(1985).
[15] Severs, L. W., et al., *Am. Ind. Hyg. Assoc.*, **39**, 321 (1978).
[16] Kim W. S., et al., *Am. Ind. Hyg. Assoc.*, **41**, 334 (1980).

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测定大气颗粒物中金属元素的样品前处理方法比较

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摘要　本文对测定大气颗粒物中金属元素样品的前处理方法：硫酸-灰化法，常压混酸消解法，高压消解法，索氏提取法进行了探讨．测定了 Cu, Pb, Cd, Cr, Be, Co, Ni 元素，对各方法的空白值，精密度、准确度，以及样品测定等进行了对比与评价．

微量元素与人体健康已引起人们普遍关注，目前国内广泛开展了这方面的研究．但由于大气中微量元素含量低，测定有一定难度．本文对国内外目前广泛使用的几种样品前处理方法：硫酸—灰化法[1]，常压混酸消解法[2]，高压消解法[3]，索氏提取法[4]，就其空白值、回收率、精密度，以及样品测定对照分析进行了实验比较，并对各法作出初步评价．认为：高压消解法具有仪器设备简单，操作容易，试剂用量少，精密度好，准确度高等优点，是大气颗粒物中金属元素测定较理想的前处理方法．常压消解法若精心操作，防止沾污，也是简单易行的方法．

一、实　验

1. 主要仪器试剂

样品采集设备：KB-120D 型空气采样泵(青岛崂山)过氯乙烯滤膜(遵义化工厂)

样品前处理仪器设备：聚四氟乙烯、不锈钢高压消解瓶、石英坩埚、索氏提取器、四氟坩埚、电热板、马福炉、干燥箱、四-六联电炉等．

测试仪器：日立 170-70 型塞曼效应原子吸收分光光度计．

试剂：HNO_3、H_2SO_4、$HClO_4$、HCl(均为优纯) HF (超纯)．

2. 操作步骤

采集样品体积一般 20—30m³．样品前处理方法(个别略有改动)如下．

(1) 硫酸-灰化法[1]　样品膜置入石英坩埚，加 2mL 0.7% H_2SO_4，玻棒搅拌使样品充分润湿，浸泡 1h，然后电热板上加热小心蒸干，将坩埚置马福炉 400±10℃ 加热 4h，至有机物全部灼烧尽停止加热，冷至室温．再加 1 mL HNO_3 及少量去离子水，小心加热转入四氟坩埚，加 4—6 滴HF，在电热板上(铺石英砂)小心加热至尽干，用 0.01 mol HNO_3 溶解，转移定容 15mL．

(2) 常压消解法[2]　用不锈钢剪刀将样品膜剪成小块，放入 200mL 三角瓶中，加 2mL H_2SO_4，8mL HNO_3，瓶口放置小玻璃漏斗，在电热板上加热至膜完全炭化，取下冷却．用水吹洗瓶壁，再加入 3mL HNO_3，2mL $HClO_4$，继续加热至溶液清亮 (炭末除尽再加 HNO_3，$HClO_4$)，取下漏斗，将溶液蒸至冒 SO_3 白烟，近干，冷却，加 0.1mol HNO_3 少许，微热使残渣溶解．转移定容 15mL．

(3) 高压消解法[3]　将样品膜置入四氟乙烯瓶，加入 HNO_3 2mL，H_2SO_4，0.5mL，HF 1 mL，拧紧不锈钢外套，置入干燥箱于 190±5℃ 保温 3h 左右，冷却后取出四氟瓶置铺有石英砂的电热板上敞口加热，先缓慢

加热后提高温度至 180℃ 左右赶酸，冒白烟近干，用 0.2% HNO_3 溶解，转移定容 15mL.

(4) 索氏提取法[4]　将样品膜卷成筒置于索氏提取器内，蒸馏瓶中加入 1:1HNO_3 100mL，回流 3h，待冷却后移入烧杯中浓缩并蒸干，再用 1% HNO_3 溶解转移定容 15mL.

测定方法：塞曼效应石墨炉原子吸收分光光度法.

二、结果与讨论

1. 空白值比较

试剂连同空白滤膜一并按上述四种方法处理后测定，结果见表 1.

微量痕量分析空白值高低直接影响测试结果的准确性和精密度. 本实验四种前处理方法：索氏提取法由于用酸量大(100mL 1:1 HNO_3)，各元素空白值普遍较高 (实验直接用优纯 HNO_3，未再提纯)，部分元素如 Cu 等由于空白值高致使样品无法测定. 高压消解法，硫酸-灰化法酸用量少，又避免了沾污，空白值均较低. 对于不易被沾污的元素如 Be, Co 等，空白值各方法普遍较低.

2. 方法回收率(准确度)比较

将已知量元素的标准溶液点入滤膜上 (Be 为0.050μg，Cd 为 0.075μg. 其他元素为 0.75μg. 接近实际样品中各元素含量范围)，在烘箱内小心烘干，然后分别用上述四种方法处理后测定(见表 2).

高压消解法，常压消解法各元素的回收率都比较满意；硫酸-灰化法 Cu、Cd 等元素回收率偏低，可能是灰化损失所致；索氏提取法由于空白值高，Cu 元素无法测定，Ni 回收率偏高. 四种方法整个回收率范围在 81—119%.

3. 精密度比较

大气颗粒物，限于设备条件很难取到完全一样的多个样品，其精密度试验采用空白膜加标准溶液 (绝对量为 0.05—0.75μg 范围)平行 9 次(分二批)消解后测定，见表 3.

高压消解法各元素精密度都较好，元素 Be, Co 四种方法精密度均较好. 这两种元素各四种方法空白值均很低，决定了它的精密度.

4. 样品测定

将样品滤膜等分 4 份，使之重量相互误差很小，分别用上述四种方法消解处理测定 (表 4).

多数测定结果有较好的一致性，个别样有差别，索氏提取法测部分元素结果偏低，如 Be 等，是提取不完全所致.

5. 各种消解方法的优缺点

各种消解方法的优缺点见表 5.

表 1　空白值比较 (μg/L)

方法 \ 元素		Cu	Pb	Cd	Cr	Be	Co	Ni
高压消解	平均值	1.7	1.6	0.18	5.4	0.07	0.4	1.8
	cv%	5.7	17.1	13.3	5.3	24.8	16.0	10.1
常压消解	平均值	2.6	2.7	0.55	6.2	0.09	0.5	2.7
	cv%	15.5	27.1	5.6	9.5	35.8	18.2	7.1
硫酸灰化	平均值	2.7	2.9	0.11	4.2	0.05	0.5	1.6
	cv%	4.0	8.1	28.8	10.9	23.3	24.0	2.1
索氏提取	平均值	77	16.8	1.18	6.4	0.13	1.1	5.2
	cv%	30.7	10.1	27.8	23.6	20.1	25.0	6.4

注：平均值为三组空白均值，每组至少平行 2 个样品.

表 2　四种方法回收率比较

		高压消解法	常压消解法	硫酸灰化法	索氏提取法
Cu	加标量(μg)	0.75	0.75	0.75	
	测得量(μg)	0.74　0.76　0.69　0.71	0.72　0.83　0.79　0.65	0.70　0.65　0.63　0.77	
	回收率(%)	99　101　92　95	96　110　105　87	93　87　84　103	
Pb	加标量(μg)	0.75	0.75	0.75	0.75
	测得量(μg)	0.74　0.75　0.77　0.73	0.78　0.69　0.83　0.61	0.71　0.75　0.80　0.83	0.85　0.85　0.85　0.60
	回收率(%)	99　100　103　97	104　92　110　81	95　100　107　110	113　113　113　80
Cd	加标量(μg)	0.075	0.075	0.075	0.075
	测得量(μg)	0.086　0.087　0.088　0.088	0.081　0.088　0.083　0.086	0.064　0.063　0.074　0.075	0.087　0.080　0.081　0.078
	回收率(%)	115　116　117　117	108　117　111　115	85　84　99　100	116　107　108　104
Cr	加标量(μg)	0.75	0.75	0.75	0.75
	测得量(μg)	0.72　0.70　0.70　0.71	0.71　0.84　0.82　0.67	0.71　0.79　0.68　0.72	0.74　0.79　0.80　0.68
	回收率(%)	96　93　93　95	95　112　109　89	95　105　91　96	99　105　107　91
Be	加标量(μg)	0.050	0.050	0.050	0.050
	测得量(μg)	0.053　0.052　0.051　0.053	0.049　0.051　0.051　0.050	0.049　0.049　0.051　0.048	0.048　0.053　0.052　0.052
	回收率(%)	106　104　102　104	98　102　102　100	98　98　102　96	96　106　104　104
Co	加标量(μg)	0.75	0.75	0.75	0.75
	测得量(μg)	0.75　0.74　0.75　0.73	0.74　0.75　0.78　0.75	0.70　0.75　0.74　0.68	0.74　0.74　0.74　0.70
	回收率(%)	100　99　100　97	99　100　104　100	93　100　99　91	99　99　99　93
Ni	加标量(μg)	0.75	0.75	0.75	0.75
	测得量(μg)	0.68　0.70　0.70　0.75	0.74　0.83　0.74　0.62	0.75　0.72　0.89　0.83	0.88　0.78
	回收率(%)	91　93　93　100	99　110　99　83	100　96　119　110	117　104

表3　四种方法精密度（CV%）比较

元素 / 方法	Cu	Pb	Cd	Cr	Be	Co	Ni
高压消解法	5.9	7.1	2.9	2.3	2.8	3.1	5.8
常压消解	13.2	11.8	7.0	11.3	4.1	4.7	9.6
硫酸灰化	8.1	8.9	11.9	7.9	5.8	5.2	8.1
索氏提取		14.5	8.1	9.2	4.6	6.0	27.9

表4　样品测定结果比较（$\mu g/m^3$）

元素	样号	高压消解	常压消解	硫酸灰化	索氏提取
Cu	1#-1	0.066	0.065	0.081	
	1#-2	0.025	0.034	0.023	
	2#-1	0.032	0.042		
	2#-2	0.025	0.033	0.029	
	3#-1	0.026	0.037	0.021	
	3#-2	0.025	0.036	0.030	
Pb	1#-1	0.038	0.047	0.054	0.052
	1#-2	0.037	0.024	0.035	0.027
	2#-1	0.085	0.094		0.074
	2#-2	0.039	0.045	0.043	0.045
	3#-1	0.037	0.040	0.053	0.050
	3#-2	0.038	0.037	0.045	0.039
Cd	1#-1	0.00050	0.00049	0.00083	0.00075
	1#-2	0.00050	0.00037	0.00040	0.00051
	2#-1	0.00182	0.00116		0.00126
	2#-2	0.00064	0.00065	0.00059	0.00068
	3#-1	0.00081	0.00066	0.00083	0.00116
	3#-2	0.00069	0.00054	0.00059	0.00095
Cr	1#-1	0.066	0.074	0.053	0.036
	1#-2	0.023	0.034	0.021	0.018
	2#-1	0.031	0.043		0.017
	2#-2		0.044	0.024	0.016
	3#-1	0.026	0.033	0.025	0.016
	3#-2	0.036	0.039	0.032	0.021
Be	1#-1	0.0019	0.0017	0.0014	0.0010
	1#-2	0.0008	0.0008	0.0007	0.0005
	2#-1	0.0014	0.0013		0.0008
	2#-2	0.0011	0.0011	0.0009	0.0007
	3#-1	0.0010	0.0009	0.0009	0.0006
	3#-2	0.0013	0.0012	0.0011	0.0008
Co	1#-1	0.012	0.017	0.011	0.010
	1#-2	0.005	0.006	0.005	0.004
	2#-1	0.009	0.010		0.008
	2#-2	0.008	0.008	0.007	0.006
	3#-1	0.006	0.007	0.006	0.006
	3#-2	0.007	0.008	0.007	0.007

续表 4

元素	样号	高压消解	常压消解	硫酸灰化	索氏提取
Ni	1#-1	0.053	0.050	0.053	0.066
	1#-2	0.019	0.021	0.021	0.023
	2#-1	0.022	0.027		0.020
	2#-2	0.068	0.024	0.027	0.040
	3#-1	0.019	0.018	0.025	0.023
	3#-2	0.030	0.022	0.031	0.045

表 5　各种消解方法的优缺点

	优　　点	局　　限
高压消解法	设备简单，操作容易，试剂用量少(单样耗酸 3.5mL)空白值低，避免沾污，样品处理完全彻底，精密度好，准确度高，适用于同时处理大批量样品(一批至少 20 个样品)	样品处理周期稍长
常压消解法	设备简单，操作容易，试剂用量 15mL 准确度尚可，工作周期短，可大批量处理样品	易沾污，精密度欠佳试剂用量稍多
硫酸灰化法	试剂用量少，(单样 3—4mL)空白值低，样品处理彻底，精密度、准确度满足要求	设备昂贵，操作繁，工作周期长，处理样品批量小，(受设备限制)部分元素易损失
索氏提取法	密闭体系迴流，不易沾污，准确度一般	酸用量大(单样 100mL 1:1HNO_3) 空白值高，部分元素提取不彻底．精密度差，操作较繁，周期长，处理样品批量小

参 考 文 献

[1] 环境监测分析方法编写组，环境监测分析方法，第 263 页，城乡建设环境保护部环保局，1983.

[2] 大气监测检验方法科研协作组，大气监测检验方法，第 158 页，人民卫生出版社，1979.

[3] 李振声，环境研究与监测，4，39(1988).

[4] 李廷安等，环境科学，7(1)，64(1986).

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模拟实验测定江河中有机物的挥发速率

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摘要　本文模拟生态体系，测定 37 种有机物的挥发速率常数，得出有机物的挥发符合一级动力学过程；并用改进的双膜理论模型预测挥发速率常数，结果表明预测值和实测值符合较好；同时介绍了几种参数的测定和估算方法.

挥发是有机物在水环境中迁移转化过程的主要环节之一，国内外有关报道较多[1-4]，但模拟江河条件进行模拟实验研究有机物的挥发速率则不多见[5].

本文针对第二松花江污染状况，选取 37 种有机污染物为研究对象，在室内和江边进行模拟实验，测定并用双膜理论预测有机物的挥发速率.

Bi Mutian Li Xin(Environmental Science Center, Peking University, Beijing): *Chin. J. Environ. Sci.*, **11**(3), 1990, pp.43—49

The method was based on collection of formic and acetic acids in solid sorbent tubes containing Red Chromosorb (40/60 mesh) impregnated with potassium hydrate. The analytes were desorbed with deionized water in an ultrasonic bath and analyzed via IC analysis. This method was applied successfully to determination of formic and acetic acids in the ambient air of Beijing and some areas in Guangdong and Guangxi provinces. In the case of 2.4 m^3 sample gas volume, the minimum detectable concentrations were about 0.2 $\mu g/m^3$ and 0.4 $\mu g/m^3$ for formic and acetic acids respectively.

A Discussion of Four Pretreatment Methods of Analysing Elements in Atmospheric Particulates. Li Zhensheng,Lang Yongshe (Environmental Protection Institute of the Ningxia Hui Autonomous Region, Yinchuan): *Chin. J. Environ. Sci.*, **11**(3), 1990, pp.49—53

This article presents a discussion on four pretreatment methods of analysing metal elements in air particulate samples. In determination of Cu, Pb, Cd, Cr, Be, Co and Ni, the four methods that are sulfate-ash method, acid mixture digestion, high pressure wet digestion and Soxhlet's extraction have beeen compared. The results demonstrate that the method of high pressure wet disgestion with low blank is easy to handle and has a desirable precision (CV% 2.3—7.1%) and high recovery (91 – 117%).

Determination of Volatile Rates of Organic Compounds in a Simulated River Ecosystem. Zhao Yuanhui, Lang Peizhen, Long Fenshan (Dept. of Environmental Science, Northeast Normal University, Changchun): *Chin. J. Environ. Sci.*, **11**(3), 1990, pp.53—57

Studies were carried out in a simulated river ecosystem for determination of volatile rates of 37 kinds of organic compounds. The results showed that volatile process of organic compounds was in line with first-order kinetics. Volatile rate constants were predicted with modified two-film mass transfer model. The predicted constant values approach the values determined practically. In addition, the methods for determining and estimating parameters have been introduced in this paper.

Some Viewpoints on Constructing Dual Water System in Hotels. Shen Guanfan (Beijing Municipal Institute of Environmental Protection): *Chin. J. Environ. Sci.*, **11**(3),1990, pp.58—63

This article describes that in order to ease urban water supply, Beijing Municipality has provided that dual water system should be constructed in the newly-built hotels for treating and reusing a partial sewage on the spot. In China some water-shorted cities have been constructing dual water system one after another. According to researches and practice concerned, the author makes a suggestion in the following aspects: the importance of constructing dual water system; choice of treatment process adapted to differant sewage; technical and economic assessment of the system, and implementing the system in a planned way.

Study on Environmental Capacity of a Tidal River. Zheng Yingming, GaoJianqun (Hohai University, Nanjing): *Chin. J. Environ. Sci.*, **11**(3), 1990, pp.63—69

This paper introduces a methodology on computing environmental capacity of a tidal river in variable conditions of water quality. The main factors affecting the capacity of a tidal river, design of the key factors for computation, a suitable calculating method have been discussed. Finally, a case study has been performed with the hydrologic data of the Suzhouhe River (Shanghai) and the result shows that the method is rational.

An Investigation on Community Response to Environmental Vibration. Tu Ruihe et al. (Beijing Municipal Institute of Labour Protection, Beijing):*Chin.J. Environ. Sci.*,**11**(3),1990, pp.70—73

Based on the investigations into environmental vibration caused by industrial machines in five cities in China, the paper analyzes the community responses in terms of subjective evaluation. The annoyance percentage increases with the Z-weighted vibration level and tendency behaves in the shape of S. The annoyance thresholds calculated by the u-test, the principle of psychological physics and turning point of the S-shaped curve are in the range from 70 to 76 dB(Z-weighted vibration level). The results have provided the national standard "GB10070-88 Standard of Environmental Vibration in Urban Area" on this basis.

Application of Photoionization Detector to Gas Chromatography. Jing Shilian et al. (Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing): *Chin. J. Environ. Sci.*, **11**(3), 1990, pp.84—86

This paper describes gas chromatography with photoionization detector to be applied in three fields: analysis of environmental samples, detection of drugs and identification of specific organic compounds. The instrument has its remarkable features with high sensitivity, low detection limit and selective measurements. The GC with PID has been designed and made by the authors.

A New Type of Hydrogen Fluoride Generator. Wu Changnian, Chen Shuyuan (Jiangsu Institute of Botany, Nanjing): *Chin. J. Environ. Sci.*, **11**(3), 1990, pp.87—91

Reported in this paper is a new type of HF generator which has been developed in Jiangsu Institute of Botany in 1989. The process of producing HF is substantially improved in the generator, so that HF solution of a specified concentration can be vaporized at a high temperature to form HF gas of a desirable concentration. The generator is suitably applied to the field experiments with the open-top chamber.