秸杆燃烧中 OCS 的排放因子和排放估算 *

曹美秋　　　庄亚辉

（中国科学院生态环境研究中心，北京　100085）

摘要　建立了痕量羰基硫采样及分析方法，利用低温预捕集和被捕集样直接释放进入分离柱技术，对压缩空气进行采样测定，得出了压缩空气中 OCS 约在 2.94×10^{-3} μg/L，方法精度以标准误差系数计为 ±0.72%。利用此采样及分析方法对实验室规模的生物质封闭燃烧系统，稻草、玉米秸、麦杆燃烧过程中排出痕量 OCS 进行了采样分析，得出稻草、玉米秸、麦杆燃烧排气中 OCS 的排放量，以排放因子表示分别是：1.80 g/t，2.75 g/t，2.05 g/t。详细统计了作物秸杆量，建立了全国各县各种作物秸杆燃烧释放痕量气总体和网格排放计算的数学模式。利用排放因子计算了几种主要作物秸杆燃气中 OCS 的释放量。

关键词　羰基硫，生物质燃烧，排放因子，排放估算。

　　羰基硫（OCS）是影响气候变化和生态变化的痕量气体，是很重要的大气化学成分。在大气中气态硫化物除 CS_2 外以 OCS 的浓度最高，其主要来源于海洋、土壤、火山爆发、沼泽地、生物质燃烧等。生物质燃烧是主要的人为源，为了解生物质燃烧中 OCS 的排放，科学工作者观测了生物质燃烧释放的 OCS 和 CO_2[1]，并从 OCS/CO_2 的平均比率推算出生物质燃烧中 OCS 的全球排放量大约是 0.2 Tg/a。笔者研究了中国生物质燃烧释放的 OCS。在国内首先建立了痕量 OCS 的分析方法，并建立封闭燃烧系统和低温富集采样装置，通过几种主要作物秸杆的燃烧实验，得出燃气中 OCS 的排放因子，利用此因子和对全国主要作物秸杆的统计量，建立了计算 OCS 排放量的数学模式，并对全国 OCS 的排放量进行了估算。

1　实验

　　实验分 2 部分，生物质在系统中的燃烧和样品的采集。燃烧装置及燃烧实验与已报道的生物质燃烧释放 N_2O 的测定及分布[2]相同为封闭式。对燃烧释放气的采集是：把一端置于燃烧室内的采样管从燃烧室引出后，经冷阱、过滤装置、$CaCl_2$ 管和样品富集管，富集管于液氮温度下，待生物质燃完，排空系统空气、即抽燃烧室内气体以 500 ml/min 流速吸取 3 min，富集好的样品在液氮温度下保存至测定。样品中的痕量 OCS 用带有双火焰光度检测器（SP-501，山东腾县），硫特征光谱滤光片（394 nm）的气相色谱测定。从液氮中取出富集管直接放入仪器的进样口内在 200℃ 以上 OCS 被解析进入玻璃填充色谱柱（4mm×1.8 m i. d.）。

　　OCS 样需预浓集[3]，其富集玻璃管[（3—4）mm×1.0 m i. d.]内装 60—80 目 Tenax-GC 约 200 mg。

　　为了验证仪器的灵敏度与精确度，以同样的方法采集测定了压缩空气中 OCS 的浓度。

　　排气中的 OCS 用 2.0%（克分子比）OCS/N_2（美国 Scott Specialty Gases Inc）标定其色谱测定值，进样量是 1 μl。

2　结果和讨论

　　以压缩空气为稳定的排放源采集测定了其中 OCS 的量，由色谱分析得到压缩空气中 OCS 的色谱峰高和浓度值列于表 1，典型的色谱峰表

表 1　压缩空气中 OCS 测定值[1)]

OCS 色谱峰高(cm)	13.5	13.7	14.0	10.3	9.0	9.8	10.2	9.2	11.4
OCS 标气峰高(cm)	17.4	17.4	17.4	13.0	11.5	12.6	12.6	11.6	14.4
[OCS]($\mu g/L \times 10^{-3}$)	2.94	2.96	2.99	2.96	2.98	2.94	3.00	2.96	2.97

1) 压缩空气中 OCS 浓度平均值($\bar{a}$)为 2.97×10^{-3} $\mu g/L$，精确度以测定值的标准误差系数($\delta_{n-1}/\bar{a} \times 100\%$)计为 $\pm 0.72\%$
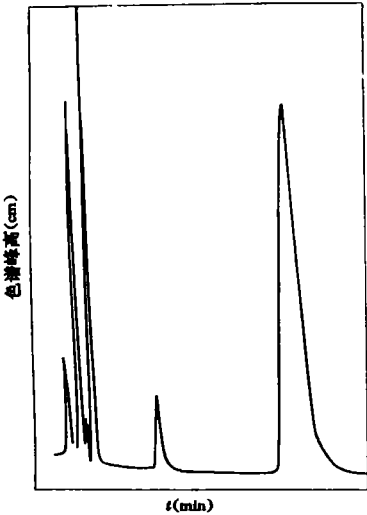
示如图 1。

图 1　典型压缩空气中 OCS 谱峰图

实验前对系统可能出现的物理和化学吸附采取了预防措施。物理吸附，主要是系统表面对被测定组分的吸着。化学吸附，本实验采用玻璃系统可能存在—OH 基与 OCS 的反应(OH+OCS→CO$_2$+HS)[4]。为了消除玻璃表面的活性基团，用二甲基二氯硅烷的甲苯溶液对采样和富集用的玻璃管以及燃烧装置中的玻璃表面进行了钝化处理并燃烧一定量的生物质使其吸附饱和，由此减免吸附的损失。

燃烧中产生的 HC 在火焰中有氧化并产生光辐射，在检测器上有响应。由于在室温下气相 HC 为 C$_1$—C$_4$，其沸点分别为 C$_1$：-100，C$_2$：$-100 \sim -50$℃，C$_3$：-50—0℃　C$_4$：0—30℃。为了避免 HC 的影响，首先在实验系统中加冷井(冰-盐)除去 C$_4$ 和部分 C$_3$ 的 HC，对 C$_1$—C$_3$ 的组分是否有干扰？笔者做了系统加入的 C$_3$ 组分实验，结果得到 C$_3$ 色谱峰在 OCS 谱峰之前大约 30 s 出现而没有干扰 OCS 的测定。

采集后的样品需注意保存，测定前一直被保持在液氮温度下，报道[5]中指出样品在液氮温度保存一周没有挥发损失。

要特别注意的是，严格控制采样时间保持在燃烧室升温和保温过程中[2]以免降温带来的浓度损失。

由色谱分析得到农业废弃物秸秆燃烧释放气中 OCS 的色谱峰高和浓度值列于表 2，其典型的色谱峰表示于图 2，其中 a 是空白样中 OCS 的峰，b 是燃气中的 OCS 谱峰。用表 2 中 OCS 的浓度值计算出生物质燃烧过程中 OCS 的排放因子列于表 3。
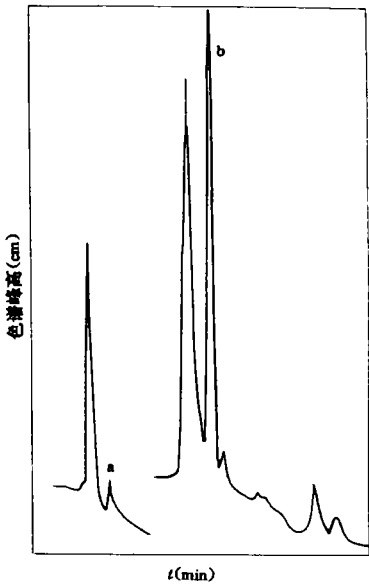

图 2　生物质燃烧色谱峰图

表 2 为燃烧不同量(g)生物质各次取样测定值，它是根据火焰光度检测器测硫化物特性，其色谱峰高与[S^{2-}]的平方成正比，即 $\sqrt{H} = ac$，a 为常数取决于实验条件，在相同实验条件，常数 a 在计算中相消，得出样品浓度($c_{\text{样}}$)计

表 2　生物质燃气中 OCS 的测定结果

生物质	OCS 测定值($\mu g/L \times 10^{-2}$)								
玉米秸	3.75	3.68	5.10	5.39	4.78	4.31	4.09		
稻　草	2.94	3.09	3.23	3.50	3.58	3.53	3.58	4.21	3.50
麦　杆	3.43	3.21	2.92	2.86	2.72	3.55	2.79		

表 3　生物质燃气中 OCS 的排放因子

生物质	OCS 排放因子平均值 (g/t)	标准误差系数 ($\pm\%$)
玉米秸	2.75($n^{1)}=7$)	8.36
稻　草	1.80($n=9$)	6.67
麦　杆	2.05($n=7$)	9.27

1) 表中 n 为测定次数

算式：

$$c_{样} = \sqrt{H_{样}} \cdot c_{标} \Big/ \sqrt{H_{标}}$$

　　测定标样和测定样品相同也经过 Tenax-GC 再进色谱柱,因此可不计算回收率。

　　利用表 3 中 OCS 的排放因子计算 OCS 在全国的排放量,计算式为:

$$Q = E \times Z \times R \times B$$

式中,Q 为生物质燃烧释放的 OCS(Tg/a),E 为本实验得到的 OCS 的排放因子(g/t),Z 为作物产量(t),R 为秸谷比[6],B 为用于生物质燃烧的秸杆量(60%)[2]。由方程计算出中国主要作物秸杆燃烧释放 OCS 量大约是 6.0×10^{-4} Tg/a。

　　研究中详细统计了全国 2370 个县、市的主要农作物产量,根据比例系数 R 值得到相应的秸杆量,作出 $1° \times 1°$ 秸杆分布图(略)。

　　利用秸杆分布量和排放因子,计算出 OCS 气体从一个网络中排放的总量(Q_T)。Q_T 是该网格中 m 个县 n 种作物收割后燃烧秸杆释放气体的和。

$$Q_T = \sum_{i=1}^{n} \sum_{j=1}^{m} Q_{i,j}$$
$$= \sum_{i=1}^{n} \sum_{j=1}^{m} Y_{i,j} \times A_{i,j} \times R_i \times f_{i,j} \times E$$

式中,$Y_{i,j}$ 是县 j 内作物 i 的单位面积产量(t/hm^2);$A_{i,j}$ 是县 j 内作物 i 的播种面积(hm^2);R_i 是作物 i 的秸谷比;$f_{i,j}$ 是 j 县内烧去作物 i 的百分数,E 是该痕量气体的排放因子(g/t)。

3　小结

　　(1)建立了痕量 OCS 的采样及分析方法,利用低温预捕集和被捕集样直接释放进入分离柱技术对压缩空气进行采样测定,得出了其中痕量 OCS 气体的浓度,方法精确度以标准误差系数计为 $\pm 0.72\%$。

　　(2)利用建立的采样和分析方法,对实验室规模的生物质封闭燃烧系统中,燃烧农业废弃物的释放气进行采样分析,得出了稻草、玉米秸、麦杆燃气中 OCS 的排放量,以排放因子表示分别为 1.80 g/t、2.75 g/t、2.05 g/t,精确度以标准误差系数表示分别为 $\pm 6.67\%$、$\pm 8.36\%$、$\pm 9.27\%$。

　　(3)建立了生物质燃烧中痕量气体全国和网格排放计算模式,详细统计了 2370 个县的相关秸杆量,作了 $1° \times 1°$ 秸杆分布图和 OCS 排放空间分布图。

参 考 文 献

1　KHALIL M A K et al.. Atmosph. Environ., 1984, **18**(9): 1805

2　Cao Meiqiu and Zhuang yahui. J. Environ. Sci.. 1994, **16**(3): 261

3　PRZYJAZNY A. J. Chromatog., 1985, **333**(2): 327

4　NIEN DAK SZE et al.. Atmosph. Environ., 1980, **14**(11): 1223

5　TANGERMAN A. J. Chromatog., 1986, **366**: 205

6　马世骏等。中国的生态工程。北京:科学出版社, 1987: 141

that PCP removal by granular sludge in UAD reactors was due to biodegradation rather than adsorption and volatilizaiton.

Key words: pentachloropenol, biosorption, de-sorption, biodegradation, anaerobic.

Photocatalytic Oxidation of Benzene Hexachloride and Pentachlorophenol in Aqueous Solution.

Li Tian and Qiu Yanling (School of Environ. Eng., Tongji Univ., Shanghai 200092): Chin. J. Environ. Sci., **17**(1), 1996, pp. 24—26

Photocatalytic oxidation of low concentration of benzene hexachloride (BHC) and pentachlorophenol (PCP) in aqueous solution is studied with a high pressure mercury lamp as radiation resource and TiO_2 as a catalyst. BHC can be oxidized easily, half life periods of the 4 isomers of BHC are all around 20 minutes. Oxidation rate of γ-BHC is higher under neutral condition. Chlorinated medium products formed in the photocatalytic oxidation of BHC can be gradually removed by further reaction. For PCP reaction rate of photocatalytic oxidation is much higher than that of photolysis. Dechlorination of PCP can be completed within 30 minutes. As the reaction process continues, PCP will be oxidized into simple small molecules and finally mineralized completely. It is predicable that photocatalytic oxidation has bright prospect in advanced treatment of drinking water.

Key words: photocatalytic oxidation, benzene hexachloride, pentachlorophenol, aqueous solution.

The Dissipation and Residue of Quinclorac in Rice Field Water, Soil and Rice Plant.

Wang Yiru et al. (Institute of Agro-environmental Protection, Tianjin 300191): Chin. J. Environ. Sci., **17**(1), 1996, pp. 27—30

Quinclorac is a new herbicide with high efficiency and low toxicity. The field experiments were carried out both in Tianjin and Jilin Province in 1993 and 1994, respectively. It has been found that the herbicide dissipated rapidly from water and leaves. Its half life values in the water was 0. 8 days in Tianjin and 2 days in Jilin, and the half life in rice leaves was less than 1 day. The residure in sediment remained quite low during 6 days of half life. No metabolite was detected in soil. Applied to rice field as a 50% WP formulation at the recommended rates of 412. 5 g—525 g/hm², one application, preharvest interval 96—105 days, the residue remaining in unpolished rice was less than 0. 005 mg/kg, far below MRL, and was safe to humanbeing.

Key words: Quinclorac, metabolite, dissipation, final residue, water, rice, soil.

Wet Air Oxidation Treatment of H-acid Production Waste Liquor.

Wang Yongyi et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084): Chin. J. Environ. Sci., **17**(1), 1996, pp. 31—33

Under the condition of reaction temperatures of 200—250℃, initial oxygen partial pressures of 1—3 MPa, the wet air oxidation (WAO) of H-acid has 2-step process, including rapid reaction step, in which during the first 10 minutes after the beginning of the reaction COD is decreased rapidly, and UV/Vis. absorbance is increased drastically at first and then reduced rapidly, and slow reaction step, in which, both COD and UV/Vis. absorbance are decreased slowly during about 20 minutes.

WAO treatment can improve biodegradability of H-acid significantly. After 1 hour reaction carried out at 160 C and 3 MPa initial oxygen pressure, COD was decreased by 50%, and the BOD_5/COD ratio of 10 g/L H-acid solution was increased from 3. 4% to 33. 3%. The offgas from the WAO treatment of H-acid contains undetectable amount of SO_2 and nitrogen oxides.

Key words: wet air oxidation, H-acid, biodegradability.

Emission Factors of Trace OCS from Crop Residues Burning and Estimation Its Amount in China.

Cao Meiqiu and Zhuang Yahui (Research Center for Eco-Environmental Sciences, CAS, Beijing 100085): Chin. J. Environ. Sci., **17**(1), 1996, pp. 34—36

A method of sampling and analysis for trace carbonyl sulfide has been described. The sample is trapped and concentrated at temperature of liquid N_2 and liberated directly into a gas chromatographic column. The concentration of OCS in compressed air as determined as 2.94×10^{-3} μg/L. The method accuracy expressed in term of standard deviation coefficient is $\pm 0.72\%$. The emission factors of carbonyl sulfide, which were measured during the combustion of rice straws, maize stalks and wheat stalks in an enclosed combustion system, are 1. 80, 2. 75 and 2. 05 g/t for rice straws, maize stalks, and wheat stalks, individual. Standard deviation coefficient are $\pm 6.67\%$, $\pm 8. 36\%$, and 9. 27% for rice straws, maize stalks, and wheat stalks, respectively. Distribution of the amount of crop residues burned in China is presented with a resolution 1° latitude × 1° longitude. The amount of trace OCS could be calculated with their emission factors.

Key words: carbonyl sulfide, biomass buring, emission factor.

The Study of Trace Elements in Human Hair from the Area of Endemic Arsenism.

Jiang Ling et al. (Institute of Environ. Medicine, Tongji Medical Univ., Wuhan 430030): Chin. J. Environ. Sci., **17**(1), 1996, pp. 37—39

217 hair samples and environmental samples from endemic arsenism in Linhe, Inner Mongolia were analyzed. The results showed that the levels of As, Cu and K in hair in studied area were higher than that in control area, but Zn and Se was opposite. The relationship between the typical symptoms of arsenism and the levels of As, Cu, K and Se in hair were found. There were rank correlations between the concentration of Se, Zn, Cu in hair and As in hair (the coefficient = -0.988, -0.794, 0.783, respectively).

Key words: endemic arsenism, trace elements, hair.

Research for the Problem about the Environmental Discount Rate.

Wang Yonghang and Fu Guowei (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): Chin. J. Environ. Sci., **17**(1), 1996, pp. 40—43

This paper presents a new formula, which describes the relation between private rate or return and social rate of return. The formula includes two environmental parameters, λ, the fraction of national income spent on environmental investment, and η, the elasticity of environmental improvement with respect to environmental spending. From the formula it can be seen that social rate of return or environmental discount rate should decline systematically over time from the point of view of environmental