的影响,实验结果见图3. 图3表明变色柱长度与进样体积呈直线关系,实验结果验证了式 (3) 予示的结果,即 L 与 Ft 成正比. 在允许的限度内增加进样量,可提高检气管分析灵敏度.
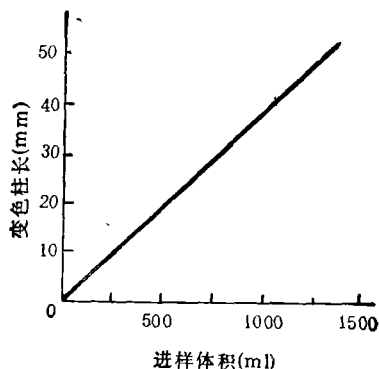

图 3　SO_2 进样体积与变色柱长度关系

(4) 进样速度的影响

进样速度太慢,则影响分析时间;进样速度太快,赶上甚至超过了化学反应速度,则变色界限不清,轻则影响定量分析准确度,重则无法定量. 实验表明本文条件下, 进样速度选择为 50—70 ml/min 较合适.

三、结　论

1. 本文对检气管方法进行了最基本的理论分析,首次推导出检测灵敏度与相关参数之间的理论关系式,从而对检气管相关参数 (包括操作参数) 的选取,给予了明晰的指导.

2. 研制出 SO_2 检气管,并对上述理论关系式给出了满意的实验验证.

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表 5　样品的回收率

样　品	样品数 (个)	样品钍含量 (μg)	加入钍量 (μg)	测得钍量 (μg)	回收率 (%)
土壤	5	10.7±0.9	5	14.5±1.1	92.3
煤	5	12.1±1.0	5	15.7±0.9	91.8
大米	5	1.1±0.2	5	5.5±0.6	90.2
青菜	5	1.3±0.1	5	5.7±0.5	90.5

回收率都在 90% 以上. 在样品分析时固体样品如土壤、煤、煤渣等用 92% 的回收率,植物样品用 90% 的回收率.

用本方法分析微量钍经济、灵敏、方便,检测下限低,能适合环境本底水平样品分析. 使用过的 N_{263} 萃取剂用 5% 碳酸钠溶液洗一次,再用 3.5 mol/L 硝酸平衡两次,即可重复使用,一般重复使用 8—10 次. 在比色时加入草酸可以有效掩蔽铀的干扰,加入抗坏血酸可以排除其它稀土干扰,由于 N_{263} 萃取剂粘度较大,所以在萃取及反萃取时缓慢地摇动,以免水相与有机相分层不清,影响分析结果.

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and PAC in PACT Sludge. Zang Bingqi, Zhang Lindi, Xiao Zhicheng (Environmental Protection Research Institute, Shanghai Petrochemical Complex): *Chin. J. Environ. Sci.*, 12(6), 1991, pp. 52—54

Based on mass balance relationship of activated sludge process this paper presents a method for the calculation and determination of biomass and powdered activated carbon (PAC) in PACT sludge. The results of the calculation show that the concentration of PAC in mixed liquor of aeration tank increased with the raise of the dosage of PAC and the ratio of sludge age to hydraulic retention time. From the weight loss of sludge and PAC at different temperatures, the basic coefficients of three simultaneous equation were obtained. These equations were used to predict the concentration of biomass and PAC in actual PACT sludge samples.

Key Words: PACT; activated sludge; biomass; PAC mass.

Comprehensive Utilization of Manganese Sulphate Containing Waste water from Hydroquinone Production.

Gu Xianghe (Sheyang Chemical Plant of Jiangsu): *Chin. J. Environ. Sci.*, 12(6), 1991, pp. 55—57

Waste water containing manganese sulphate was firstly neutralized to remove Fe and then sulphurated to remove Co and Ni from the water so as to obtain electrolysis liquid up to standard. After addition of Se, the liquid underwent electrolysis for 24 hrs and inactivation to get metallic manganese. Manganese Carbonate was prepared from anode waste water resulting from the electrolysis of mangar se sulphate and then ammonium sulphate was recovered from the waste water of manganese carbonate. The purity of the manganese produced herefrom can reach 99.8%. The process proved to be simple and feasible and possess tangible economical and environmental benefit.

Key Words: manganese sulphate; manganese carbonate; electrolysis.

Plutonium-239, 240, Americium-241 and Cesium-137 in Soils from Some Areas in China.

Sha Lianmao (China Institute for Radiation Protection, Taiyuan, China) M. Yamamoto, K. Komura, K. Ueno (Low Level Radioactivity Laboratory Kanazawa University, Japan): *Chin. J. Environ. Sci.*, 12(6), 1991, pp. 58—63

The surface soil samples with a set of 0-5cm and 5-20 cm depth were collected from Beijing,

Taiyuan, Shijiazhuang, and Jinan of China in early 1990. The samples were analyzed for ^{239,240} Pu, ^{241}Am and ^{137}Cs, including naturally occurring radionuclides, to estimate their present levels and distributions. From these results, the average accumulated depositions were estimated roughly to be $24 \pm 13 MBq/km^2$ for ^{239,240}Pu, $10 \pm 5 MBq/km^2$ for ^{241}Am and $1.2 \pm 0.7 GBq/km^2$ for ^{137}Cs, respectively. The activity ratios of ^{239,240}Pu/^{137}Cs and ^{241}Am/^{239,240}Pu ranged from 0.016 to 0.026 (with a mean value of 0.020 ± 0.004) and 0.35 to 0.49(with a mean value of 0.43 ± 0.05), respectively. The relation between the inventories of these nuclides and excess^{210}Pb in soils was also discussed.

Key Words: plutonium; americium; cesium; radionuclide.

Studies on Flow Injection Chemiluminescence Analysis of Trace Nitrite——I$_2$-EDTA-NO$_2^-$ Photochemical Reaction System.

Liu Renmin and Liu Daojie (Department of Chemistry, Liaocheng Teacher's College, Shandong): *Chin. J. Environ. Sci.*, 12(6), 1991, pp. 64—66

A flow injection chemiluminescent method for the determination of trace nitrite was developed based on its inhibitory effect on the photochemical reaction between I_2 and EDTA and the chemiluminescent reaction between I_2 and luminol. Optimum analytical conditions were established. The linear range for nitrite determination is 1.0×10^{-7} —4.0×10^{-6} mol/L and the detection to limit is 1.1×10^{-8} mol/L. The method was applied to the determination of nitrite in natural water and recoveries of the method were determined to be 93—103.5%.

Key Words: nitrite; flow injection analysis; chemiluminescence analysis; photochemical reaction.

Analysis of Trace Radioactive Thorium in Environmental Samples with N 263 Solvent Extraction Technique.

Wu Jinhai, Chou Tienpao, Li Jinquan (Institute of Radiation Medicine, Shanghai): *Chin. J. Environ. Sci.*, 12(6), 1991, pp. 67—68

This paper describes a method for the analysis of trace thorium by using N263 solvent extraction technique to separate the element from other elements like uranium, radium and rare earth in the environmental samples. Such influencing factors as extraction, reverse extraction, interfering ion, ect. were examined. The method was used for

analysing soil, water, coal, plant samples collected in Shanghai.

Key Words: Thorium analysis.

Basic Theoretical Analysis of Gas-Detector Method Used for the Detection of Atmospheric Pollutants. Wang Hongdao, Zhao Pingya (Research Laboratory of Environmental Chemistry Dalian Railway Institute), Zhang Junxiang, Zhang Lairong (Dalian Institute of Chemical Physics Chinese Academy of Science): *Chin. J. Environ. Sci.,* 12(6), 1991, pp. 69—71

According to the basic theory of gas-detector, the relationship between the detection sensitivity and related parameters was derived as follows: $L = C.F.t/C.A.$ From the equation, the controlling parameters for the operation of gas-detector can be selected easily. The relationship was experimentally verified using the developed H_2S detector.

Key Words: gas-detector; detection sensitivity.

Study on Biodegradability of Coal Gasification Waste water. Jin Chengji, Liu Xuehong, Ou Shanci, Shi Guangmei (Harbin Achi. & Civil Eng. Inst.): *Chin. J. Environ. Sci.,* 12(6),1991, pp. 72—76

Experimental research on characteristics of waste water resulting from coal gasification and bio-reactor for its treatment was carried out. The research shows that when the ratio of phenol to COD is in the range of 43.7—47.7%, biodegradability of the waste water is high (m = 0.62, n = 0.13). Whereas when phenol is removed and ammonia is stripped, biodegradability of the waste water becomes much lower (m = 0.34, n = 0.22) due to the removal of phenolic maters, but it is still biodegradable.

Key Words: coal-gasification wastewater; biodegradability; phenol.

Some Problems about Wind Erosion and the Environment. Lü Yuelai (Northwestern Forestry College): *Chin. J. Environ. Sci.,* 12(5), 1991, pp. 77—78

Soil wind erosion is one of the major environmental problems. This paper reviews the influence of wind erosion on plant growth environment, and the relation between wind erosion and dust storms, and analyses the anthropocentric factors causing the wind erosion. Some proporsals are also offered to control soil erosion by wind and water in certain reaches of the Yellow River Basin.

Key Words: wind erosion, environment.

An Approach to the Sensitivity and Errors of the Air Quality Model of Mountainous Region. Tang Shibao, Chen Meifang (Environmental Monitoring Station of Panzhihua, Sichuan): *Chin. J. Environ. Sci.,* 12(5), 1991, pp. 79—83

This paper analyses the relative significance of parameters of the air quality model of mountainous regions and their influence on the output of the model, based on the analysis of sensitivity and the simulation of errors of the model. It is suggested that great attention should be paid to the selection of correct model and reasonable use of parameters, particularly those like intensity of source, wind direction, wind speed, diffusion parameters, correcting factor of topography and the height of source.

Key Words: air quality modelling.

期的观测数据。因此，建立永久性的监测网点不仅对土壤风蚀与环境质量的评价而且对土壤风蚀的防治都是非常必要的。

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