第17卷第1期　　环　境　科　学　　Vol. 17, No. 1
1996年2月　　ENVIRONMENTAL SCIENCE　　Feb., 1996

多氯联苯焚烧处置时烟灰中的二噁唔*

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摘要　专门用于销毁含多氯联苯(PCBs)固体废弃物的中试焚烧炉，焚烧排放物中含有微量剧毒二噁唔(PCDD/Fs)．应用同位素稀释HRGC/HRMS方法测定了烟灰中的PCDD/Fs含量，以17种有毒同族体的含量可计算出样品的2，3，7，8-TCDD毒性当量为47.2 ng/g。

关键词　焚烧，多氯联苯，二噁唔排放，PCDO/Fs测定。

微量的二噁唔类化合物(dioxins)在低剂量时也危及人体健康[1-3]，发达国家的二噁唔污染有95%是焚烧造成的。

国内生产的多氯联苯(PCBs)大多数用作电力电容器的浸渍剂[4]，有些进口变压器油中PCBs含量高达50%[5]。焚烧过程中PCBs容易转换成更毒的二噁唔[2]，为了避免二次污染，测定了焚烧炉烟灰中多氯二苯并二噁唔(PCDDs)和多氯二苯并呋喃(PCDFs)的含量，计算出其2，3，7，8-TCDD毒性当量为47.2 ng/g，并和焚烧原料作了比较。

1　实验

(1) 试验焚烧炉　沈阳环境科学研究所制造。

(2) 焚烧原料　国产YL、CL、RL系列电力电容器中的国产商品1号PCB多氯联苯。

(3) 烟道灰取自烟囱内壁、100目过筛(采自1993年)。

(4) 提取　139 mg烟灰样品加入由9种^{13}C PCDD/Fs组成的混合内标[6]，在索氏提取器中用甲苯溶剂提取16 h。

(5) 分离纯化　按照USEPA 1613方法[7]将提取液用多级硅胶柱[8]和碱性氧化铝柱处理。应用含3%二氯甲烷的己烷溶剂洗脱硅胶柱，依次用己烷、含2%和50%二氯甲烷的己烷溶剂洗脱氧化铝柱，PCDD/Fs存在于最后一部分洗脱液中。

(6) GC/MS测定前在样品提取液中再加入各1 ng ^{13}C-1，2，3，4-TCDD和^{13}C-1，2，3，7，8，9-H_6CDD内标，用以测定先前9个内标的前处理回收率。定容50 μl，进样1 μl，用HRGC/HRMS定量。

(7) VG Autospec毛细管色谱/高分辨质谱(HRGC/HRMS)仪器。DB-5柱，30 m×0.32 mm(i.d.)，柱上进样；程序升温：70℃(1 min)，40℃/min至200℃，3℃/min由200℃升至235℃，235℃(10 min)，8℃/min升至310℃，310℃(15 min)；质谱参数：EI(35 eV)，在m/z 304.9824处的分辨率(10%峰谷)>10 000，选择离子监测(SIM)[9]，用3个特征离子定性，质量色谱峰面积定量。

(8) PCDD/Fs标样由加拿大环保局提供。溶剂：己烷、二氯甲烷、甲苯和异辛烷(农药级)，硅胶(Bio-SiL A，100—200目)，碱性氧化铝(AG10，100-200目)。

(9) 质量控制和保证[9]同系物中各异构体的分离，各同系物的保留时间窗口，线性定量校正曲线，系统空白试验，加标回收率，盲样及平行样品的相对误差，GC峰保留值误差，氯同位素丰度比。

2　结果和讨论

加入^{13}C PCDD/Fs内标的烟灰提取物，应用HRGC/HRMS得到的部分质量色谱见图1—5。采用的色谱保留值窗口，检测限，^{13}C标记物回收率及同系物含量列于表1。烟灰中PCDDs总量为0.80 mg/g，PCDFs总含量为4.8 mg/g，PCDD/Fs总含量为5.6 mg/g。17个有毒PCDD/Fs同族体的测定结果列于表2，表明了氯同位素丰度比的实测值、含量及由毒性当量因子(TEF)计算的2，3，7，8-TCDD毒性当量值(TEQ)。

* 国家"八五"科技攻关项目
收稿日期：1995-08-09

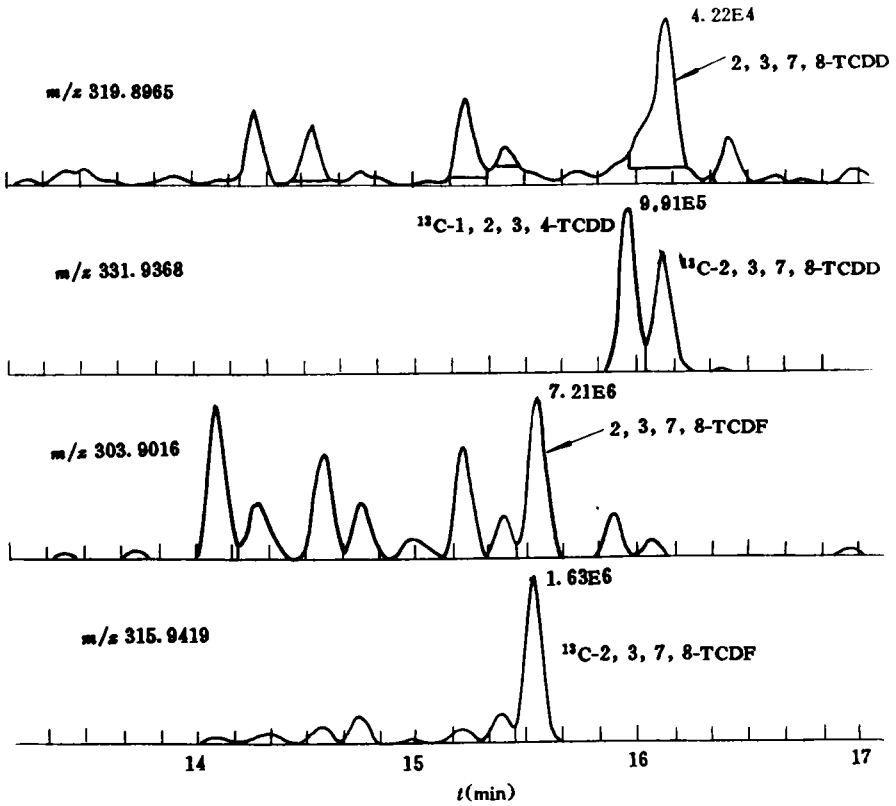

图 1　焚烧烟灰提取物中 PCDD/Fs 的高分辨质量色谱图

该试验性焚烧炉主要用于销毁含 PCBs 的废旧国产电容器，它焚毁 PCBs 的效率已达到 99.9999%[10]，焚烧过程中的热反应使烟灰中的 PCDDs、H_6CDF、H_7CDF 和 OCDF 的含量明显高于焚烧原料 1 号 PCB[9]，焚烧烟灰的总毒性当量值降为原料的 1/5(1 号 PCB 的 2，3，7，8-TCDD TEQ 值为 217 ng/g)，其中，2，3，7，8-TCDF，1，2，3，7，8 和 2，3，4，7，8-P_5CDF 所贡献的 TEQ 值其中，2，3，7，8-TCDF，1，2，3，7，8 和 2，3，4，7，8-P_5CDF 分别减少到原料的 1/51，1/3.3 和 1/10。但是不容忽略的是：残留 PCBs 作为二噁唔的前体化合物[11]在燃烧过程中形成了一些更毒的二噁唔类化合物，使烟灰中 PCDDs 贡献的 TEQ 比原料高了 35 倍[10]。

此烟灰样品中的二噁唔类化合物贡献的 2，3，7，8-TCDD TEQ 值为 47.2 ng/g，超过 USEPA 规定的排放标准(1 ng TEQ/g)，建议妥善处置这些烟囱灰，防止污染环境。

表 1　焚烧烟灰中 PCDD/Fs 同系物的含量

PCDD/Fs 同系物	色谱保留值窗口 (min)	定量的色谱峰数	检测限 (ng/g)	^{13}C 标记物的回收率 (%)	焚烧烟灰中含量 (ng/g)
TCDD	12.0—17.2	5	0.05	68	0.7
P_5CDD	17.2—23.0	5	0.05	59	2.6
H_6CDD	23.0—30.5	6	0.13	84	20.9
H_7CDD	30.5—34.5	2	0.13	109	154
OCDD	34.5—40.0	1	0.2	280	624
TCDF	12.0—17.2	13	0.03	77	131
P_5CDF	17.2—23.0	11	0.05	67	143
H_6CDF	23.0—30.5	12	0.13	90	389
H_7CDF	30.5—34.5	4	0.2	161	713
OCDF	34.5—40.0	1	0.2		3453

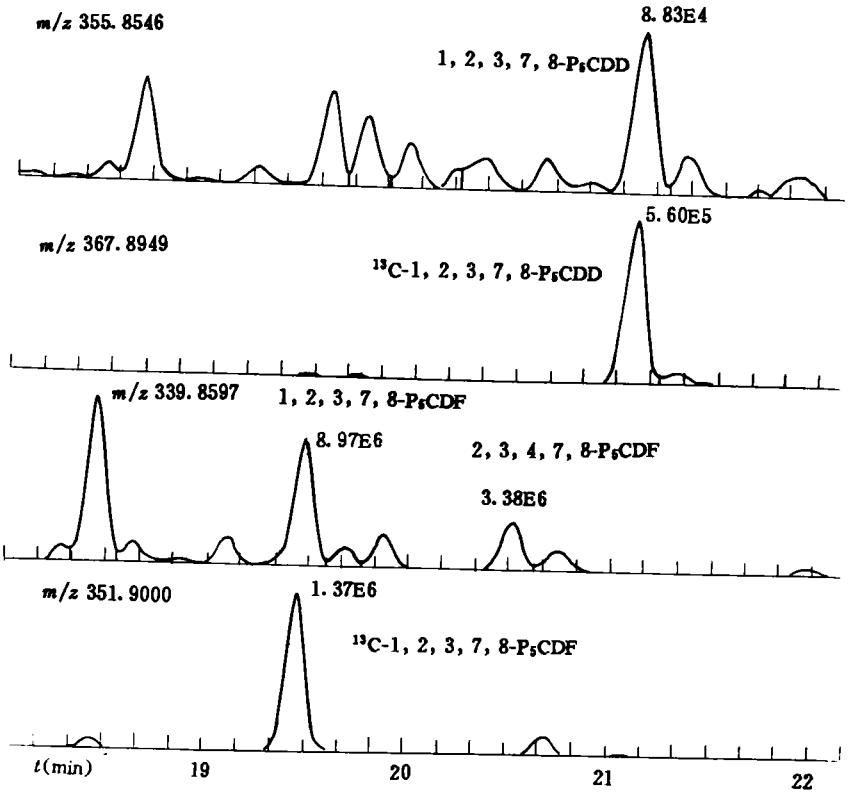

图 2 焚烧烟灰提取物中 P_5 CDD/F 的高分辨质量色谱图

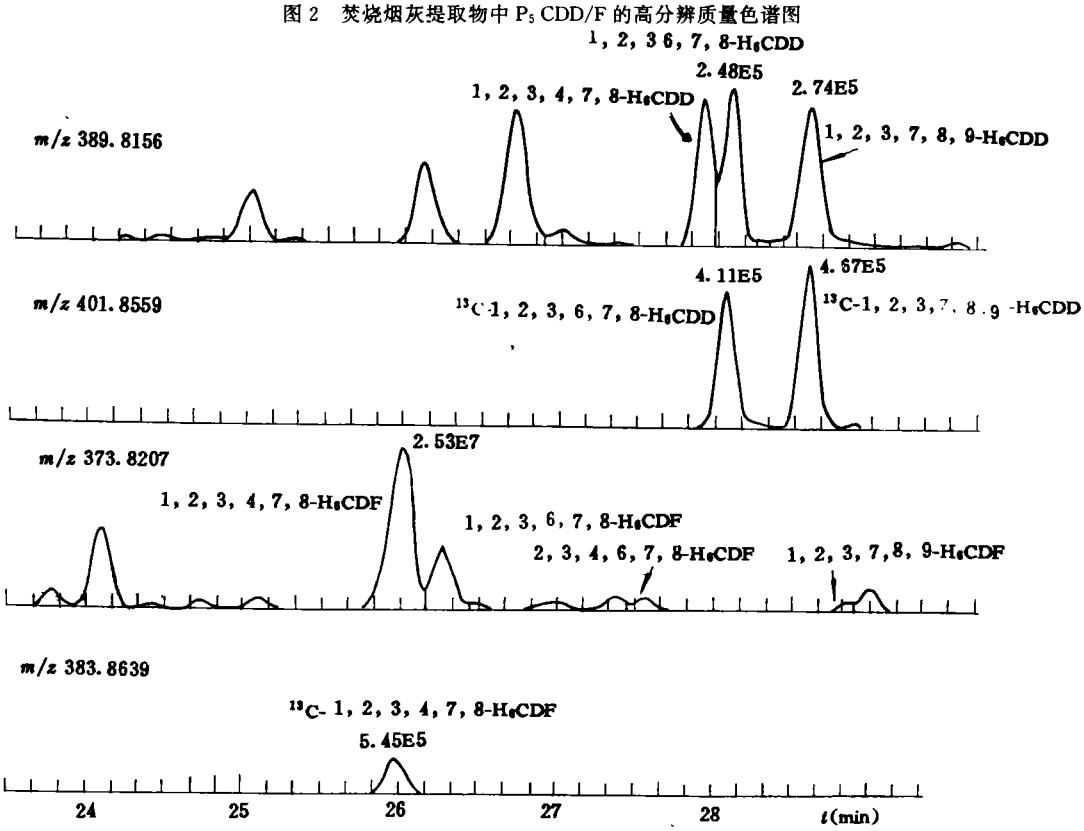

图 3 焚烧烟灰提取物中 H_6 CDD/Fs 的高分辨质量色谱图

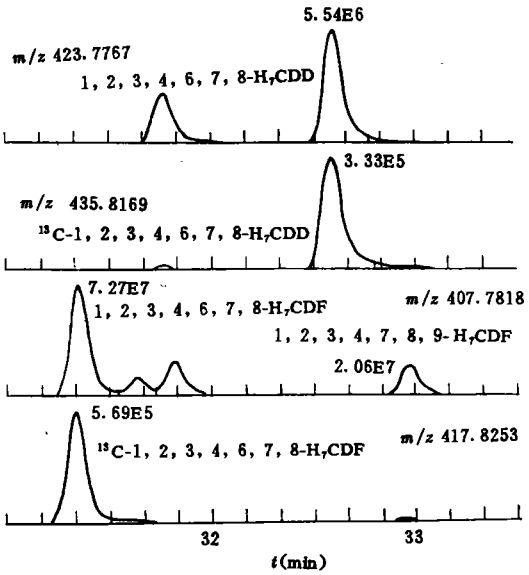

图 4　焚烧烟灰提取物中 H_7 CDD/Fs 的高分辨质量色谱图

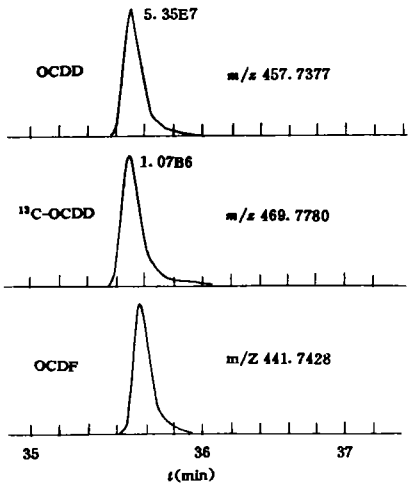

图 5　焚烧烟灰提取物中 OC CDD/Fs 的高分辨质量色谱图

表 2　焚烧烟灰中二噁唠同族体的含量及毒性当量

PCDD/Fs 同族体	实测的氯同位素峰丰度比		含量	毒性当量因子	毒性当量
	M/M+2	M+2/M+4	(ng/g)	TEFs	TEQ (ng/g)
2, 3, 7, 8-TCDD	0.87		0.4	1.0	0.4
1, 2, 3, 7, 8-P_5CDD		1.20	1.2	0.5	0.6
1, 2, 3, 4, 7, 8-H_6CDD		1.28	4.2	0.1	0.42
1, 2, 3, 6, 7, 8-H_6CDD		1.24	3.7	0.1	0.37
1, 2, 3, 7, 8, 9-H_6CDD		1.49	4.5	0.1	0.45
1, 2, 3, 4, 6, 7, 8-H_7CDD		1.07	107	0.01	1.07
OCDD		0.91	624	0.001	0.62
2, 3, 7, 8-TCDF	0.82		27.1	0.1	2.71
1, 2, 3, 7, 8-P_5CDF		1.57	38.8	0.05	1.94
2, 3, 4, 7, 8-P_5CDF		1.54	14.1	0.5	7.05
1, 2, 3, 4, 7, 8-H_6CDF		1.29	165	0.1	16.5
1, 2, 3, 6, 7, 8-H_6CDF		1.24	46.9	0.1	4.69
2, 3, 4, 6, 7, 8-H_6CDF		1.32	11.4	0.1	1.14
1, 2, 3, 7, 8, 9-H_6CDF		1.26	9.5	0.1	0.95
1, 2, 3, 4, 6, 7, 8-H_7CDF		1.04	336	0.01	3.36
1, 2, 3, 4, 7, 8, 9-H_7CDF		1.04	148	0.01	1.48
OCDF		0.88	3453	0.001	3.45
PCDDs			8.0×10^2		3.93
PCDFs			4.8×10^3		43.28
总 PCDD/Fs			5.6×10^3		47.21

致谢　沈阳环境科学研究所协助采样，加拿大环保局协助 HRGC/HRMS 分析，在此谨表谢意。

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to fluidize easily in the reactor. The treatment system can resist the loading fluctuation and possess high dehydrogenase activity.

Key words: fludized, biofilm, treatment, phenolic wastewater, carrier.

Development of a New Type Dispelling Smoke Silencer of Diesel Engine. Zeng Defang (Turbine College, Wuhan University of Science and Technology of Traffic, Wuhan 430063): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 63—64

This paper introduces a kind of method of making a new type dispelling smoke silencer of diesel engine. The method includes adding a kind of solution which can clean the end gas of diesel engine to the buttom of the old silencer of diesel engine. The end gas of diesel engine can be both cleaned and silenced by passing through the dispelling smoke silencer. A comparison of new silencer with the old one under the same condition on the type 135 diesel engine has shown that the dispelling smoke silencer can reduce 80% of smoke and 14.1% of noise (from 99 dB to 85 dB).

Key words: diesel engine, dispelling smoke silencer, noise, end gas of diesel engine.

A Study on Treatment of Traditional Chinese Medicine Wastewater by SBR Process. Han Xiangkui et al. (Jilin Architectural and Civil Engineering Institute, Changchun 130021): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 65—67

Experimental resutls showed that at the concentration range of COD in influent from 1000 mg/L to 2500 mg/L, effluent COD can be reduced to less than 250 mg/L, BOD_5 and SS less than 100 mg/L. These levels comform to discharge permission standard of pharmaceutical wastewater. The variation behavior of dehydrogenase during the process of aeration is also discussed in this paper.

Key words: SBR process, wastewater treatment, traditional Chinese medicine wastewater.

Dioxins in Stack Ash from PCBs Incinerator. Ke Jiang et al. (Research Center for Eco-environmental Sciences, CAS, Beijing 100085): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 68—71

The PCDD/Fs in stack ash from a experimental incinerator for destruction of PCBs waste have been determined by ^{13}C isotope HRGC/HRMS method. Seventeen 2, 3, 7, 8-substituted toxic dioxins congeners were quantitatively measured. The TEQ value of the stack ash is 47.2 ng/g.

Key words: stack ash, PCBs, dioxins.

Releasing of PAHs from Coal-ash in Seawater. Fu Yunna and Liu Yiwen (Inst. of Mar. Environ. Prot., SOA, Dalian 116023): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 72—74

Releasing of PAHs from coal-ash in seawater was determinated by fluorescence spectrophotometer. The amounts of PAHs from coal-ash soaked before and after in seawater were also analysed by reversed high performance liquid chromatography with UV or fluorescence detectors. The results show that the static state releasing and adsorption of PAHs from coal-ash in seawater are reversible, releasing of PAHs is pool, and PAHs in the fine coal-ash dumped into sea from heat and power plant have little effect to the marine environment.

Key words: coal-ash, PAHs, releasing, seawater.

Spectrophotometric Determination of Anionic Surfactants in Water with Bromocresol Green and Cetylpyridinium Bromide. Wang Yongsheng et al. (Hengyang Medical College, Hengyang 421001): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 75—77

In this paper a spectrophotometric method has been developed for the determination of anionic surfactants in water with bromocresol green (BCG) and cetylpyridinium bromide (CPB). Sodium dodecylbenzenesulfonate (SDBS) and sodium dodecylsulfate (SDS) were determined at 614 nm and pH range of 5.5—9.0. In the concentration range of 0—80 μg/10 ml for SDBS and 0—75 μg/10 ml for SDS, both of them obey Beer's law in the presence of 86 μg CPB. The apparent molar absorptivities are 2.9×10^4 $L\cdot mol^{-1}\cdot cm^{-1}$ for SDBS and 3.1×10^4 $L\cdot mol^{-1}\cdot cm^{-1}$ for SDS. The proposed method has been applied to the determination of anionic surfactants in river water and wastewater. The average recovery of environmental water samples was 99.3% and the relative standard deviation was less than 3.0%.

Key words: anionic surfactants, bromocresol green, cetylpyridinium bromide, spectrophotometry.

Photometric Determinations of Nickel and Copper in Wastewater by Reversed Flow Injection Ana-lysis. Wang Peng et al. (Department of Applied Chemistry, Harbin Institute of Technology, 150006): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 78—79

The new wastewater monitoring system by use of reversed flow injection spectrophotometry has been developed with injection of different reagents to produce similar color compounds by chemical reactions. The system has been used to simultaneous determination of nickel and copper in wastewater. The detection freqency of the method is 60 sampels h^{-1}, the minimum detection limits are 0.03 μg Ni ml^{-1} and 0.04 μg Cu ml^{-1} respectively.

Key words: environmetnal monitoring, flow injection analysis, nickel, copper.

Acidification Models and Their Application to the Determination of Critical Load for Acid Deposition. Xie Shaodong et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 80—84

This paper briefly discusses different models developed abroad in the study of precipitation effects to predict the long-term effects of acid deposition on soil, surface water, ground water and lakes in the past ten years. The basic methods to establish these models and the principles to apply them to the determination of critical load for acid deposition are presented based on through comparisions and analyses.

Key words: acidification model, critical load, acid depostion, acid rain.

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