

北京市燕山地区大气颗粒物中 NO_3^- 和 SO_4^{2-} 浓度变化规律及其与 O_3 的关系

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摘要 用KB-120型大气颗粒采样器采样, 离子色谱法分析其中水溶性无机阴离子组分。结果表明, 北京市燕山石油化工区大气颗粒物中 NO_3^- 和 SO_4^{2-} 浓度随季节变化显著, 夏季 NO_3^- 和 SO_4^{2-} 平均浓度分别为 $9.40 \mu\text{g}/\text{m}^3$ 和 $28.22 \mu\text{g}/\text{m}^3$; 秋季分别为 $4.12 \mu\text{g}/\text{m}^3$ 和 $3.80 \mu\text{g}/\text{m}^3$ 。

关键词 颗粒物, NO_3^- , SO_4^{2-} , 离子色谱, 北京燕山地区。

大气颗粒物中的 NO_3^- 和 SO_4^{2-} 一般是由大气中的一次污染物 NO_x 和 SO_2 经过一系列物理、化学变化形成; 有时, 它们又作为光化学烟雾的最后归宿之一停留于大气中, 它们对大气环境有明显的影

响。燕山石化公司炼油厂地处山区, 每年7—8月份光照强时, O_3 浓度明显增高。7月份 O_3 浓度约为元月份 O_3 浓度的10倍左右^[1]。 O_3 是重要的光化学氧化剂之一, 在环境大气中吸收紫外光发生光解产生的OH自由基, 在 NO_x 和 SO_2 气相转化成 NO_3^- 和 SO_4^{2-} 过程中起着十分重要的作用^[2]。为此, 笔者与燕山石化公司炼油厂合作, 于1991-07和1991-09分别对颗粒物中 NO_3^- 和 SO_4^{2-} 和 O_3 、甲醛、烃类等气体污染物进行了2次集中观测。对该地区颗粒物中 NO_3^- 和 SO_4^{2-} 浓度变化规律及其与 O_3 浓度关系进行了初步探讨。

1 实验

1.1 样品的采集

(1) 采样地点 厂前、胜利小学和凤凰亭生活区。

(2) 采样时间和采样方法 1991-07-19—07-25和1991-09-11—09-21, 2段时间采样。每天采样时段为08:00—10:45, 11:00—13:45和14:00—16:45。2次集中采样共117个。

用KB-120型大气颗粒物采样器和有机膜采集粒径小于 $100 \mu\text{m}$ 的颗粒物。采样器的流量控制在110—120 L/min之内。

1.2 样品的前处理与分析方法

(1) 仪器与试剂 超声波清洗机(H66005, 无锡超声电子设备厂); 2010i型离子色谱仪, HPIC-AS4型分离柱, HPIC-AG4型保护柱和AFS型抑制柱(均为美国Dionex公司产品); $0.2 \mu\text{m}$ 微孔滤膜(北京化工学校附属工厂), K_2SO_4 , 无水 Na_2CO_3 , NaOH , 浓 H_2SO_4 和 KNO_3 等试剂均为优级纯(除 KNO_3 为上海化工专科学校实验工厂生产外, 其余均为北京化工厂制)

(2) 分析方法 样品分析前用去离子水在超声波清洗器中浸取20 min, 浸取液用 $0.2 \mu\text{m}$ 微孔滤膜过滤后定容到25 ml。按此方法浸取水溶性 NO_3^- 和 SO_4^{2-} 的浸取效率均在96%以上。浸取液按文献[3]提供的离子色谱条件测定 NO_3^- 和 SO_4^{2-} 的浓度。

2 结果与讨论

2.1 SO_4^{2-} 和 NO_3^- 的浓度及其变化规律

(1) 随季节变化的趋势 今将该地区夏、秋

2 季大气颗粒物中 SO_4^{2-} 和 NO_3^- 浓度的平均值、最高值和中值分别列于表 1 和表 2 中。

表 1 燕山地区大气颗粒物中 SO_4^{2-} 浓度 ($\mu g/m^3$)

样 点	平均值		最高值		中 值	
	7 月	9 月	7 月	9 月	7 月	9 月
厂 前	26.30	4.03	135.1	12.22	17.26	2.70
凤凰亭	34.30	2.95	120.5	13.07	25.51	1.03
胜利小学	24.05	4.43	112.8	15.83	12.73	1.43
平均值	28.22	3.80	122.8	13.71	18.50	1.72

表 2 燕山地区大气颗粒物中 NO_3^- 浓度 ($\mu g/m^3$)

样 点	平均值		最高值		中 值	
	7 月	9 月	7 月	9 月	7 月	9 月
厂 前	10.97	3.32	33.15	13.40	6.79	1.90
凤凰亭	11.61	5.70	23.79	27.29	11.08	4.08
胜利小学	5.63	3.34	27.57	16.11	2.39	1.89
平均值	9.40	4.12	28.17	18.93	6.75	2.62

从表 1 和表 2 看出, 由于季节不同, SO_4^{2-} 和 NO_3^- 浓度的平均值、最高值和中值, 夏季都高于秋季。7 月份 NO_3^- 的浓度主要分布在 $0.01-20 \mu g/m^3$ 范围内, 约占样品总数的 89%; 9 月份其浓度主要分布在 $0.01-10 \mu g/m^3$ 范围内, 约占样品总数的 90.3%。7 月份 SO_4^{2-} 的浓度主要分布在 $0.15-40 \mu g/m^3$ 范围内, 约占样品总数的 81.5%; 9 月份其浓度主要分布在 $0.01-10 \mu g/m^3$ 范围内, 约占样品总数的 85.5%。将此结果与采样期间的气温变化(参看图 1)相对照, 不难看出由于 7 月份日照较强, 排放到大气中的 NO_x 在日光作用下更易经过多步氧化成 HNO_3 , 形成 HNO_3 后与大气中的碱性物质中和形成硝酸盐, 以使 NO_3^- 的浓度随之上升。与此同时, 强日照下的 SO_2 氧化作用 ($SO_2 \xrightarrow[H_2O(g)]{日光, O_2} H_2SO_4, SO_2 \xrightarrow[OH]{NO_x} H_2SO_4$) 也均得到加速。因而 SO_4^{2-} 的浓度也易出现高值。另一方面, 夏季闷热、干燥、静风天气较多, 污染物形成后不易被稀释并扩散到远方, 容易在附近积累; 到秋季日照明显减弱, 加上风的传输与稀释作用, 污染物的浓度得以减小。

(2) 采样点不同的差异 7 月份, 厂前

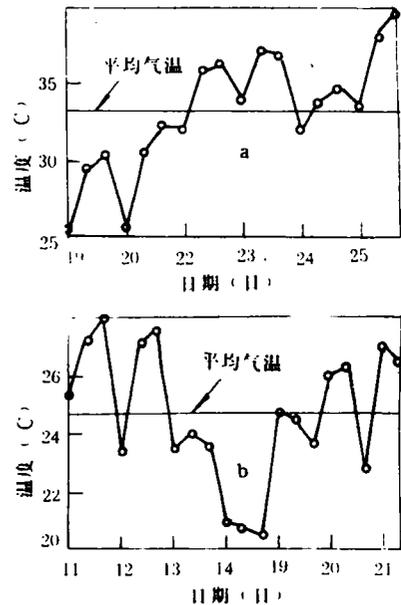


图 1 一周内温度变化图
a. 七月 b. 九月

NO_3^- 的浓度主要分布在 $0-10 \mu g/m^3$ 范围内, 约占样品总数的 61%; 胜利小学 NO_3^- 的浓度主要分布在 $0-5 \mu g/m^3$ 范围内, 约占样品总数的 76.2%, 而凤凰亭的浓度主要分布在 $5-15 \mu g/m^3$ 范围内, 约占样品总数的 72.2%。从其平均

浓度来看,也以凤凰亭为最高。9月份与7月份的结果其总的趋势基本相同。这一现象的产生可能与其所处的地理位置及气象因素有关。凤凰亭位于炼油厂加氢车间的东南方向,其西北方向又有多个化工厂和聚脂厂等。所以,不论刮东南风还是西北风,都很容易将NO_x由污染源处带到凤凰亭来,出现该地区虽无污染源但其污染程度却很高的异常现象。在美国的Connecticut地区也有类似的情况^[4]。颗粒物中SO₄²⁻浓度的分布范围普遍高于NO₃⁻(最高为40 μg/m³),但总的趋势与NO₃⁻的情况相类似。

2.2 NO₃⁻、SO₄²⁻与O₃浓度间的相关关系

各采样点大气颗粒物中NO₃⁻和SO₄²⁻浓度随天气状况的变化趋势如图2和图3所示。

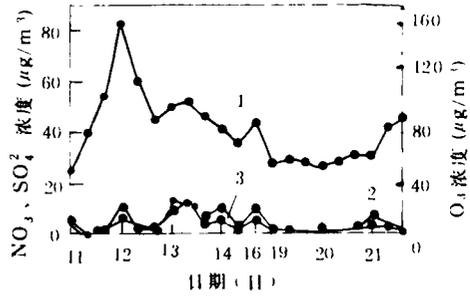


图3 SO₄²⁻、NO₃⁻和O₃随时间变化(一周内,厂前,九月)
1. O₃ 2. SO₄²⁻ 3. NO₃⁻

从图2和图3上可以看出,在采样期间NO₃⁻、SO₄²⁻与O₃浓度的变化趋势大体相同。各种污染物基本上都在同一天出现高峰。而且厂前采样点各种污染物浓度的总体水平一般都高于生活区。经进一步统计回归分析结果表明,NO₃⁻和SO₄²⁻浓度之间有明显的相关关系。这说明二者可能具有共同的来源,而且受天气状况的影响也表现出相类似的趋势。此外,NO₃⁻浓度与O₃浓度的统计回归分析计算结果是95%置信水平上有较显著的线性相关性^[5];反之,SO₄²⁻浓度与O₃浓度之间却没有这种明显的线性相关性,虽然由于样品数的限制,目前尚不能得出最终的结论,但这一现象仍可反映出该地区的地形特点和夏季的高温、强日照以及静风天气为主的气象特点成为大气光化学反应活跃的适宜条件。这一趋势应该十分重视,由于NO_x气相转化形成NO₃⁻可能比SO₂气相转化形成SO₄²⁻的形式更为重要,NO_x的气相反应更易于受光氧化剂O₃的影响,而SO₂转化反应还与大气相对湿度密切相关。在相对湿度较高情况下,其转化率也较高^[6],这说明SO₂的液相氧化可能是更为重要的途径。

燕山地区石油、化工工厂较为集中,根据地形和天气条件等特点均有助于化工区直接或间接排放的大量烃类化合物通过光化学反应生成O₃并造成O₃的积累。从表3中所列出的数据可以看出,燕山地区夏、秋季O₃的浓度远远高于北京市其它地区同期O₃的浓度数值。此外,该地区的含硫污水池和制硫车间等都是含

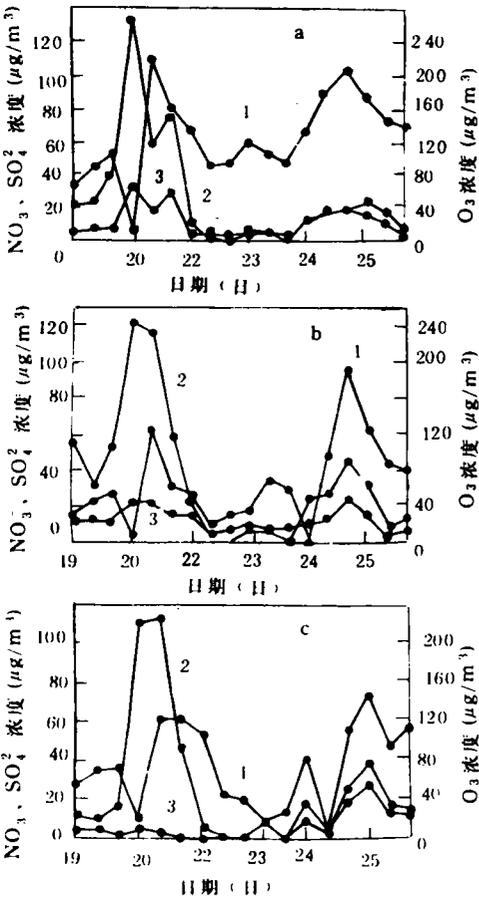


图2 SO₄²⁻、NO₃⁻和O₃随时间变化(一周内)
a. 厂前(七月) b. 凤凰亭(七月) c. 胜利小学(七月)
1. O₃ 2. SO₄²⁻ 3. NO₃⁻

硫化合物的重要来源。

表 3 几种污染物浓度的比较(μg/m³)

污染物	燕山	黄庄 ²⁾	昌平 ²⁾	大兴 ²⁾
NO ₃ ⁻	9.40	10.74	6.83	7.19
SO ₄ ²⁻	28.22	18.63	16.09	12.96
O ₃	122.90	79.60	97.50	63.30
SO ₂	15.80 ¹⁾	9.50	10.40	19.00
NO _x	26.80 ¹⁾	19.90	27.00	38.50

1) 为历年平均值(由燕山石化公司监测站提供)

2) 为北京地区 1986 年的实测结果

3 小结

(1) 该地区大气颗粒物中 NO₃⁻ 和 SO₄²⁻ 的浓度随季节的变化而发生急剧的变化。这一事实说明在 NO₃⁻ 和 SO₄²⁻ 的气相形成过程中日照的影响尤为显著;

(2) 在不同采样地点 NO₃⁻ 和 SO₄²⁻ 的浓度分布不同, 这说明其浓度与采样地点的地理位置和气象条件密切相关;

(3) 在该地区的大气中, 颗粒物中 NO₃⁻ 和

SO₄²⁻ 的浓度之间存在着较为明显的相关关系。二者随时间的变化趋势与 O₃ 基本一致。因 NO_x 的气相转化反应与 SO₂ 的气相转化反应相比更为重要, 且更易于受光氧化剂浓度的影响。因此, NO₃⁻ 与 O₃ 浓度之间的线性相关趋势不容忽视, 应作进一步长期监测和考察。

致谢 燕山石化公司炼油厂及监测站在采样过程及提供有关数据等方面都给予了大力协助与支持, 在此致以诚挚的谢意。

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(3) 根据淮河流域实际情况, 编制了非点源污染模型, 并同 QUAL2EU 进行接口, 解决了污水灌溉、农业施肥造成的非点源污染问题。

(4) 此综合模型应用于淮河流域, 计算结果与实际监测值吻合良好, 此模型是开发者和使用者反复交流共同开发的, 已经作为淮河流域的水质管理和决策的有力工具。

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ments in batch experiments. A COD removal of 98.4% was given when a gentamycin wastewater with a COD concentration of 19240 mg/L was subjected to an anaerobic treatment for 3 d and then to an aerobic treatment for 10 h. A COD removal of 95.8% was given when a mixture of gentamycin wastewater and aureomycin wastewater (1 : 2) with a COD concentration of 7740 mg/L was subjected to an anaerobic treatment for 2 d and then to an aerobic treatment for 10 h. The COD concentration in final effluent could be reduced to less than 300 mg/L when the gentamycin wastewater after an anaerobic treatment for 3 d was combined with the aureomycin wastewater after an anaerobic treatment for 6 h and then subjected to an aerobic treatment for 4 h.

Key words: gentamycin wastewater, aureomycin wastewater, refractory organics, anaerobic-aerobic treatment.

Chemical Valence States of Sulfur Measured with a High Resolution Two Crystal X-ray Fluorescence Method. Wang Qingguang et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085), Ji Ang (Shanghai Institute of silicates, Chinese Academy of Sciences, Shanghai 200050), Ma Guangzu (Institute of Rock and Mineral Analysis, Ministry of Geology and Mineral Resources, Beijing 100037); *Chin. J. Environ. Sci.*, **16** (5), 1995, pp. 48-50

With a high resolution two crystal X-ray fluorescence (HRXRF) method, the chemical valence states of sulfur in pure elemental sulfur, sulfites, sulfates and sulfides and in some of unknown samples were determined, the range of energy differences of the spectral peaks for sulfur in different valence states were identified, and then the range of energy differences was used to identify the chemical valences of sulfur in unknown samples. Each of chemical valence states of sulfur in standard samples had essentially no change after they had been subjected to repeated HRXRF measurements. Sulfur in various chemical valence states had the following ranges of energy differences for spectral peaks; S^{6+} , +1.10 to +1.25 eV; S^{4+} , +0.61 to +0.93 eV; and S^{2-} , -0.12 to -0.21 eV. This method was found useful in the measurement of sulfur in a single chemical valence state, and in the identification of different chemical valence states of sulfur.

Key words: HRXRE, chemical valence state, sulfur, sulfur-bearing compounds, energy

change.

Application of Black-box Theory to GC Analysis of Waste Containing Methanol. Qin Jinping et al. (Nanjing Institute of Chemical Technology, Nanjing 210009); *Chin. J. Environ. Sci.*, **16** (5), 1995, pp. 51-53

The GC optimal conditions were estimated based on black-box theory. GC/MS was used for qualitative analysis of methanol wastewater. On the GPX-203 (60-80 mesh) coated with 5% PEG-20 M, C_1-C_5 alcohols in methanol wastewater were quantitatively analyzed by means of FID. The detection limits were 1 μ /ml for C_1-C_3 alcohols, 3 μ g/ml for C_4 alcohols, and 4 μ g/ml for C_5 alcohols.

Key words: methanol, wastewater, C_1-C_5 alcohols, black-box theory, gas chromatography.

Flame Atomic Absorption Spectrometric Determination of Copper, Lead, Cadmium, and Manganese in Natural Waters Using a Flow Injection System with On-line Ion Exchange Preconcentration. Wang Peng et al. (Dept. of Applied Chemistry, Harbin Institute of Technology, Harbin 150006); *Chin. J. Environ. Sci.*, **16** (5), 1995, pp. 54-56

The title method was developed, and some practical considerations in the design of on-line column preconcentration FIA system for FAAS were studied. The relative standard deviation was about 2.0% ($n=11$) at a sampling frequency of 45 h^{-1} with an enrichment of around 20 times. The advantages, such as high-efficiency, on-line, accuracy, precision, micro-amount of sample, automation et al., made it possible to be applied to the routine analysis of natural waters.

Key words: flow injection analysis (FIA), ion exchange preconcentration, atomic absorption spectrometry, copper, lead, cadmium, manganese.

Study on the Seasonal Variations in the Atmospheric Particulate Nitrate and Sulfate Concentrations in the Yanshan District of Beijing. Li Xin, Guo Huajie et al. (Dept. of Technical Physics, Peking Univ., Beijing 100871); *Chin. J. Environ. Sci.*, **16**(5), 1995, pp. 57-60

The title study was carried out in summer and autumn, in which the seasonal variations were also related to the atmospheric concentration of ozone as a major photochemical oxidant. The results show that the concentrations of nitrate and sulfate in atmospheric particulates varied significantly with seasons, and were higher in summer than in

autumn. In addition, the concentration of nitrate and sulfate were often of high values in one or two days before raining and in 3 or 4 days after raining. This indicates that rainfall had a significant effect of scavenging particulates. The level of nitrate in particulates was found to have a much better correlation with ozone concentration than the level of sulfate in particulates.

Key words: particulate, nitrate, sulfate, ozone, ion chromatography.

Study on the Photocatalytic Degradation of Organo-Phosphorus Pesticides. Chen shifu et al. (Dept. of Chemical Eng., Zhengzhou Institute of Technology, Zhengzhou 450002); *Chin. J. Environ. Sci.*, **16**(5), 1995, pp. 61–63

The feasibility of photocatalytic degradation of three different structures' organophosphorus pesticides using TiO_2 powders as a photocatalyst was studied. The results show that different structures of organophosphorus pesticides had different photodegradation efficiencies, and four organophosphorus pesticides of 1.0×10^{-4} mol/L were completely photocatalytically degraded into inorganic phosphate after 40 min illumination with a medium pressure mercury lamp of 375 W. Some intermediate products of photocatalytic degradation of monocrotophos were detected and the effects of the parameter, such as amount of TiO_2 , flow rate of air and Fe^{3+} concentration, on the photocatalytic degradation were also investigated. The mechanism were discussed preliminarily.

Key words: organophosphorus pesticides, photocatalytic degradation, TiO_2 powders.

Preliminary study on the relationship between seasonal dynamics of microfauna in the root system of water hyacinth and their effects on the purification of waterbody. Li Baolin (Beijing Municipal Research Academy of Environmental Protection, Beijing 100037); *Chin. J. Environ. Sci.*, **16**(5), 1995, pp. 64–66

Seasonal variation characteristics of microfauna in the root system of water hyacinth has been primarily studied when it was used to treat sewage water from the Beijing Zoo. 70 species of microfauna was found in the water-root system in 1992, with the largest number of 60 species in 49 genera in August. Biomass (by relative quantity and average wet weight) of microfauna was heavier in July and August, and the weight percentage of protozoa in the same two months were 76.9% and 64.1%. The dominant species (po-

pulation) examined in each month (June to October) was reported. The main physical and chemical indexes such as TN, TP and BOD varied seasonally. The removal of TSS was up to 82.9% and those of BOD and TP were 66.6% and 91.6%. This study demonstrates that the purifying efficiency of water-hyacinth system was in a relationship with the seasonal characteristics of the microfauna built up in its rootsystem.

Key words: water hyacinth, root system, microfauna, purification.

Study on the Decolourization Activity of Activated Sludge with Immobilized Decolourization Bacteria. Zhang Lin et al. (Dept. of Environ. Eng., Taiyuan Univ. of Technology, Taiyuan 030024), Ma Minghuan (Shanxi Textile Industry Designing Institute, Taiyuan 030002); *Chin. J. Environ. Sci.*, **16**(5), 1995, pp. 67–69

The highly efficient decolourization bacteria were selected and immobilized on an activated sludge by using an aggregated/cross-linked immobilization method to form a microstructure of cross-linked floccule-granule. The activity of decolourization enzyme increased by about 70% as compared with a non immobilized activated sludge. The results of textile dyeing wastewater treatment under anaerobic condition show that there was an average colour removal 77.3% with an average COD_{Cr} removal of 65.1%.

Key words: aggregated/cross-linked immobilization, the activated sludge with immobilized decolourization bacteria, activity of decolourization enzyme, dyeing wastewater.

Study on Environmental Etiology Among a Population at a High Risk of Gastric Cancer in Xianghuangqi County of Inner Mongolia: An Appraisalment on the Endogenous Synthesis of Nitrosamines in Human Body. Song Xiuxian et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085), Liu Kezhong (Inner Mongolia Autonomous Region's Hospital, Huhhot 010017); *Chin. J. Environ. Sci.*, **16**(5), 1995, pp. 70–71

The contents of nitrites in water from 15 rural areas in Xianghuangqi, Xilinguole Meng, Inner Mongolia Autonomous Region, were measured. The results show that the contents of nitrites in water widely varied and could be classified broadly into three groups with an average nitrite level of 0.186, 0.640 and 3.840 $\mu\text{g}/\text{ml}$ respectively. The contents of amines in mildewed cheese were