可以认为，污泥是一种生物能源和原料，它具有和泥炭相当的发热量，有能源利用价值。污泥对热极不稳定，热解起始温度低，挥发份高，适于用热解方法转化成气体、液体燃料和化工原料。

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国产五氯酚中痕量 PCDFs 杂质的鉴定*

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摘要 五氯酚生产过程中会产生一些剧毒的副产物——多氯二苯并呋喃（PCDFs），应用质谱/质谱（MS/MS）法直接鉴定出国产五氯酚工业品中含有4—8个氯原子的二苯并呋喃类化合物，这可能是我国PCDFs污染的主要来源之一。本方法可用于工业化学品的普查及潜在污染源的调查。

多氯二苯并呋喃（简称 PCDFs）是和多氯二苯并二噁唔（简称 PCDDs）在化学结构、性质和生物毒性方面都很相似的一组化合物，都是由三个环组成的含氯的芳香族化合物（图1），它共有135个位置异构体，其中有些是剧毒的，一些 PCDFs 的毒性效应[1]见表1。

F. W. Karasek[2] 建议动物和人对 T_4CDDs 和 T_4CDFs 的允许接触水平见表2。据认为，在侧位（2,3,7,8 位置）存在氯原子取代的 PCDDs 和 PCDFs 是最毒的一些异构体，它们会导致氯痤疮等皮肤疾病，心血管和消化系统病症，降低免疫力，神经障碍和精神疾病以及致癌致畸等。

表1 一些含氯苯并呋喃的毒性效应

PCDFs	侧位氯原子数	相对活性(%)		胸脉萎缩
		AHH 诱导[1]	键亲合性[2]	
2,3,7,8 T_4CDF	4	20	35	+++
2,3,4,7,8 P_5CDF	4	100	100	+++
1,2,3,7,8 P_5CDF	4	25	20	++
1,2,3,4,7,8 H_6CDF	4	7.0	8	++
2,3,6,8 T_4CDF	3	<1.0	7	+
2,8 D_2CDF	2	<0.1	<0.1	−

1) Aryl Hydrocarbon Hydroxylase Induction Receptor

2) abbinity binding of this compound to a cytosolic protein

* 本工作得到北京中关村地区联合分析测试中心部分资助.

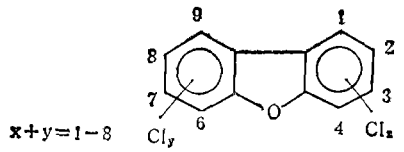


图 1　多氯二苯并呋喃 (Polychlorinated Dibenzofurans) 的化学结构

表 2　人和动物接触 T_4CDD 和 T_4CDF 时的许可极限

效应	NOEL—动物 (ng/kg/day)	暴露—人 (pg/50kg/day)
慢性致毒	1	100
致胎毒	30	3 000
影响生殖	1	100
致畸	100	10 000
致癌	1	2

虽然城市垃圾和工业废物焚烧、金属冶炼过程及使用含铅汽油的汽车排放等也会生成 PCDFs，但是我国 PCDFs 的主要来源可能是某些含氯工业化学品，如氯酚、多氯联苯及除草剂等生产过程中形成的副产物．先前的工作中，我们已鉴定出国产五氯酚工业品中含有约 3ppm 的 T_4CDF（四氯二苯并呋喃），最近应用质谱/质谱法（MS/MS）又鉴定出了另一些 PCDFs：P_5CDF（五氯二苯并呋喃），H_6CDF（六氯二苯并呋喃），H_7CDF（七氯二苯并呋喃）和 O_8CDF（八氯二苯并呋喃）．

一、实验

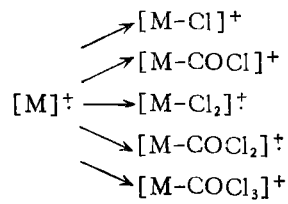
1. 国产五氯酚工业品由铁道部劳动卫生所王世伟同志提供，标准样品 2，3，7，8-T_4CDD 由美国环保局（EPA）提供．

2. Finnigan MAT TSQ 三级四极质谱计，样品在直接进样杆中快速升温至 270℃，气化后在电子轰击源内电离成离子（EI，70eV），正离子在第一级四极杆中被分离，挑选出的母离子在第二级中被氩气碰撞（碰撞能量为－20 伏）碎裂成有关子离子，第三级四极杆中再分离它们，从而获得这些母离子的子离子谱．利用计算机控制的多离子检测（MID），本方法的最小检测量为 20pg（标样，2,3,7,8-T_4CDD）．

五氯酚工业品配成 100μg/μl 溶液，直接加入进样管．

二、结果和讨论

TCDFs 质谱中的特征离子为：



在 2,3,7,8-T_4CDD 标样的 MS/MS 子离子谱中可以清晰地看到上述离子．实验中，选择 $[M-COCl]^+$ 及 $[M-COCl_2]^+$ 离子作为特征离子，为了使鉴定结果可靠，也核对了氯同位素峰的丰度比（[M + 2]/[M] 或 [M + 4]/[M + 2]）．用 MS/MS 法直接测定未加任何处理的五氯酚样品，检测 T_4CDF，

表 3　MS/MS 法测 PCDFs 时所选择的母离子和子离子

待测化合物	所选母离子 (m/z)			待测子离子 (m/z)					
	M^+	$[M+2]^+$	$[M+4]^+$	M^+-COCl	$[M+2]^+$-COCl	$[M+4]^+$-COCl	M^+-$COCl_2$	$[M+2]^+$-$COCl_2$	$[M+4]^+$-$COCl_2$
T_4CDF	304	306		241	243		206	208	
P_5CDF	338	340		275	277		240	242	
H_6CDF		374	376		311	313		276	278
H_7CDF		408	410		345	347		310	312
O_8CDF		442	444		379	381		344	346

P_5CDF, H_6CDF, H_7CDF, O_8CDF 实验中所选定的母离子和子离子见表 3.

为了保证测定灵敏度，测 H_6CDF, H_7CDF, O_8CDF 时选择分子离子簇中的 [M + 2] 及 [M + 4] 离子作为 MS/MS 中的母离子.

用 MS/MS 方法快速鉴定出国产五氯酚工业品中痕量不纯物 T_4CDF, P_5CDF, H_6CDF, H_7CDF 和 O_8CDF 含氯二苯并呋喃化合物，图 2 是 m/z 304 (母离子)，241 和 206 (子离子)离子强度随时间的变化. 图 3, 4, 5, 6 分别是 T_4CDF, P_5CDF, H_6CDF, H_7CDF 分子离子的子离子谱.

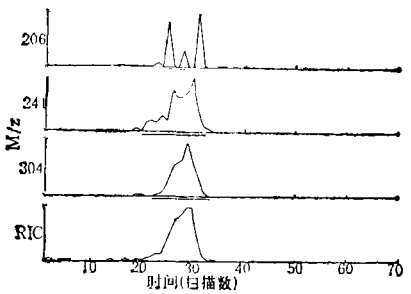


图 2 m/z304 ,241, 206 离子强度随时间的变化

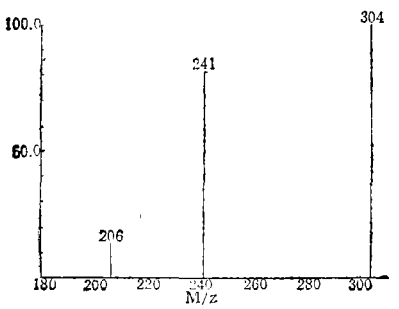


图 3 m/z 304 的子离子谱

实验中测定了各分子离子簇的 MS/MS 质谱图，母离子和相应子离子峰的同时性(离子强度随时间的变化) 及氯同位素峰的丰度比，可靠地鉴定了国产五氯酚工业品中除了含有约 3ppm 的 T_4CDF 外(用 2, 3, 7, 8-TCDD 标样估算)，也含有 P_5CDF, H_6CDF, H_7CDF 和 O_8CDF.

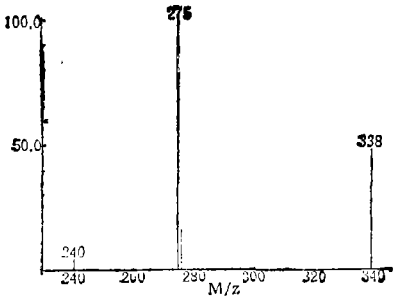


图 4 m/z 338 的子离子谱

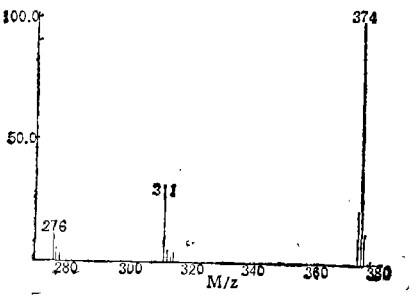


图 5 m/z 374 的子离子谱

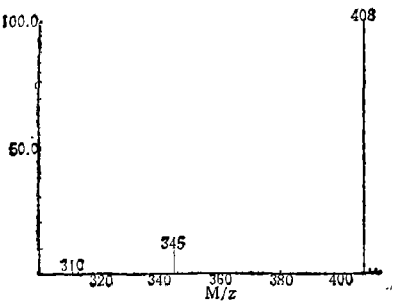


图 6 m/z 408 的子离子谱

三、结论

PCDFs 和 PCDDs 具有脂溶性，容易被土壤吸附，可以通过食物链浓缩，在环境中自然降解代谢速度缓慢，增加了环境残留的复杂性，有些国家的土壤、大气和漂尘、水生物、人体脂肪组织、人血和人奶中均已发现含有 ppt—ppb 量级的 PCDDs 和 PCDFs 存在[3]. MS/MS 法可以直接测出五氯酚中含量为 10^{-7} 的 PCDFs 杂质，样品无需任何预处理，测定方便、快速和可靠，适用于大量工业

化学品的普查和污染源的调查. 首次在国产五氯酚工业品中鉴定出含 4—8 个氯原子的剧毒苯并呋喃类化合物，具有重大的环境生态学意义.

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(收稿日期：1989 年 6 月 8 日)

牛奶样品中 ^{90}Sr、^{137}Cs、Ca 和 K 的测定

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摘要　本文介绍了用放射化学和化学方法分析 WHO-IRC 提供的低水平环境放射性测量比对样品的主要程序和得到的结果. 结果表明，^{90}Sr、^{137}Cs 和 Ca 的分析结果达到了较高的准确度. 文中对分析中影响准确度的几个问题进行了讨论.

目前，有关分析测定环境中 ^{90}Sr、^{137}Cs、Ca 和K的方法很多. 但是，试图获得经得起时间和空间考验的准确的分析结果并不是很容易的事情. 为了达到这个目的，有很多的途径. 其中的一个有效途径就是参加实验室之间的分析测量的比对. 通过比对，可以纠正自身难以发现的系统误差，完善分析方法. 为此，我们于 1985 年参加了世界卫生组织国际放射性参考中心 (WHO-IRC) 组织的环境样品放射性活度测量比对活动. 本文主要介绍这次牛奶样品的测量比对中我们所采用的分析程序和得到的结果，并讨论了分析中影响准确度的几个问题.

一、比对样品和测定程序

(一) 比对样品

IRC 提供的比对样品为牛奶，取自法国中部山区的牛奶场. 样品分装到容积为 1L 的聚乙烯塑料瓶中，每L 牛奶中加入 5ml 福尔马林(30% 溶液)防腐剂. 最后分发给每个参加比对的实验室. 比对样品编号为 No. 42 L300.

当我们收到样品后，先对原包装样品用带计算机的 S-88 Ge(Li)r 谱仪进行粗测，发现 ^{137}Cs 含量很低，难以直接测定. 开瓶后发现牛奶已部分变质，呈块状. 为了消除和减少体积测量带来的误差，首先将牛奶剧烈搅拌，捣碎，用比重计测量其比重为 1.030 g/cm^3，然后用称重法确定取样的体积.

(二) 测定程序

由于样品中 ^{90}Sr 和 ^{137}Cs 的含量很低，在 1L牛奶中要求分析的项目又较多，包括 ^{90}Sr、^{137}Cs、Ca 和 K，IRC 提供的牛奶样品量仅有 2L. 为此进行了 2 个样品的平行测定. 将每L牛奶分成两份，其中一份的体积约 900 ml，供 ^{90}Sr 和 ^{137}Cs 的联合分析用；另一份约 100ml，统一灰化、酸溶和定容后，分别进行 Ca 和K的测定.

1. ^{90}Sr 和 ^{137}Cs 的联合分析

量取 900ml 牛奶在红外线干燥箱中蒸发至干，在本院自制的生物样品快速灰化炉[1]中 400℃ 下灰化 2h. 获得的灰样按图 1所示的流程图进行 ^{90}Sr 和 ^{137}Cs 的联合分析[2].

Wang Xunling, Guo Qingxia (Biology Department, Lanzhou University): *Chin. J. Environ. Sci.*,**11**(2), 1990, pp. 31

The plants, *Fuchsia hybrida* Voss. and *Vicia faba* L., were fumigated with ozone at different concentrations. It was observed that the lower level of ozone would stimulate respiration. Such effect did not easily disappear for a long time after stopping fumigation. However, the higher concentration of ozone inhibited respiration. If the injury caused by ozone was not so severe that the plant respiration could recover to normal.

It is suggested that there might be two kinds of mechanism which control the rise and fall of respiration. These two actions compensate and adjust each other under the conditions of controlling ozone doses, resulting in various phenomena of respiration intensity, such as increasing, decreasing or unremarkable changes, recoverable or irrecoverable, etc.

A Study of Photochemical Pollution with a Box Model. Yu Jinxiang (Department of Atmospheric Sciences, Lanzhou University): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 34

A box model for simulating the atmospheric photochemical pollution in a valley region has been developed and verified by using real source emission, meteodological and pollutant concentration data for Xigu district in Lanzhou in August of 1983. The model is utilized to study the impact of source density on the photochemical smog concentration.

Anaerobic Fermentation for Fur Processing Wastewater. Qui Rongchu, Liang Wensheng, Wu Dongfeng (Department of Environmental Engineering, Lanzhou Railway College, Lanzhou): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 37

Batch bioassays have been applied to determine the feasibility of anaerobic treatment for two main flows of wastewater from fur processing: for soaking wastewater and for scouring wastewater. The former does not restrict methanogens and can be biodegraded easily under the anaerobic conditions with the methane production of 1.02 m^3/m^3 while the COD removal percentage as high as 87.6%. In the latter with the methane production of 0.82 m^3/m^3, detergent DG7 can not be biodegraded anaerobically, but can be adsorbed on sludge and shows effects of restriction to methanogens that can be acclimated, even there is no influence on the anaerobic process when the concentration of DG7 is less than 50—100 mg/L. It is reasonable for the scouring wastewater to be treated anaerobically with the soaking wastewater or other sewage at the same process.

Heat Feedback in the Catalytic Combustion and Safe-Controlling Technology. Su Jianhua, Wang Boduo (The Seven Design and Research Institute of the Ministry of Mechanical-Electronical Engineering Industry, Xi'an): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 41

This paper deals with the problem of heat feedback and safe control in catalytic combustion of organic waste gas. The increase of gas concentration will lead to the increase of temperature in catalyst bed entrance. If ignition temperature is higher than 350°C, normal heat equilibrium will be destroyed. The authors have concluded that in order to guarantee safety of the system, concentration of waste gas entering into the catalyst bed should be controlled by means of continuous quantative detection of the gas.

Analysis of Chemical Composition of Activated Sludge. Liu Lifen, Zhao Shuchang, Deng Yizhao (Dalian University of Technology, Liaoning Province): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 45

This work is to analyse chemical composition and related characteristics of the sludge sampled from Tianjin Sewage Plant with infrared spectrophotometry and thermogravimetry. The activated sludge derived from wastewater treatment process contains the elements of C, H, O, N, S, P, and mainly belongs to aliphatics in structurs. There exist organic groups known as proteins, oil, fibre and humic acid, which will be potential sources of raw material of chemical engineering and alternative fuel.

Detection of Trace PCDFs in China-made Pentachlorophenol. Jiang Ke et al. (Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing); Deng Lin, Li Zhongmin (Beijing Institute of Technology): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 48

Extremely toxic PCDFs (polychlorinated dibenzofurans) can be formed in the production of pentachlorophenol as by-products. PCDFs including 4—8 chlorine atoms have been identified in China-made Pentachlorophenol using MS/MS method It is considered as one of the main sources of PCDFs contamination in china. This analytical method has been recommended for application

in general survey of technical chemicals and investigation of potential pollution sources.

Determination of ^{90}Sr, ^{137}Cs, Ca and K in Milk by Radiochemical and Chemical Method. Sha Lianmao, Wang Zhihui, Wang Fenghua (China Institute for Radiation Protection, Taiyuan): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 51

A method for determining low-level radioactive nuclides in milk for intercomparison by WHO-IRC is presented in this paper. The results show that the values of ^{90}Sr, ^{137}Cs, Ca concentration appear to be agreement with IRC reference values. Some problems concerning the effect on analytical accuracy have been discussed as well.

A Survey of $^{239+240}Pu$ and ^{238}Pu in Main Foodstuff of China. Han Shouling et al. (Liaoning Provincial Institute of Labour Hygiene, Shenyang): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 55

Radioactive plutonium isotopes in 16 samples of the main foodstuff collected from nine provinces and autonomous regions of China have been determined by means of radiochemical separation, electrodeposition and alpha-spectrum measurements. The results show that specific radioactivities of both $^{239+240}Pu$ and ^{238}Pu in the foodstuff vary from 1×10^{-4} Bq/kg to 1×10^{-3} Bq/kg, the concentrations of ^{238}Pu in foodstuff are less than $^{239+240}Pu$. However, by way of exception, the specific radioactivities of $^{239+240}Pu$ and ^{238}Pu in tea samples are 7.41×10^{-3} Bq/kg and 1.33×10^{-3} Bq/kg respectively.

Advances of Quantitative Structure Activity Relationship (QSAR) in Environmental Chemistry and Its Methodology. Bai Naibin (Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 62

QSAR is a useful means in safety assessment of chemicals. This article describes its application background, fundamental principles, evolution, conception model, mathematical model and algorithm, from which the author and his assitants have developed a software package of applied quantum chemistry with a purpose of producing the molecular structure descriptors. In the software a chemical substance toxicity database has been carried out so as to acquire lots and lots of biological activity data of chemicals, and in order to set up the relationship between molecular structure and its biological activity, a pattern recognition software has been applied. Finally, the perspective of QSAR research in environmental chemistry has been discussed in this article.

Microbial Degradation of Pesticides. Zheng Zhong (Zhejiang Agricultural University, Hanzhou): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 68

A general description on microbial degradation of pesticides is given in this review. The subject covers following aspects: isolation of the microbe-degraders, biodegradation pathway of some pesticides, and characteristics of microbial metabolism and involved enzymes. The practical approaches to biological detoxification of pesticides have also been discussed.

On the Environmental Characterics and Changes in Northwestern Arid Area of China. Ma Ruijun (Department of Geography, Northwest Normal University, Lanzhou): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 76

With a comparative approach, the author discusses theoretically the arid causes in the northwestetern area of China from the viewpoints of its formation course, space structure, heat and moisture conjunction, natural factors and human activities on the environment as well.

Fuzzy Comprehensive Assessment of Environmental Quality by Computer Performance. Liu Hui, Wang Feiyue (Wuhan University): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 81

This paper presents a fuzzy mathematical model designed for comprehensive assessment of environmental quality by means of IBM PC computer. The model has been applied successfully to the atmospheric environmental assessment in Wuhan.

Radiactive Impact Assessment of Returning the Coal-Ash Storage Sites of the Power Stations into Farmland. Wang Bing (Society of Environmental Protection of Handan Prefecture, Hebei Province): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 84

The radionuclide contents of coal ash from the power stations in Handan Area are higher than that in the local soil except ^{40}K. However, this situation doesn't affect the sites to be reformed into farmland. The results of detection show that radionuclide contents in wheat, maize and rice which were planted on the farmland are not different from those planted on ordinary ones, and the additional radiation dosage received annually by the peasants working in the coal-ash storage sites is only 1% of the limit stipulated by Chinese authorities concerned.