

毛细管气相色谱法测定人参中五氯硝基苯及六六六异构体残留量

白求恩医科大学预防医学院(长春130021) 袁 兰* 陈秋丽

吉林省东方制药公司

王雅丽 姜茁松

摘要 建立了同时测定人参中五氯硝基苯及四种六六六异构体的方法。人参经丙酮-正己烷(1:2)提取、浓硫酸纯化后,采用OV-1701弹性玻璃毛细管柱、电子捕获检测器测定上述5种有机氯农药。方法快速、简便、准确。

关键词 人参 五氯硝基苯 六六六异构体 毛细管气相色谱法

人参中残留五氯硝基苯(PCNB)、六六六异构体等有害有机氯农药[Searle CE, Cancer Res, 1966, 26(1):12]已引起关注,并已成为国际上评价人参质量的标准之一。

在人参有机氯农药含量的分析过程中,通常难于用普通玻璃柱同时在GC上分离、测定PCNB及六六六异构体。目前在国内的文献中未见报道。今采用毛细管柱气相色谱法能很好地解决这一问题,并建立了测定人参中上述5种有机氯农药的前处理方法。

1 仪器及试剂

带有ECD的岛津GC-9A型气相色谱仪,并配有SPL-G9分流/不分流装置, C-R 3A数据处理机, OPGU-500S氢气发生器(岛津产)。

PCNB、六六六异构体(α -666, γ -666, β -666, δ -666)及狄试剂贮备液:均用苯配成100 μ g/ml的贮备液,使用时用正己烷稀释至所需浓度。

实验所用有机溶剂均用全玻璃蒸馏器2次蒸馏,所用蒸馏水用正己烷(按500:20比例)萃取2次,而且做试剂空白试验无干扰峰存在。

2 样品处理

2.1 样品制备:取200g 60℃干燥的人参,粉碎后过40目筛,保存于干燥器中备用。

2.2 提取:准确称取上述样品10g(W),置于250ml厚壁磨口具塞三角瓶中,加入100ml丙酮-正己烷(1:2),放置浸泡30min,于超声振荡仪中流水冷却下,振荡提取10~15min,取出静置5min,立即过滤,弃去初始10ml滤液后,准确分取出20ml滤液($n=1/5$, 占总滤液100ml的1/5)于125ml分液漏斗中,用20ml 2% Na_2SO_4 溶液振荡1min,弃去水相,上层正己烷相供净化用。

2.3 净化:向上述分液漏斗中小心加入1.5ml浓 H_2SO_4 (正己烷:浓 H_2SO_4 约为10:1),轻振3min,分层后弃去酸相。反复净化1~3次(视酸相黄颜色杂质深浅而定)后,加入25min 2% Na_2SO_4 洗涤残存酸3次。将正己烷相通过3cm高的无水 Na_2SO_4 柱,并用3ml正己烷溶剂洗涤 Na_2SO_4 柱,并将正己烷溶液合并于具塞刻度管中,供浓缩用。

2.4 浓缩:于40℃水浴中,用 N_2 气在管中近液面上轻吹,浓缩至管中剩4~5ml溶液后取出试管,冷却,用正己烷定容至5ml(V),上机测定。

3 气相色谱测定

3.1 GC条件:OV-1701弹性玻璃毛细管柱(25m $\times$ 0.25mm);ECD检测器温度:260℃;

*Address: Yuan Lan, Department of Preventive Medicine, Norman Bethune University of Medical Sciences, Changchun

柱温50℃，保持2.7min，以40℃/min升至180℃，然后再以5℃/min升至230℃，保持20min；载气：高纯氢气，线速23.5cm/s；尾吹气：高纯氮气，流速55ml/min；进样量0.5μl；分流比1:12

3.2 色谱性能：上述GC条件，PCNB与4种六六六异构体能很好地分离，出峰顺序见图。

3.3 定量测定：a) 标准曲线的绘制：配制所测农药的系列混合标准溶液，其中各种农药标准的浓度见表。以200μg/L狄试剂作内标，以各农药的浓度与内标浓度之比(Kc)为横座标，以相应的峰面积比(Ka)为纵座标，在双对数座标图纸上绘制峰面积比-浓度比(Ka-Kc)曲线。求得α-666，γ-666，β-666，δ-666及PCNB依次在4~200，4~200，10~200，8~200及4~12μg/L的浓度范围内，Ka-Kc曲线线性良好；其最小检出浓度依次为2，2，10，8及2μg/L。b) 测定样品时，浓缩后的样品浓度应控制于Ka-Kc图线线性范围所对应的浓度，按下式计算人参中各农药的含量。

表 PCNB、六六六异构体标准溶液的配制

农药	浓 度 (μg/L)						
	1	2	3	4	5	6	7
PCNB	4	10	20	40	60	100	128
α-666	4	20	40	80	128	160	200
γ-666	4	20	40	80	128	160	200
β-666	10	20	40	80	128	160	200
δ-666	8	20	40	80	128	160	200
狄试剂	200	200	200	200	200	200	200

$$\text{含量}(\mu\text{g/kg}) = \frac{K_{ci} \cdot Co \cdot V}{W \cdot n}$$

Kci-在Ka-Kc标准曲线求得之

样品溶液的农药浓度与内标浓度之比

Co-加入至样品溶液中内标浓度(200μg/L)

3.4 方法回收率与准确度：按样品处理及测定方法，在各农药的线性范围内作高、中、低浓度的加标回收率实验(n=7)。求得回收率范围、平均回收率、相对标准偏差范围如下：α-666，94.7%~104%，96.7%，0.21%~4.3%；γ-666：98%~105%，99.7%，0.2%~5.8%；β-666：96.2%~104%，98.9%，0.3%~5.5%；δ-666：96.1%~101%，98.2%，0.05%~1.4%；PCNB：91%~98%，94.0%，0.08%~1.73%。

4 讨论

- 4.1 步骤2.4可用K-D法浓缩，本法可避免溶液转移。易控制浓缩条件与体积，简单快速。
- 4.2 经对多种标准物质进行试验，我们发现狄试剂在酸中不稳定，若样品中含有，经酸净化后可消除。因此，各溶液在GC测定前加入狄试剂作内标。
- 4.3 在探索提取人参中上述农药的方法时，曾将超声振荡提取法与处理有机氯农药常用的索氏提取法相比较，两者结果一致，在精密度与准确度上均符合农药残留分析方法要求。但引入超声法提取仅需不到1h，而索氏法则需8h。可以认为本法是一种快速、准确的方法。

(1993-12-27收稿)

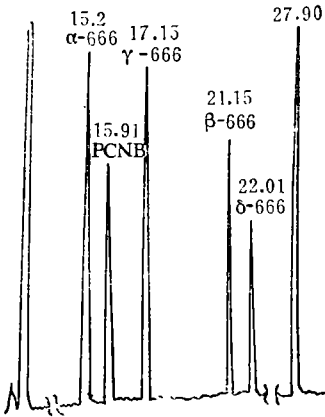


图 PCNB、六六六异构体色谱图

**Method for the Determination of Residual PCNB and Benzené
Hexachloride Isomers in Ginseng (*Panax ginseng*) by Capillary
Column Gas Chromatography**

Yuan Lan, Wang Yali, et al

A method for the detection of residual amount of pentachloro nitro benzene (PCNB) and benzene hexachloride isomers, in Ginseng was developed. The pesticides in Ginseng was extracted with acetone-n-hexane (1 : 2), purified with H_2SO_4 , separated on ov-1701 flexible glass capillary column and determined by electron capture detector (ECD).

(Original article on page 519)

**Beneficial Effect of Gastrodia on Some Aging Disorders
Induced by D-Galactose in Mice**

Gao Nannan, Yu Shuren, Liu Ruihong, et al

A model of senile state was established in mice by successive retrobulbar injection of 80 mg/kg D-galactose for 50 days. Concomitant oral administration of 4 g/kg and 8 g/kg gastrodia can effectively recover the decreased ability of the passive avoidance reaction in the model animals.

The activity of RBC SOD and the contents of hydroxyproline in the animals skin were markedly increased as well as the lipofuscin of myocardium. However, gastrodia was less effective to lower lipofuscin in liver and brain.

(Original article on page 521)

**Inhibitory Effect of Soyasaponin on Virus Replication
and Its Use in Clinic**

Li Jingbo, Hu Jisheng, An Zhanyuan

Experiment demonstrated that total soyasaponin (TS) possessed significant inhibitory effect on replication of HSV-1 and CoxB3 viruses and showed marked protective effects on the infected cells ($P < 0.05$ and $P < 0.01$). Preliminary studies on the mechanism of its action showed that TS had a direct killing effect on the viruses. A preparation of TS cream was tried in patients suffering from herpes labialis and oral ulcer. The treatment was highly effective with a cure rate of 88.8% and 76.9% respectively.

(Original article on page 524)

**Studies on the IR Spectra of Lobed Kudzuvine (*Pueraria lobata*)
and Xiaoji (*cirsium setosum*) Collected at Different Times**

Tian Jinguo, He Xinliang, et al

Extracts of *Radix Pueraria* and *Herba Cirsii*, obtained by the same isolating procedure, were examined with IR spectra. Results showed that the IR spectra of *Radix Pueraria lobata* and *Herba Cirsii*, collected at different times had distinct characteristics, consistency and repeatability. The spectra of *Radix Pueraria thomsonii* also showed characteristic evidence. Accordingly, *Radix pueraria* and *Herba Cirsii* may be well distinguished by means of IR spectra.

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