

监测分析

大气中几种痕量烃类化合物连续自动检测

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摘要 本文报道在环境大气中有机污染物的全自动新分析方法。本方法采用由计算机控制的 GC、大气样品浓缩管、电磁六通阀、真空泵及微处理机组成的全自动连续分析装置、完成定性定量分析。连续三周在呼和浩特市以每小时为分析周期,用此装置检测了环境大气中正己烷、苯、甲苯、O-甲苯、M-甲苯、P-甲苯等 16 种有机污染物,获得较满意的结果。

关键词: 大气;烃类化合物;连续自动检测。

在城市大气中烃类化合物的存在极为普遍,在工业发达国家,其主要来源是汽车尾气^[1],而在我国可能主要是来自家庭及工业用煤的不完全燃烧。分析这些在环境中含量甚微、种类繁多的有机污染物,一般采用以毛细管色谱的高分离性与质谱的高分辨性能相结合的方法,这在目前是比较有效的分析手段^[2]。但是,在分析时常需要手动操作,并且处理大量的环境样品有一定的局限性,尤其是大气中的污染物浓度受气象,时间以及季节的影响,变化很大^[3]。因此,我们用内藏微机的气相色谱、开发了能够自动浓缩样品,分析,定量的装置,将这装置用于呼和浩特市环境大气中烃类化合物的检测。

一、实 验

1. 分析装置及色谱条件

自动分析装置^[4]由 GC-MiNi2 便携式气相色谱仪、SUPELCOWAX 10 毛细管柱、FID 检测器大气样品浓缩管(自制),AU-SF 型电磁六通阀,PG-15 采样泵及内存微机的 GC-3A 积分仪等组成。其分析程序如图 1、2。

色谱条件: 本实验改装了岛津 GC-MiNi2 气相色谱仪。色谱柱为 SUPELCO-

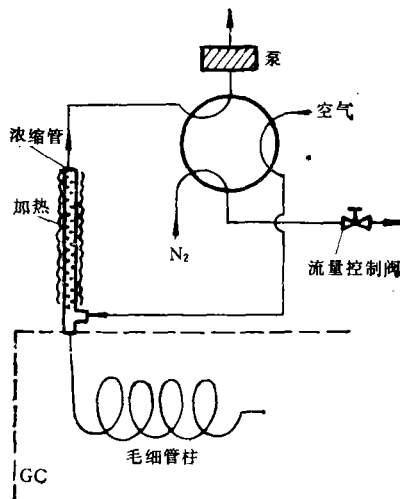


图 1 浓缩流路

WAX 10 Fused Silica Capillary Column, $\phi 0.32\text{mm} \times 25\text{m} \times 0.25\mu\text{m}$; 柱温: 初温 35°C , 以 $5^\circ\text{C}/\text{min}$ 程序升温至 220°C ; 载气进口压力 $1.2\text{kg}/\text{cm}^2$ 。氢气压力 $0.5\text{kg}/\text{cm}^2$, 空气压力 $1\text{kg}/\text{cm}^2$ 。大气样品浓缩管: 内径 3.5mm , 外径 6mm , 长 30cm 的硼硅酸盐玻璃管, 管中填充 Tenax GC (60—80 目) 10cm , 两头用玻璃棉堵住, 直接与 GC 进样口连接。

2. 分析步骤

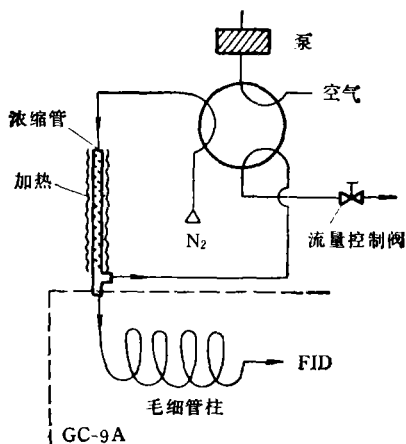


图2 分析流程

自动分析由时间程序来控制。首先（打开继电器 6）清洗 2mm ϕ \times 4m Teflon 采样管道。1min后，（打开继电器 1），浓缩管在室温下以 0.2L/min 的流速进行大气采样及浓缩。采气量视大气中污染物含量来调节，本实验采用20min 采气 4L。20min 后采样泵停止，同时（打开继电器 4）浓缩管中通入载气，21.5min（打开继电器 5）控温器的电源自动接通，10s 后使浓缩管温度升到 220℃，将浓缩管中被测样洗脱进毛细管色谱系统，24.5min 柱温以 5℃/min 的速率升温，分析开始。55min（关闭继电器 4），将柱温冷却至初始温度，打印分析结果。60min 分析装置再次自动启动，重复以上全过程（自动循环周期为 1h）。

二、结果与讨论

1. 分离效果

本实验所用的 16 种标准样品均由日本横滨国立大学环境科学研究中心提供。文献 [5] 报道用 HP-Crosslinked 5% Phenyl Methyl Silicone Capillary Columu (ϕ 0.32mm \times 25m \times 0.25 μ m) 较难分离邻二甲苯和间二甲苯。但我们改用 SUPELCOWAX 10 Fused Silica Capillary Columu ϕ 0.32mm \times 25m 柱，并对分离多种烃类化合物曾进行多

次程序升温条件的选择，其最佳条件是 35—230℃，5℃/min，当柱温升到 200℃ 时，待测样品的峰全部出完，柱温上升到 230℃（保持 10min）时可除去高沸点的杂质，从而检测器不被沾污。从图 3 可见，标样中各化合物均可分离完全，邻二甲苯和间二甲苯也能清晰的被分辨。定量分析时，用注射器将 16 种标样分别取 10 μ l 于 10ml 丙酮中溶解，再从此混合液中取 100 μ l 于 10ml 甲醇中稀释配制成工作液。取稀释液 3 μ l 直接注入浓缩管中，在

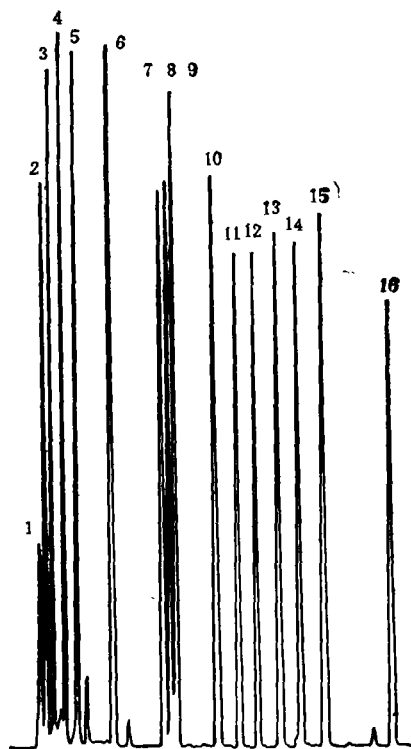


图3 标准样品的色谱图

序号及标准混合溶液浓度 (ppb): ①正己烷(139) ②庚烷(123) ③辛烷(111) ④壬烷(99) ⑤苯(202) ⑥甲苯(169) ⑦乙苯(147) ⑧邻-二甲苯(149) ⑨间-二甲苯(146) ⑩对-二甲苯(146) ⑪ n-丙基苯(165) ⑫二乙基苯(132) ⑬1,3,5-三甲基苯(129) ⑭1,2,4-三甲基苯(131) ⑮对-乙基苯(176) ⑯1,2,3-三甲基苯(175)

大气采样口接上充满 N₂ 气的 5L 气袋，其它步骤与分析大气样品相同。

2. 空白与干扰

将 5L 气袋用高纯 N₂ 气冲洗 3 次后充满

表 1 16 种化合物相对标准偏差 (C-V%)

化 合 物	相对标准偏差(%)	化 合 物	相对标准偏差(%)
正 己 烷	2.6	间-二甲苯	4.8
庚 烷	2.1	对-二甲苯	2.2
辛 烷	4.6	n-丙基苯	1.6
壬 烷	3.7	二乙基苯	1.1
苯	0.8	1,3,5-三甲基苯	2.1
甲 苯	0.9	1,2,4-三甲基苯	3.8
乙 苯	2.2	对-乙基苯	1.7
邻-二甲苯	0.4	1,2,3-三甲基苯	0.5

高纯 N_2 气, 接在大气采样口, 仍与分析大气样品一样浓缩 20min 进行分析, 待测物出峰时而均未发现有杂质峰干扰。本实验最低检出限均可达 0.1ppb。

3. 精密度

在用高纯 N_2 冲洗过的 5L 气袋中, 同时取大气样品 6 个, 同样以 0.2L/min 的流速进行浓缩 20min 后分析, 观察了自动分析系统对 16 种化合物的再现性。16 种烃类化合物均得到较满意的结果, 将 6 次分析的相对偏差结果列于表 1。

4. 回收率

本实验对其中 10 种化合物进行了加标回收实验, 结果列于表 2, 加标量为 10ppb, 回收率为 86.2%—113.3%。

5. 现场实测结果

我们于 1989 年 2 月 1 日—2 月 20 日在呼和浩特市对环境大气中 16 种烃类化合物进行了现场测定。在 21 天内, 该装置运转正常, 从未间断。连续自动(基本上无人看管情况下)分析了冬季呼和浩特市大气中环己烷、苯、甲苯等 16 种烃类化合物, 取得 8064 个(16

种 $\times 24h \times 21d$) 数据, 每种化合物都获得连续 504 个 h 的 (21d $\times 24h$) 分析数据。其准确度与精密度均达到较满意的结果。

从分析数据可知, 呼和浩特市大气中确实存在着上述 16 种烃类化合物, 其检出率达 100%, 其中苯含量最高, 平均浓度为 12.24 ppb, 实测浓度在 11.04—36.53ppb 之间。甲苯的平均浓度为 5.78ppb, 实测浓度在 4.65—7.98ppb 之间。其它 14 种化合物含量较低, 平均值均在 1ppb 左右, 详细结果参见表 3、图 4、图 5。

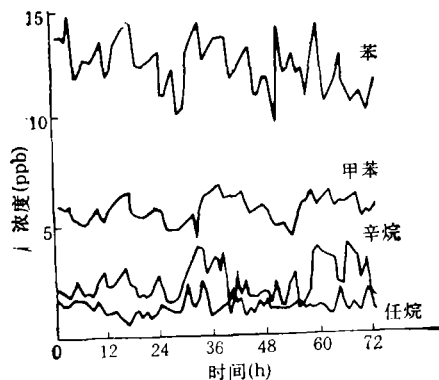


图 4 呼和浩特市大气浓度变化

表 2 回收率实验结果

化合物	苯	乙苯	n-丙基苯	1,3,5-甲基苯	1,2,3-甲基苯
回收率(%)	87.0	98.5	113.3	90.0	102.8
化合物	甲苯	邻二甲苯	2-乙基苯	1,2,4-甲基苯	二乙基甲苯
回收率(%)	86.2	112.5	106.8	106.3	90.0

表 3 大气中芳香烃化合物分析结果

名 称	平均值 (ppb)	最大值 (ppb)	最小值 (ppb)	标准偏差	变异系数(%)
正 己 烷	1.35	2.99	0.67	0.59	37
庚 烷	2.02	4.15	1.70	0.54	37
辛 烷	2.06	4.21	1.42	0.77	30
壬 烷	1.33	2.13	0.81	0.34	25
苯	12.24	36.53	11.04	1.43	12
甲 苯	5.78	7.98	4.65	0.75	13
乙 苯	1.49	3.50	0.84	0.72	44
对-二甲苯	1.55	2.14	1.02	0.28	17
间-二甲苯	2.04	2.81	1.36	0.75	18
邻-二甲苯	1.29	2.43	0.88	0.93	24
n-丙基苯	1.00	1.77	0.78	0.24	9.0
乙基苯	0.99	2.53	0.69	0.40	36
甲基苯	1.06	2.37	0.77	0.35	31
邻乙基苯	1.44	2.44	0.81	0.51	27
1,2,4-甲基苯	1.43	2.18	0.82	0.33	21
1,2,3-甲基苯	1.81	2.81	1.47	0.50	24

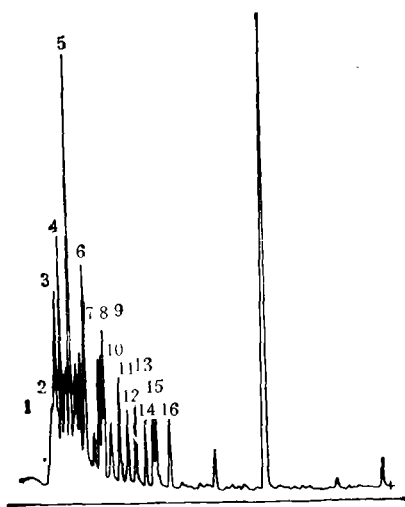


图 5 大气样品色谱图

呼和浩特地区苯浓度平均值为 12.24 Ppb, 甲苯为 5.8ppb。苯与甲苯比例为 2:1, 与兰州地区的苯与甲苯比值较接近; 而与日本横滨地区的苯与甲苯比值正好相反, 见表 4。在日本, 甲苯含量高是由汽车尾气污染所致, 而呼和浩特市的苯含量高于甲苯是否与煤烟污染有关? 有待进一步研究。

采用 Tenax GC 为吸附剂的常温连续自动分析方法, 运用微机控制全分析系统, 解决了从采集大气样品、富集导入毛细管色谱

表 4 不同地区苯、甲苯浓度(ppb)

地区	苯	甲苯	备注
呼和浩特市	12.24	5.80	平均值
兰州市	33.9	19.5	
日本	3.10	6.35	平均值

分离到数据处理的自动化、连续化问题, 便于研究随气象、时间、季节等因素所引起的污染物浓度变化趋势及规律。实际应用表明:

(1) 该方法具有快速、灵敏、准确的优点, 而且无需繁琐的化学前处理, 节省大量的溶剂, 省人力物力, 简便经济。

(2) 采用了无分流直接进样法, 不通过气化室, 没有样品损失, 使灵敏度相对提高, 也不存在死体积问题。

(3) 由于自动采样、浓缩进样弥补了人工操作时的偶然误差, 有良好的再现性。

(4) Tenax GC, 在室温下 (25℃) 虽然

对沸点低于 30℃ 的化合物吸附力不强,但是对沸点高于正己烷的(C₆以上)烃类化合物,其捕集率为 100%^[1],并且能耐 380℃ 的高温,使用过程中再生很简单。

本研究说明,以 Tenax GC 为吸附剂的常温浓缩自动分析系统是测定环境大气中挥发性痕量有机污染物的行之有效的手段,至今在国内未见报道。该方法为我国环境大气监测提供了简便、可靠的先进手段。

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甲醇燃料发动机排气中的亚硝酸甲酯和硝酸甲酯的分析*

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摘要 为了测定使用甲醇燃料的发动机排气里的亚硝酸甲酯(MeONO)和硝酸甲酯(MeONO₂)含量,建立了色谱分析方法。本方法的最小检测限 MeONO 为 20ppb, MeONO₂ 为 50ppb。对自制的 MeONO 和 MeONO₂ 进行了质谱鉴定,并对所制备的一定浓度的样品进行了稳定性考察。应用本方法测定了甲醇机排气中的 MeONO 含量为 5ppm—250ppm, MeONO₂ 含量为 <50ppb。

关键词: 亚硝酸甲酯;硝酸甲酯;气相色谱法;色谱-质谱联用。

使用甲醇燃料的发动机排气中含有一定量未燃的甲醇,它在排气管中或大气里能与氮氧化物反应生成亚硝酸甲酯(MeONO)。MeONO 致变作用明显^[1]。在紫外光照射下可变成硝酸甲酯(MeONO₂)^[2]进而生成甲氧基成为光化学烟雾源^[3]。因而引起人们的关注。瑞典的 Jonsson 等^[4]、日本的 K. Ito^[5]研究了甲醇燃料车排气里的亚硝酸甲酯。日本的 Kyokuo 等报导了甲醇、乙醇燃料小汽轮机排气里有亚硝酸甲酯和硝酸甲酯的生成^[6]。国内尚未看到有关报道。近年来,我国开展了 M₁₀₀ 甲醇燃料在内燃机上的应用研究。为了评价甲醇燃料发动机排放对大气的污染,测定 M₁₀₀ 甲醇发动机尾气中 MeONO 和 MeONO₂ 的含量建立了本分析方法。

一、仪器和试剂

仪器: SC-1001 气相色谱仪带有 Ni⁶³ ECD (四川仪表九厂)

JMS-D300S 色谱-质谱仪(日本 JEOL 公司)

试剂: 硫酸(分析纯)(北京化工厂)
硝酸(分析纯)(北京化工厂)
甲醇(分析纯)(北京化工厂)
亚硝酸钠(分析纯)(济南化学试剂厂)

二、实验和结果

(一) MeONO 和 MeONO₂ 的制备:

* 籍志松同志参加了部分工作。

standard concentration.

Directed by the model, the plant species and afforestation pattern were designed, and the capacity of plants for SO_2 and the amount of SO_2 released in Yiyang were established.

Key Words: model, vegetation, control, air pollution.

The Avoidance of Eel Larvae (*Anguilla japonica* Tem. et Schl.) in the Solution Containing Copper Ions. Zhen Jiang (Institute of Zoology, Academia Sinica, Beijing): *Chin. J. Environ. Sci.*, 11(4), 1990, pp.31—34

The avoidance of eel larvae (*Anguilla japonica*) in the solution containing copper sulfate (as Cu^{2+}) has been studied in a flowing water system under the laboratory conditions: water temperature 16.5°C, pH 7.43, water hardness (CaCO_3 and others contained) 220 mg/L and saturation of DO 62—68%. The larvae used for the experiment were collected from the Minjiang River, Fujian Province. Their lengths ranged 46—69.5 mm, and their weights 174—227 mg. The experiment illustrated that the eel larvae was highly sensitive to copper, because the avoidance action was observed at the level of 0.001 ppm of copper ions. However, below the level of 0.001 ppm, the avoidance was not so obvious, but the larvae all avoided the test solution as its concentrations increased to 0.064 ppm. The results indicated that the concentrations of avoidance against copper was much lower than that of MATC derived from acute toxicity test.

Key Words: avoidance, eel larvae, (*Anguilla japonica*), copper.

Estimation of Fishery Losses Caused by Water Pollution in a Country of Jiangsu Province. Ge Jigi (Department of Agricultural Economics, Nanjing Agricultural University): *Chin. J. Environ. Sci.*, 11(4), 1990, pp. 34—37

Based on the fundamental principles of environmental economics, the fishery losses caused by water pollution in the area can be calculated in three parts: loss of resources, loss of accidents and expense of protection from pollution impact. The calculative methods of the said every items of losses and a case study are also presented, according to the author.

Key Words: fishery losses, water pollution.

Improvement of Removing Rate of Nitrate in

Drinking Water with the CARIX Process. Gong Wenli (Institute of Nuclear Energy Technology, Tsinghua University): *Chin. J. Environ. Sci.*, 11(4), 1990, pp.38—41

The paper describes treatment of drinking water using CARIX ion exchange process. The combined application of a weakacid ion exchanger in the free acid form and an anion exchanger in the bicarbonate form provides a combined removal of nitrate, sulfate and hardness from drinking water. Carbon dioxide is used for the simultaneous regeneration of both resins. In order to improve the regeneration efficiency of nitrate, the application of additives like CaCO_3 or MgO has been studied. The dosage of different quantities of MgO has been investigated with respect to an optimization. MgO should be added at the concentrations above 0.4%. Furthermore, the usual mixed bed was compared with a compound bed, consisting of several short single beds. Under the raw water conditions of the test, over 50 BV of water could be treated, whereas regeneration required about 5 BV of water.

Key Words: CARIX process, nitrate, drinking water.

Research on the Starting Conditions of an Anaerobic Digester. Xu Chunlan, Yan Dacheng, Wu Chibo (Department of Environmental Engineering, Huangshi University, Hubei Province): *Chin. J. Environ. Sci.*, 11(4), 1990, pp. 42—48

The primary intent of this research is to explore optimal starting conditions of an anaerobic digester. Anaerobic treatment of wastewater has many advantages, but it takes a long time for the digester to start running, so that the equipment cannot bring into full play. The authors investigated starting conditions of anaerobic treatment in a citric acid factory, found that the conditions were optimized by using orthogonal design. The experimental results were applied to the industrial equipment for treating wastewater and got a satisfactory benefit.

Key Words: starting conditions, anaerobic digester.

Automatic and Continuous Determination of Aromatic Compounds in the Ambient Air Using Capillary Column Gas Chromatograph. Wulan Sendan, Tong Qing, Liu Yansen (Inner Mongolia Monitoring Center for Environmental Protection, Huhehot): *Chin. J. Environ. Sci.*, 11(4), 1990, pp.49—53

An automatic and continuous analysing device of aro-

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 exhaust gas from the engine fuelled with methanol has been established. The minimal concentrations of MeONO and MeONO₂ determined by this method are 20ppb and 50ppb respectively. The prepared MeONO and MeONO₂ 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 MeONO₂.

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 nitrochlorobenzenes, 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 (SF₆) technique was used. SF₆ concentration $C(t)$ at time t in the measured building is described as

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

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, SF₆ concentrations were analyzed by using a portable gas chromatograph. The λ values were taken from 0.6 h⁻¹ to 2.8 h⁻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 University)