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can be extended to general locally compact groups. In this paper we give an answer to Reiter's question within the more general context of double algebras.

## 2. DOUBLE ALGEBRAS

In this paper we need a weakened version of the approximate units usually defined for topological algebras.

**Definition 2.1.** Let  $R$  be an algebra which is also a topological space with topology  $\mathcal{J}_R$  (Note that  $(R, \mathcal{J}_R)$  need not necessarily form a topological algebra). Then  $R$  is said to have right approximate units if, given any  $f \in R$  and any neighborhood  $V$  of  $f$ , there exists  $u \in R$  such that  $fu \in V$ .

It is clear that  $R$  has right approximate units if and only if  $f \in$  the closure of  $fR$ , for all  $f \in R$ .

**Definition 2.2.** Let  $A$  be a topological algebra with topology  $\mathcal{J}_A$  and let  $B$  be a subalgebra of  $A$ . Then the pair  $(B, A)$  is called a double algebra if

- (D1)  $B$  is a dense left ideal of  $A$ .
- (D2)  $B$  is a topological space with respect to some topology  $\mathcal{J}_B$ .
- (D3)  $\mathcal{J}_B$  is stronger than the relative topology on  $B$  induced by  $\mathcal{J}_A$ .
- (D4) For any  $g \in B$ , the mapping  $f \rightarrow fg$  ( $f \in A$ ) is continuous from  $(A, \mathcal{J}_A)$  into  $(B, \mathcal{J}_B)$ .

Moreover, if both  $A$  and  $B$  have right approximate units, then  $(B, A)$  is called a D-algebra.

Note that Definition 2.2 is slightly different from [12; Definition 1.2]. The class of double algebras includes a wide variety of interesting special cases such as Segal algebras ([8; §5], [10], [11]), normed ideals [5], and A-Segal algebras [4; Examples 15-24].

Because there are two topologies involved in a double algebra  $(B, A)$ , to avoid confusion, we make the following convention:

For a set  $S \subset A$ ,  $\bar{S}$  denotes the closure of  $S$  in  $(A, \mathcal{J}_A)$ , while for a set  $S \subset B$ ,  $\bar{S}^B$  denotes the closure of  $S$  in  $(B, \mathcal{J}_B)$ .

Before going to our main analysis, we observe the following basic facts: Let  $(B, A)$  be a double algebra and let  $S$  and  $T$  be subsets of  $A$ . Then we have

- (a)  $\overline{S} + \overline{T} \subset \overline{S + T}$ .
- (b)  $\alpha\overline{S} = \overline{\alpha S}$ , where  $\alpha$  is a scalar.
- (c)  $\overline{S} \overline{T} \subset \overline{ST}$ .
- (d)  $\overline{SA} = \overline{SB}$ .
- (e)  $\overline{S}^B \subset \overline{S}$ , provided  $S \subset B$ .
- (f)  $\overline{ST} \subset \overline{ST}^B$ , provided  $T \subset B$ .

Though these facts are elementary, they will make the proofs simpler and more lucid.

### 3. CANONICAL CORRESPONDENCE PROPERTY

For a double algebra  $(B, A)$ , there is a natural mapping from the set of all ideals of  $A$  into the set of all ideals of  $B$  which takes  $I$  to  $I \cap B$ . For any specific class of ideals, if this natural mapping restricted to it on both domain and range is bijective, then  $(B, A)$  is said to have the canonical correspondence property on that specific class. For instance,  $(B, A)$  is said to have the canonical correspondence property on closed right ideals if  $I \rightarrow I \cap B$  is a one-to-one mapping from the set of all closed right ideals of  $A$  onto the sets of all closed right ideals of  $B$ .

As we shall see below, any  $D$ -algebra has the canonical correspondence property on closed right ideals. In the next section we will study the canonical correspondence property on some other important classes of ideals.

**Lemma 3.1.** Let  $(B, A)$  be a double algebra.

- (i) If  $I$  is a closed (right, left, or two-sided) ideal of  $A$ , then  $I \cap B$  is a closed (resp. right, or two-sided) ideal of  $B$ .
- (ii) If  $J$  is a closed (right, left, or two-sided) ideal of  $B$ , then  $\overline{J}$  is a closed (resp. right, left, or two-sided) ideal of  $A$ .

**Proof.** (i) Clear, since the topology  $\mathcal{J}_B$  is stronger than the topology  $\mathcal{J}_A$ .

(ii) We prove the assertion for right ideals, the proofs for left or two-sided ideal being completely analogous. Observe:

$$\bar{J} + \bar{J} \subset \overline{J + J} \subset \bar{J},$$

$$\alpha \bar{J} = \overline{\alpha J} \subset \bar{J}, \text{ where } \alpha \text{ is a scalar,}$$

$$\bar{J}A = \bar{J} \bar{B} \subset \overline{JB} \subset \bar{J}.$$

Therefore  $\bar{J}$  is a closed right ideal of  $A$ .

**Lemma 3.2.** Let  $(B, A)$  be a double algebra.

(i) If  $A$  has right approximate units, then  $\overline{I \cap B} = I$  for each closed right ideal  $I$  of  $A$ .

(ii) If  $B$  has right approximate units, then  $\bar{J} \cap B = J$  for each closed right ideal  $J$  of  $B$ .

**Proof.** (i) Since  $I$  is a right ideal of  $A$  and  $B$  is a left ideal of  $A$ , we have  $IB \subset I \cap B$  and therefore

$$\overline{IB} \subset \overline{I \cap B} \subset \bar{I} = I. \quad (1)$$

Since  $A$  has right approximate units, we have

$$I \subset \overline{IA} = \overline{IB}. \quad (2)$$

By (1) and (2), we have  $\overline{I \cap B} = I$ .

(ii) Note that

$$\bar{J}B \subset \overline{JB^B} \subset \bar{J}^B = J \subset \bar{J} \cap B. \quad (3)$$

On the other hand, since  $\bar{J} \cap B \subset B$  and  $B$  has right approximate units, we have

$$\bar{J} \cap B \subset \overline{(\bar{J} \cap B)B^B} \subset \overline{JB^B}. \quad (4)$$

By (3) and (4), we have  $\bar{J} \cap B = J$ .

**Theorem 3.3.** (Reiter's ideal theorem). Let  $(B, A)$  be a D-algebra. Then  $(B, A)$  has the canonical correspondence property on closed right ideals.

**Proof.** Lemma 3.1 (i) shows that  $I \rightarrow I \cap B$  ( $I$  being a closed right ideal of  $A$ ) is a mapping from the set of all closed right ideals into the set of all closed right ideals of  $B$ , and Lemma 3.2 (i) shows that the mapping is injective. Finally, Lemma 3.1 (ii) and Lemma 3.2 (ii) together show that the mapping is surjective. Therefore the mapping is bijective and the theorem is proved. Incidentally we also proved that the inverse of this mapping is  $J \rightarrow \bar{J}$ ,  $J$  being a closed right ideal of  $B$ .

As a matter of fact, Theorem 3.3 (including Lemmas 3.1 and 3.2) was already established in [12; Theorem 1.4]. We have stated (in a different way) and proved it again, just for the convenience of our latter development.

**Remark.** It is interesting to note that among two-sided normed ideals  $N$  on a locally compact group  $G$ , the double algebra  $(N, L^1(G))$  having the canonical correspondence property on closed right ideals is a characterization of symmetric Segal algebras. For the details see [6; Theorem 4.3].

It follows from Theorem 3.3 that if  $(B, A)$  is a D-algebra, then  $(B, A)$  has the canonical correspondence property on closed right ideals, in particular  $(B, A)$  has the canonical correspondence property on closed two-sided ideals. Reiter [8; §16, Theorem 1) proved that this canonical correspondence preserves the existence of approximate units for closed ideals, under the case of Segal algebras on locally compact abelian groups. His proof is based on some non-trivial preparation. Happily enough, as we shall see below, an elementary proof is actually available even under the more general case of D-algebras.

**Theorem 3.4.** Let  $(B, A)$  be a D-algebra. Then a closed two-sided ideal  $I$  of  $A$  has right approximate units if and only if the closed two-sided ideal  $I \cap B$  of  $B$  has right approximate units.

**Proof.** Suppose  $I$  has right approximate units. Let any  $f \in I \cap B$  be given, then  $f \in \bar{f}I$  and then  $f \in \bar{f}I \cap B$ . Since  $\bar{f}I \cap B \subset B$  and  $B$  has right approximate units,

$$\begin{aligned} \overline{fI} \cap B &\subset \overline{(\overline{fI} \cap B) B^B} \subset \overline{fI B^B} \subset \overline{(fI) B^{B^B}} \\ &= \overline{(fI) B^B} = \overline{f(IB)^B} \subset \overline{f(I \cap B)^B}. \end{aligned}$$

Therefore  $f \in \overline{f(I \cap B)^B}$  and this proves that  $I \cap B$  has right approximate units.

Conversely, suppose  $I \cap B$  has right approximate units. Given any  $f \in I$ , then we have  $fB \subset I \cap B$ . Since  $I \cap B$  has right approximate units, we have

$$fB \subset \overline{(fB) (I \cap B)^B} \subset \overline{f[B(I \cap B)]} \subset \overline{f(BI)} \subset \overline{fI}.$$

On the other hand, since  $A$  has right approximate units, we have

$$f \in \overline{fA} = \overline{fB} \subset \overline{fI}.$$

This proves that  $I$  has right approximate units.

When specialized to Segal algebras, Theorem 3.4 yields the following corollary.

**Corollary 3.5.** Let  $G$  be a locally compact group and let  $S(G)$  be a symmetric or pseudo-symmetric Segal algebra on  $G$ . Then a closed two-sided ideal  $I$  of  $L^1(G)$  has right approximate units if and only if the closed two-sided ideal  $I \cap S(G)$  of  $S(G)$  has right approximate units.

**Proof.** [8; Proposition 1] implies that  $(S(G), L^1(G))$  is a  $D$ -algebra and the corollary follows immediately from Theorem 3.4.

Corollary 3.5 combined with Lemma 3.2 gives an answer to Reiter's question [8; p. 92, lines 6-8].

#### 4. STRUCTURE SPACE

For any term not explained in this section, we refer the reader to [2; Ch. III, Ch. IV] or [9; Ch. II].

**Definition 4.1.** Let  $R$  be an algebra which is also a topological space with topology  $\mathcal{J}_R$ . Then  $R$  is said to be modular closed if every maximal modular left ideal of  $R$  is closed in the topology  $\mathcal{J}_R$ . A double algebra  $(B, A)$  is said to be modular closed if both  $A$  and  $B$  are modular closed.

Every Banach algebra is modular closed. Also any modular annihilator topological algebra [1] is modular closed. Since every primitive ideal (and hence every maximal modular two-sided ideal) of an algebra is the intersection of the maximal modular left ideals containing it [2; §24, Proposition 12 (iv)], all primitive ideals and all maximal modular two-sided ideals are also closed in a modular closed algebra.

The goal of this section is to show that every modular closed double algebra  $(B, A)$  has the canonical correspondence property on maximal modular left ideals, on maximal modular two-sided ideals, and on primitive ideals; and that  $A$  and  $B$  have homeomorphic (strong) structure spaces.

In the following, notations  $E(1-u)$  and  $(1-u)E$  denote respectively the sets  $\{f-fu \mid f \in E\}$  and  $\{f-uf \mid f \in E\}$ .

**Lemma 4.2.** Let  $(B, A)$  be a double algebra.

- (i) If  $J$  is a closed left ideal of  $B$ , then  $J$  is a left ideal of  $A$ .
- (ii) If  $J$  is a proper modular closed left (two-sided) ideal of  $B$  with  $u$  as a right (two-sided) modular unit, then  $\bar{J}$  is a proper modular left (two-sided) ideal of  $A$  with  $u$  as a right (two-sided) modular unit.

**Proof.** (i) Observe

$$AJ = \bar{B}J \subset \bar{B}J^B \subset \bar{J}^B = J.$$

Therefore  $J$  is a left ideal of  $A$ .

(ii) By hypothesis,  $B(1-u) \subset J$  (and  $(1-u)B \subset J$ ). Therefore

$$\begin{aligned} A(1-u) &= \bar{B}(1-u) \subset \overline{B(1-u)} \subset \bar{J} \\ \text{(and } (1-u)A &= (1-u)\bar{B} \subset \overline{(1-u)B} \subset \bar{J}). \end{aligned}$$

This shows that  $u$  is a right (two-sided) modular unit for  $\bar{J}$ . Since given any  $f \in J$  we have  $fu = f - (f-fu) \in J$ ,  $Ju \subset J$ . Thus, if  $u \in J$ , then we would have

$$u^2 \in \bar{J}u \subset \bar{J}u^B \subset \bar{J}^B = J.$$

Then given any  $f \in B$  we would have

$$f = (f - fu) + [fu - (fu)u] + fu^2 \in J.$$

Thus  $J = B$  which contradicts the hypothesis. Therefore  $u \notin \bar{J}$  and therefore  $\bar{J} \neq A$ . This complete the proof.

Note that the two-sided version of Lemma 4.2 (i) does not hold. That is, if  $J$  is a closed two-sided ideal of  $B$  then  $J$  is not necessarily a two-sided ideal of  $A$ . To see this, just take  $J = B$ .

**Lemma 4.3.** Let  $(B, A)$  be a double algebra in which  $A$  is modular closed.

(i) If  $I$  is a modular left ideal of  $A$  which is dense in  $A$ , then  $I = A$ .

(ii) If  $I$  is a proper modular left (two-sided) ideal of  $A$ , then  $I \cap B$  is a proper modular left (two-sided) ideal of  $B$ .

**Proof.** (i) If  $I \neq A$ , then  $I$  could be extended to a maximal modular left ideal  $L$  of  $A$ . Since  $A$  is modular closed,  $L$  is closed in  $A$  and therefore  $\bar{L} \subset L \not\equiv A$ . This contradicts the hypothesis:  $I$  being dense in  $A$ . Therefore  $I = A$ .

(ii) If  $I \cap B = B$ , then  $B \subset I$  which would imply that  $I$  is dense in  $A$ . Then  $I = A$  by (i). This leads to a contradiction. Hence  $I \cap B \neq B$ . Next note that  $I + B$  is a left ideal of  $A$  which contains both  $I$  and  $B$ . Therefore  $I + B$  is a modular dense left ideal of  $A$  and therefore  $I + B = A$  by (i). Now let  $u$  be a right (two-sided) modular unit for  $I$ , then there exist  $f \in I$  and  $v \in B$  such that  $u = f + v$ . Clearly  $v$  is also a right (two-sided) modular unit for  $I$ . That is,

$$A(1-v) \subset I \quad (\text{and } (1-v)A \subset I),$$

in particular, we have

$$B(1-v) \subset I \quad (\text{and } (1-v)B \subset I).$$

On the other hand, since  $v \in B$ , we have

$$B(1-v) \subset B \quad (\text{and } (1-v)B \subset I).$$

Therefore

$$B(1-v) \subset I \cap B \quad (\text{and } (1-v)B \subset I \cap B)$$

and this proves that  $I \cap B$  is modular.

**Theorem 4.4.** Let  $(B, A)$  be a modular closed double algebra. Then  $(B, A)$  has the canonical correspondence property on maximal modular left (two-sided) ideals.

**Proof.** Let  $L$  be a maximal modular left (two-sided) ideal of  $A$ . We will show that  $L \cap B$  is a maximal modular left (two-sided) ideal of  $B$ .

By Lemma 4.3 (ii),  $L \cap B$  is a proper modular left (two-sided) ideal of  $B$ . Now let  $J$  be any left (two-sided) ideal of  $B$  such that

$$L \cap B \subsetneq J \subset B.$$

Without loss of generality, we may assume that  $J$  is closed in  $B$ , since  $B$  is modular closed. Then  $J \not\subset L$  and then  $\bar{J} \not\subset L$ . Since  $\bar{J}$  is a left (two-sided) ideal of  $A$ ,  $L + \bar{J}$  is a left (two-sided) ideal of  $A$  properly containing  $L$ , and therefore  $L + \bar{J} = A$ . Observe

$$\overline{L + J} \supset \bar{L} + \bar{J} = L + \bar{J} = A$$

which implies that  $L + J$  is dense in  $A$ . By Lemma 4.2 (i),  $J$  is a left ideal of  $A$ , therefore  $L + J$  is a modular dense left ideal of  $A$ . By Lemma 4.3 (i),  $L + J = A$ . Thus for any  $b \in B$ , there exist  $l \in L$  and  $j \in J$  such that  $b = l + j$ . By this we have  $l = b - j \in B$ . Therefore  $l \in L \cap B \subset J$  and therefore  $b = l + j \in J$ . Thus  $J = B$  which implies that  $L \cap B$  is maximal.

Conversely let  $M$  be a maximal modular left (two-sided) ideal of  $B$ . We will show that  $\bar{M}$  is a maximal modular left (two-sided) ideal of  $A$ :

Let  $u$  be a right (two-sided) modular unit for  $M$ , then by Lemma 4.2 (ii),  $\bar{M}$  is a proper modular left (two-sided) ideal of  $A$  with  $u$  as a right (two-sided) modular unit. Now let  $I$  be any left (two-sided) ideal of  $A$  such that  $\bar{M} \subset I \subsetneq A$ . Then by Lemma 4.3 (ii), we have

$$M \subset \bar{M} \cap B \subset I \cap B \subsetneq B.$$

Since  $M$  is maximal,  $M = I \cap B$ . Given any  $i \in I$ , we have

$$iu = i - (i - iu) \in M,$$

therefore  $iu \in I \cap B = M \subset \bar{M}$ , and therefore

$$i = (i - iu) + iu \in \bar{M}.$$

Hence  $I = \bar{M}$  which shows that  $\bar{M}$  is maximal.

Finally by the results we proved above, it is readily checked that  $\overline{L \cap B} = L$  and  $\bar{M} \cap B = M$  for any maximal modular left (two-sided) ideal  $L$  of  $A$  and for any maximal modular left (two-sided) ideal  $M$  of  $B$ . Therefore the mapping  $L \rightarrow L \cap B$  from the set of all maximal modular left (two-sided) ideal of  $A$  into the set of all maximal modular left (two-side) ideal of  $B$  is bijectie. Incidentally, like Theorem 3.3, we also proved that the inverse of this correspondence is  $M \rightarrow \bar{M}$ ,  $M$  being a maximal modular left (two-sided) ideal of  $B$ .

**Corollary 4.5.** Let  $(B, A)$  be a modular closed double algebra. Then

(i)  $\text{rad}(B) = \text{rad}(A) \cap B$  and  $\text{rad}_s(B) = \text{rad}_s(A) \cap B$ , where  $\text{rad}$  denotes radical and  $\text{rad}_s$  denotes strong radical.

(ii) If  $A$  has right approximate units, then

$$\text{rad}(A) = \overline{\text{rad}(B)} \quad \text{and} \quad \text{rad}_s(A) = \overline{\text{rad}_s(B)}.$$

**Proof.** (i)

$$\begin{aligned} \text{rad}(B) &= \cap \{ M \mid M \text{ is a maximal modular left ideal of } B \} \\ &= \cap \{ L \cap B \mid L \text{ is a maximal modular left ideal of } A \} \\ &= (\cap \{ L \mid L \text{ is a maximal modular left ideal of } A \}) \cap B \\ &= \text{rad}(A) \cap B. \end{aligned}$$

Similarly,  $\text{rad}_s(B) = \text{rad}_s(A) \cap B$ .

(ii) Note that  $\text{rad}(A)$  is a closed two-sided ideal of  $A$ , therefore, by (i) and Lemma 3.2 (i), we have

$$\text{rad}(A) = \overline{\text{rad}(A) \cap B} = \overline{\text{rad}(B)}.$$

Similarly,  $\text{rad}_s(A) = \overline{\text{rad}_s(B)}$ . Thus we complete the proof.

Recall that the left annihilator of  $A$  is the set  $\text{lan}(A)$  defined by

$$\text{lan}(A) = \{ f \in A \mid fA = \{0\} \}.$$

For the condition:  $\text{lan}(A) = \{0\}$  will appear in the following corollary as a hypothesis, it is worth noting under what conditions, we have  $\text{lan}(A) = \{0\}$ .

- (a) If  $A$  has right approximate units, then  $\text{lan}(A) = \{0\}$ .
- (b) If  $A$  is an annihilator algebra, then  $\text{lan}(A) = \{0\}$ .
- (c)  $A$  is semi-simple  $\Rightarrow A$  is semi-prime  $\Rightarrow \text{lan}(A) = \{0\}$ .

The proof of (a) is easy. (b) is just a part of the definition of annihilator algebras. For the proof of (c) see [2; §30, Lemma 4 and Proposition 5].

**Corollary 4.6.** Let  $(B, A)$  be a modular closed double algebra. If  $A$  is (strongly) semi-simple, so is  $B$ . Conversely, if  $B$  is (strongly) semi-simple and  $\text{lan}(A) = \{0\}$ , then  $A$  is also (strongly) semi-simple.

**Proof.** The first part of the corollary follows immediately from Corollary 4.5 (i). Now suppose  $B$  is semi-simple and  $\text{lan}(A) = \{0\}$ . Then

$$\text{rad}(A)B \subset \text{rad}(A) \cap B = \text{rad}(B) = \{0\},$$

and then

$$\text{rad}(A)A = \text{rad}(A)\overline{B} \subset \overline{\text{rad}(A)B} = \overline{\{0\}} = \{0\}.$$

Thus  $\text{rad}(A) \subset \text{lan}(A) = \{0\}$ . Therefore  $A$  is semi-simple.

**Theorem 4.7.** Let  $(B, A)$  be a modular closed double algebra. Then  $(B, A)$  has the canonical correspondence property on primitive ideals.

**Proof.** We first establish the following assertion (\*):

(\*) Given any maximal modular left ideal  $L$  of  $A$ , we have

$$\{f \in A \mid fA \subset L\} \cap B = \{f \in B \mid fB \subset L \cap B\}.$$

Proof of (\*): It is clear that

$$\{f \in A \mid fA \subset L\} \supset B \subset \{f \in B \mid fB \subset L \cap B\}.$$

Conversely, given any  $g \in \{f \in B \mid fB \subset L \cap B\}$ , then we have  $g \in B$  and  $gB \subset L \cap B$ . Since

$$gA = g\bar{B} \subset \overline{gB} \subset \overline{L \cap B} = L,$$

$g \in \{f \in A \mid fA \subset L\} \cap B$ . Therefore

$$\{f \in B \mid fB \subset L \cap B\} \subset \{f \in A \mid fA \subset L\} \cap B$$

and therefore

$$\{f \in A \mid fA \subset L\} \cap B = \{f \in B \mid fB \subset L \cap B\}.$$

Thus we established (\*).

Now, by (\*) and Theorem 4.4, it is clear that  $P \rightarrow P \cap B$  is a mapping from the set of all primitive ideals of  $A$  onto the set of all primitive ideals of  $B$ . To prove the mapping is injective, let  $P$  and  $P'$  be two primitive ideals of  $A$  such that

$$P \cap B = P' \cap B.$$

Then

$$PB \subset P \cap B = P' \cap B \subset P'.$$

By [2; §24, proposition 12 (iii)] we have  $P \subset P'$ , since  $B \not\subset P'$ . Similarly, we have  $P' \subset P$ . Therefore  $P = P'$ . Thus the mapping  $P \rightarrow P \cap B$  is injective. This completes the proof.

Unlike Theorem 3.3 and Theorem 4.4, we do not know whether the inverse of the correspondence in Theorem 4.7 is  $Q \rightarrow \bar{Q}$ ,  $Q$  being a primitive ideal of  $B$ . It becomes true if  $A$  has right approximate units.

**Theorem 4.8.** Let  $(B, A)$  be a modular closed double algebra. Then the structure space  $\Pi_A$  of  $A$  is homeomorphic with the structure space  $\Pi_B$  of  $B$  under the canonical correspondence:  $P \rightarrow P \cap B$ ,  $P$  being a primitive ideal of  $A$ .

**Proof.** Let  $F$  be a subset of  $\Pi_A$  and denote its image in  $\Pi_B$  by  $G$  under the canonical correspondence. Then

$$\ker(G) = \ker(F) \cap B.$$

If we can establish the following assertion (\*\*) then the proof is complete.

$$(**) \quad F = \text{hul}(\ker(F)) \Leftrightarrow G = \text{hul}(\ker(G)).$$

Proof of (\*\*):

( $\Rightarrow$ ) Let  $Q$  be any primitive ideal of  $B$  which contains  $\ker(G)$ . By Theorem 4.7, there is a (unique) primitive ideal  $P$  of  $A$  such that  $Q = P \cap B$ . Then

$$\ker(F)B \subset \ker(F) \cap B = \ker(G) \subset Q \subset P.$$

Since  $B \not\subset P$ ,  $\ker(F) \subset P$ . By hypothesis  $P \in F$ . Hence  $Q = P \cap B \in G$ . Therefore  $\text{hul}(\ker(G)) \subset G$  which forces  $G = \text{hul}(\ker(G))$ .

( $\Leftarrow$ ) Let  $P$  be any primitive ideal of  $A$  which contains  $\ker(F)$ . Then

$$P \cap B \supset \ker(F) \cap B = \ker(G)$$

and then  $P \cap B \in \text{hul}(\ker(G)) = G$ . Thus  $P \in F$ . So  $\text{hul}(\ker(F)) \subset F$  which forces  $F = \text{hul}(\ker(F))$ .

**Theorem 4.9.** Let  $(B, A)$  be a modular clouble algebra. Then the strong structure space  $\mathcal{E}_A$  of  $A$  is homeomorphic with the strong structure space  $\mathcal{E}_B$  of  $B$  under the canonical correspondence:  $L \rightarrow L \cap B$ ,  $L$  being a maximal modular two-sided ideal of  $A$ .

**Proof.** Since any maximal modular two-sided ideal is primitive, the proof of Theorem 4.8 can be transferred to here in terms of maximal modular two-sided ideals.

**Corollary 4.10.** Let  $(B, A)$  be a modular closed double algebra. Then  $B$  is completely regular if and only if  $A$  is completely regular.

**Proof.** Let  $V$  be an open set of  $\mathcal{E}_A$  and denote its image in  $\mathcal{E}_B$  by  $W$  under the canonical correspondence. Then

$$\ker(W) = \ker(V) \cap B.$$

If  $\ker(V)$  is modular then  $\ker(W)$  is also modular by Lemma 4.3 (ii). Conversely, if  $\ker(W)$  is modular, then since

$$\ker(\overline{V}) \supset \overline{\ker(V) \cap B} = \ker(W)$$

and since  $\overline{\ker(W)}$  is modular by Lemma 4.2 (ii),  $\ker(V)$  is also modular. Thus the corollary follows from the result we established above, Theorem 4.9, and the definition of complete regularity.

**Remark.** If  $A$  is commutative, then it can be proved that the carrier space of  $A$  is homeomorphic with the carrier space of  $B$ . For the proof see [3; Theorem 2.1].

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# “論雙重代數的構造空間”

何 清 人

## 摘 要

在本論文中，我們證明如下的結果：

1. 設  $(B, A)$  為一個  $D$ -代數，則  $A$  中的一個閉雙邊理想  $I$  有右近似單元若且唯若  $B$  中的雙邊理想  $I \cap B$  有右近似單元。
2. 設  $(B, A)$  為一個模閉二重代數，則在  $P \rightarrow P \cap B$  ( $P$  為  $A$  中的本原理想) 的正準對應下， $A$  的構造空間同胚於  $B$  的構造空間。對強構造空間而言，類似的結果亦成立。



# ON THE USE OF LANCZOS METHOD FOR SOLVING NONSYMMETRIZABLE LINEAR SYSTEMS

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## ABSTRACT

Solving  $Au = b$  when  $A$  is nonsymmetrizable by the idealized generalized conjugate gradient (IGCG) method requires extensive computer storage and computational effort. The IGCG method can be greatly simplified by introducing a fictitious system and we derived three variations of the Lanczos method. Among these three procedures, Lanczos/ORTHODIR is shown to be the most reliable one, but floating overflow always occurs during computation. A normalized Lanczos/ORTHODIR procedure has been developed for use on a minicomputer or microcomputer.

## 1. INTRODUCTION

In this paper we are concerned with certain iterative methods for solving the linear system

$$Au = b \tag{1.1}$$

where  $A$  is a given real  $N \times N$  nonsingular matrix which is large and sparse, and  $b$  is a given  $N \times 1$  column vector.

The conjugate gradient (CG) method, developed by Hestenes and Stiefel<sup>(1)</sup>, can be effectively used to solve (1.1) when  $A$  is symmetrizable in the sense that  $ZA$  is symmetric positive definite (SPD) for some SPD matrix  $Z$ . A number of generalizations of the CG method have been proposed for the nonsymmetrizable case. Young and Jea<sup>(5,6)</sup> considered a method called the idealized generalized conjugate gradient method (IGCG method) for this case. The IGCG method has three equivalent forms, named ORTHODIR, ORTHOMIN, and ORTHORES, each converges to the true solution in at most  $N$  iterations under very general conditions. Unfortunately,

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however, the determination of a given iteration vector requires information on all preceding iterations. Thus a tremendous amount of computer storage and computation effort is required. Jea<sup>(2)</sup> showed that the ICGG method can be greatly simplified if one has available a matrix  $H$  satisfying condition I with respect to  $A$ , i.e., if  $HA = A^T H$ . The resulting procedures are called ORTHODIR(2), ORTHOMIN(1), and ORTHORES(1), respectively, according to the number of previous vectors required for determining the present iteration vector. Although we can prove such a matrix  $H$  always exists, it is not easily constructable. Jea and Young<sup>(3)</sup> introduced a fictitious system

$$A^T \tilde{u} = \tilde{b}. \quad (1.2)$$

For the present we will not specify  $\tilde{b}$ . It is obvious that for any  $\tilde{b}$ , the vector  $\hat{u} = [u^T, \tilde{u}^T]^T$  satisfies the double system

$$\hat{A}\hat{u} = \hat{b} \quad (1.3)$$

where

$$\hat{A} = \begin{bmatrix} A & 0 \\ 0 & A^T \end{bmatrix}, \quad \hat{u} = \begin{bmatrix} u \\ \tilde{u} \end{bmatrix}, \quad \text{and} \quad \hat{b} = \begin{bmatrix} b \\ \tilde{b} \end{bmatrix},$$

if and only if  $u$  satisfies (1.1) and  $\tilde{u}$  satisfies (1.2). Moreover, if we choose

$$\hat{H} = \begin{bmatrix} 0 & I \\ I & 0 \end{bmatrix}$$

than  $\hat{H}\hat{A} = \hat{A}^T\hat{H}$ , that is  $\hat{H}$  satisfies condition I with respect to  $\hat{A}$ . Therefore, solving (1.3) by ORTHODIR, ORTHOMIN, and ORTHORES will reduce to ORTHODIR(2), ORTHOMIN(1), and ORTHORES (1), respectively. We omit formulas involving the fictitious vector  $\tilde{u}^{(*)}$  for the solution of (1.2) and give formulas for these three methods in Table 1. Here we find that ORTHOMIN(1) with  $\hat{Z} = \hat{H}$  for (1.3) turns out to be the Lanczos<sup>(4)</sup> method for solving (1.1), thus we name these resulting procedures as Lanczos/ORTHODIR, Lanczos/ORTHOMIN, and Lanczos/ORTHORES, respectively.

Table 1. The Lanczos method for the nonsymmetrizable case

$u^{(0)}$  is arbitrary,  $r^{(0)} = b - Au^{(0)}$ , and  $\tilde{r}^{(0)}$  is arbitrary.

## Lanczos/ORTHODIR:

$$q^{(0)} = r^{(0)}$$

$$\tilde{q}^{(0)} = \tilde{r}^{(0)}$$

$$u^{(n+1)} = u^{(n)} + \hat{\lambda}_n q^{(n)}$$

$$\hat{\lambda}_n = \frac{(\tilde{r}^{(n)}, q^{(n)}) + (r^{(n)}, \tilde{q}^{(n)})}{2(Aq^{(n)}, \tilde{q}^{(n)})}$$

$$q^{(n)} = Aq^{(n-1)} - a_n q^{(n-1)} - b_n q^{(n-2)}, \quad n = 1, 2, \dots$$

$$\tilde{q}^{(n)} = A^T \tilde{q}^{(n-1)} - a_n \tilde{q}^{(n-1)} - b_n \tilde{q}^{(n-2)}, \quad n = 1, 2, \dots$$

$$a_n = \frac{(Aq^{(n-1)}, A^T \tilde{q}^{(n-1)})}{(Aq^{(n-1)}, \tilde{q}^{(n-1)})}, \quad n = 1, 2, \dots$$

$$b_n = \frac{(Aq^{(n-2)}, A^T \tilde{q}^{(n-1)}) + (Aq^{(n-1)}, A^T \tilde{q}^{(n-2)})}{2(Aq^{(n-2)}, \tilde{q}^{(n-2)})}$$

$$= \frac{(Aq^{(n-1)}, \tilde{q}^{(n-1)})}{(Aq^{(n-2)}, \tilde{q}^{(n-2)})}, \quad n = 2, 3, \dots, (b_1 = 0)$$

$$r^{(n+1)} = r^{(n)} - \hat{\lambda}_n Aq^{(n)}$$

$$\tilde{r}^{(n+1)} = \tilde{r}^{(n)} - \hat{\lambda}_n A^T \tilde{q}^{(n)}$$

## Lanczos/ORTHOMIN:

$$p^{(0)} = r^{(0)}$$

$$\tilde{p}^{(0)} = \tilde{r}^{(0)}$$

$$u^{(n+1)} = u^{(n)} + \lambda_n p^{(n)}$$

$$\lambda_n = \frac{(r^{(n)}, \tilde{r}^{(n)})}{(Ap^{(n)}, \tilde{p}^{(n)})}$$

$$p^{(n)} = r^{(n)} + \alpha_n p^{(n-1)}, \quad n = 1, 2, \dots$$

$$\tilde{p}^{(n)} = \tilde{r}^{(n)} + \alpha_n \tilde{p}^{(n-1)}, \quad n = 1, 2, \dots$$

$$\alpha_n = \frac{(r^{(n)}, \tilde{r}^{(n)})}{(r^{(n-1)}, \tilde{r}^{(n-1)})}, \quad n = 1, 2, \dots$$

$$r^{(n+1)} = r^{(n)} - \lambda_n Ap^{(n)}$$

$$\tilde{r}^{(n+1)} = \tilde{r}^{(n)} - \lambda_n A^T \tilde{p}^{(n)}$$

## Lanczos/ORTHORES:

$$u^{(n+1)} = \rho_{n+1} u^{(n)} + \tau_{n+1} r^{(n)} + (1 - \rho_{n+1}) u^{(n-1)}$$

$$\tau_{n+1} = \frac{(r^{(n)}, \tilde{r}^{(n)})}{(Ar^{(n)}, \tilde{r}^{(n)})}$$

$$\rho_{n+1} = \left[ 1 - \frac{\tau_{n+1}}{\tau_n} \frac{(r^{(n)}, \tilde{r}^{(n)})}{(r^{(n-1)}, \tilde{r}^{(n-1)})} \frac{1}{\rho_n} \right]^{-1}, \quad n = 1, 2, \dots \quad (\rho_1 = 1)$$

$$r^{(n+1)} = \rho_{n+1} r^{(n)} - \tau_{n+1} Ar^{(n)} + (1 - \rho_{n+1}) r^{(n-1)}$$

$$\tilde{r}^{(n+1)} = \rho_{n+1} \tilde{r}^{(n)} - \tau_{n+1} A^T \tilde{r}^{(n)} + (1 - \rho_{n+1}) \tilde{r}^{(n-1)}$$

It is easy to show that if  $(Aq^{(n)}, \tilde{q}^{(n)}) = 0$  but  $r^{(n)} \neq 0$ , Lanczos/ORTHODIR breaks down; if  $(Ap^{(n)}, \tilde{p}^{(n)}) = 0$  or  $(r^{(n)}, \tilde{r}^{(n)}) = 0$  but  $r^{(n)} \neq 0$ , then Lanczos/ORTHOMIN breaks down; and if  $(Ar^{(n)}, \tilde{r}^{(n)}) = 0$  or  $(r^{(n)}, \tilde{r}^{(n)}) = 0$  but  $r^{(n)} \neq 0$ , then Lanczos/ORTHORES will break down. Moreover, we can prove the following

**Theorem.** Lanczos/ORTHOMIN converges if and only if Lanczos/ORTHORES converges. If these two procedures converge, then Lanczos/ORTHODIR will converge, too, and the three methods are equivalent.

The following counterexample shows that the convergence of Lanczos/ORTHODIR does not imply that of Lanczos/ORTHOMIN nor Lanczos/ORTHORES. Therefore, among these three methods, we consider Lanczos/ORTHODIR as the most reliable one.

**Example.** Solve

$$\begin{bmatrix} 0 & I \\ I & 0 \end{bmatrix} u = \begin{bmatrix} \underline{3} \\ \underline{1} \end{bmatrix}$$

where  $I$  is the  $N \times N$  identity matrix and  $\underline{k}$  denotes a  $N \times 1$  column vector whose components are constant  $k$ .

If we choose  $u^{(0)} = [\underline{1}^T, \underline{2}^T]^T$  and  $\tilde{r}^{(0)} = [\underline{0}^T, \underline{1}^T]^T$ , then  $r^{(0)} = [\underline{1}^T, \underline{0}^T]^T$  and  $(r^{(0)}, \tilde{r}^{(0)}) = 0$  but  $r^{(0)} \neq 0$ . Therefore, both Lanczos/ORTHOMIN and Lanczos/ORTHORES break down. If we apply Lanczos/ORTHODIR, we will have  $\hat{\lambda}_0 = 0$  and  $u^{(1)} = [\underline{1}^T, \underline{2}^T]^T$ . Then  $a_1 = 0$ ,  $q^{(1)} = [\underline{0}^T, \underline{1}^T]^T$ ,  $\tilde{q}^{(1)} = [\underline{1}^T, \underline{0}^T]^T$ , and  $\hat{\lambda}_1 = 1$ . Thus,  $u^{(2)} = [\underline{1}^T, \underline{3}^T]^T = \bar{u}$ , the exact solution.

We ran numerical experiments of these three procedures on PDP-11/34, computer of our College of Science and Engineering. Floating overflow always occurs for Lanczos/ORTHODIR. In order to avoid this, we propose a new algorithm named normalized Lanczos/ORTHODIR. This method does not overflow during computation, but of course, it takes a little extra work than Lanczos/ORTHODIR.

## 2. NORMALIZED LANCZOS/ORTHODIR

In the above section we claimed that Lanczos/ORTHODIR is

more reliable than Lanczos/ORTHOMIN and Lanczos/ORTHORES. Unfortunately, the following numerical experiments showed that floating overflow always occurs when we apply Lanczos/ORTHODIR on a small computer such as the PDP-11/34 in our College of Science and Engineering, whose range of real numbers is  $10^{\pm 38}$ .

Our test problem is

$$\begin{cases} u_{xx} + u_{yy} + Du_x = Dy & \text{in } R \\ u(x, y) = 1 + xy & \text{on } \partial R \end{cases} \quad (2.1)$$

where  $R$  is the unit square  $[0, 1] \times [0, 1]$ . The exact solution is  $\bar{u}(x, y) = 1 + xy$ . We use the central difference scheme to discretize the region  $R$ , and the stopping criterion is

$$K_E = \frac{\|u^{(n)} - \bar{u}\|_2}{\|u^{(0)} - \bar{u}\|_2} < \epsilon \quad (2.2)$$

where  $\epsilon$  is any desired tolerance, say  $10^{-6}$ . For convenience, we usually start with  $u^{(0)} = 0$ . We draw the graph of  $\log(K_E)$  versus  $n$ , the number of iterations, to observe the change of (2.2) during process. Figure 1 shows that if we use single precision to solve (2.1) on a small computer,  $K_E$  can reduce to  $10^{-4}$  for Lanczos/ORTHOMIN and Lanczos/ORTHORES, and reduces to  $10^{-1}$  only when we apply Lanczos/ORTHODIR. All three procedures can not achieve convergence, say  $\epsilon = 10^{-6}$ , because the round-off errors become dominant. Therefore, we used double precision for the remaining numerical tests. In Fig. 2 we find that if  $A$  is symmetric, i. e.  $D = 0$ , or  $A$  is nearly symmetric, e. g.  $D = 5$  or  $10$ , there are no problems for Lanczos/ORTHODIR to converge. For cases where  $A$  is very nonsymmetric, e. g.  $D = 50, 100, 200$  and  $500$ , floating overflow occurred, and the process could not be continued. On the other hand, Fig. 3 shows that Lanczos/ORTHOMIN converges for all these cases. Moreover, Lanczos/ORTHORES gives a similar result as in Fig. 3. Therefore, Lanczos/ORTHODIR is not suitable to be used on a minicomputer or a microcomputer.

When we apply Lanczos/ORTHODIR given in Table 1, overflow occurs since  $(Aq^{(n)}, \tilde{q}^{(n)})$  grows very large. Therefore, we normalize the direction vectors  $q^{(n)}$  and  $\tilde{q}^{(n)}$  to reduce the value  $(Aq^{(n)}, \tilde{q}^{(n)})$ ,

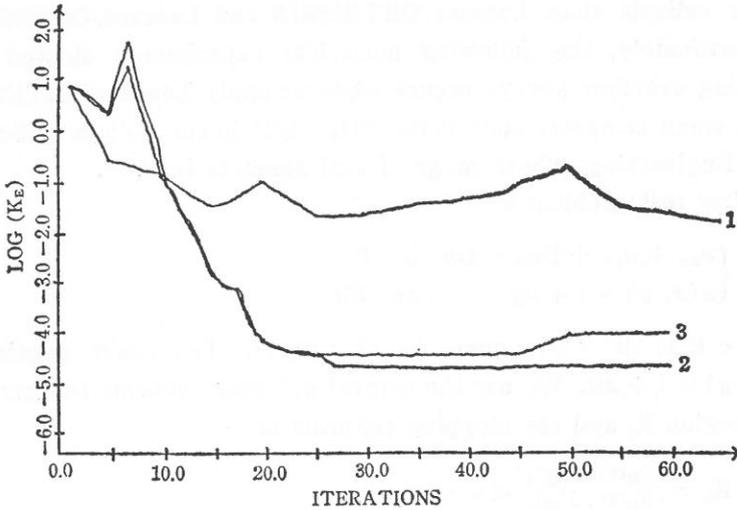


Fig. 1. Solving (2.1) with  $D = 5$  and  $h = 1/8$  by single precision. 1: Lanczos/ORTHODIR, 2: Lanczos/ORTHOMIN, and 3: Lanczos/ORTHORES.

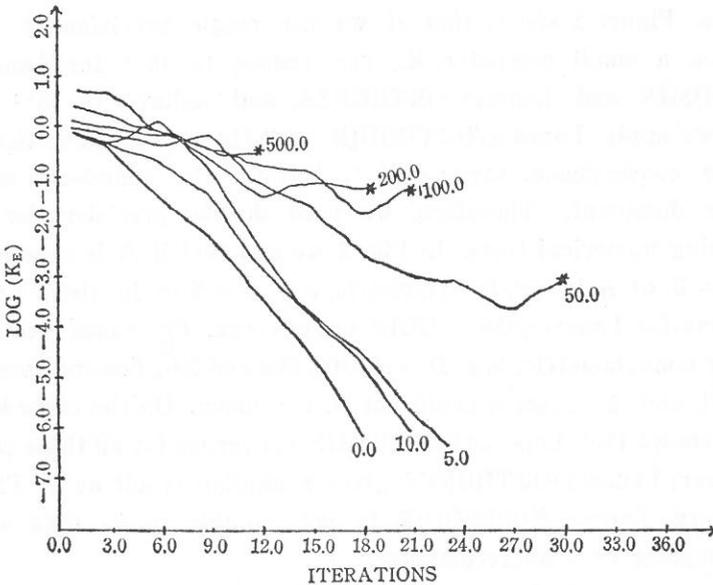


Fig. 2. Solving (2.1) with  $D = 0, 5, 10, 50, 100, 200,$  and  $500$  by Lanczos/ORTHODIR. Here,  $h = 1/8$ , and \* denotes floating overflow occurred and the process could not be continued.

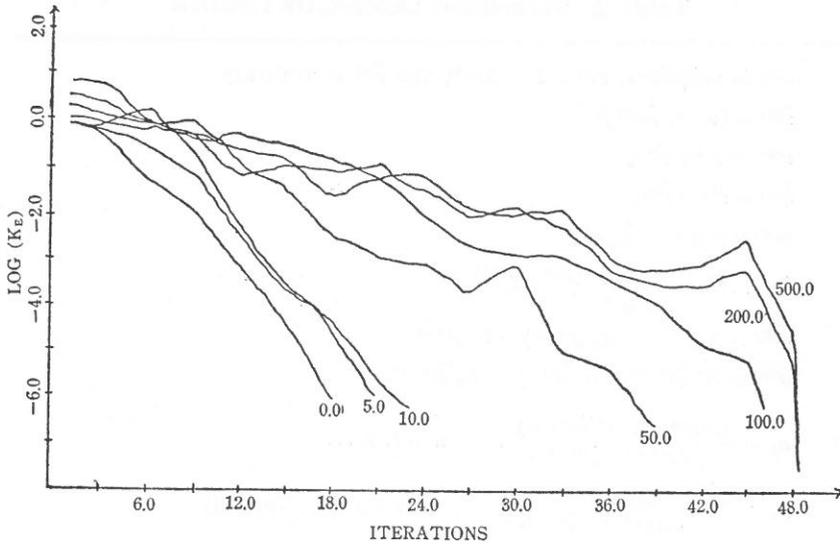


Fig. 3. Solving (2.1) with  $D = 0, 5, 10, 50, 100, 200,$  and  $500$  by Lanczos/ORTHOMIN, here  $h = 1/8$ .

according to the following

**Theorem.** Let  $v$  be any nonzero vector in  $R^N$  and let  $Z$  be any nonsingular matrix in  $R^{N \times N}$  such that  $ZA$  is positive real (PR), and let  $d$  be any nonnegative integer such that the vectors  $v, Av, \dots, A^d v$  are linearly independent. Then the set of vectors  $w^{(0)}, w^{(1)}, \dots, w^{(d)}$  defined by

$$\begin{cases} w^{(0)} = v/\|v\| \\ \tilde{w}^{(n)} = Aw^{(n-1)} + \beta_{n,n-1}w^{(n-1)} + \dots + \beta_{n,0}w^{(0)}, & n = 1, 2, \dots, d \\ w^{(n)} = \tilde{w}^{(n)}/\|\tilde{w}^{(n)}\| \end{cases}$$

where

$$\beta_{n,i} = - \frac{(ZA^2 w^{(n-1)}, w^{(i)}) + \sum_{j=0}^{i-1} \beta_{n,j} (ZAw^{(j)}, w^{(i)})}{(ZAw^{(i)}, w^{(i)})}$$

$$\begin{aligned} i &= 0, 1, \dots, n-1; \\ n &= 1, 2, \dots, d \end{aligned}$$

are linearly independent and satisfy

Table 2. Normalized Lanczos/ORTHODIR

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$u^{(0)}$  is arbitrary,  $r^{(0)} = b - Au^{(0)}$ , and  $\tilde{r}^{(0)}$  is arbitrary

$$\hat{r}^{(0)} = (r^{(0)T}, \tilde{r}^{(0)T})^T$$

$$q^{(0)} = r^{(0)} / \|\hat{r}^{(0)}\|$$

$$\tilde{q}^{(0)} = \tilde{r}^{(0)} / \|\hat{r}^{(0)}\|$$

$$u^{(n+1)} = u^{(n)} + \hat{\lambda}_n q^{(n)}$$

$$\hat{\lambda}_n = \frac{(r^{(n)}, q^{(n)}) + (\tilde{r}^{(n)}, \tilde{q}^{(n)})}{2(Aq^{(n)}, \tilde{q}^{(n)})}$$

$$q^{(n)} = Aq^{(n-1)} - a_n q^{(n-1)} - b_n q^{(n-2)}$$

$$\tilde{q}^{(n)} = A^T \tilde{q}^{(n-1)} - a_n \tilde{q}^{(n-1)} - b_n \tilde{q}^{(n-2)}$$

$$a_n = \frac{(Aq^{(n-1)}, A^T \tilde{q}^{(n-1)})}{(Aq^{(n-1)}, \tilde{q}^{(n-1)})}, \quad n = 1, 2, \dots$$

$$b_n = \frac{\|\hat{q}^{(n-1)}\|(Aq^{(n-1)}, \tilde{q}^{(n-1)})}{(Aq^{(n-2)}, \tilde{q}^{(n-2)})}, \quad n = 2, 3, \dots (b_1 = 0)$$

$$\hat{q}^{(n)} = (q^{(n)T}, \tilde{q}^{(n)T})^T$$

$$q^{(n)} = q^{(n)} / \|\hat{q}^{(n)}\|$$

$$\tilde{q}^{(n)} = \tilde{q}^{(n)} / \|\hat{q}^{(n)}\|$$

$$r^{(n+1)} = r^{(n)} - \hat{\lambda}_n Aq^{(n)}$$

$$\tilde{r}^{(n+1)} = \tilde{r}^{(n)} - \hat{\lambda}_n A^T \tilde{q}^{(n)}$$


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$$(ZAw^{(i)}, w^{(j)}) = 0, \quad j < i, \quad i, j = 0, 1, \dots, d.$$

Moreover, for each  $n = 1, 2, \dots, d$  there exist coefficients  $c_{n,0}$ ,  $c_{n,1}, \dots, c_{n,n-1}$ , and  $c_{n,n} \neq 0$ , such that

$$w^{(n)} = c_{n,0} v + c_{n,1} Av + \dots + c_{n,n-1} A^{n-1} v + c_{n,n} A^n v,$$

Also, for  $n = 1, 2, \dots, d$ , there exist coefficients  $e_{n,0}, e_{n,1}, \dots, e_{n,n-1}$ , and  $e_{n,n} \neq 0$ , such that

$$A^n v = e_{n,0} w^{(0)} + e_{n,1} w^{(1)} + \dots + e_{n,n-1} w^{(n-1)} + e_{n,n} w^{(n)}.$$

The details of proof are given in Lu<sup>(7)</sup>. We can see the above theorem defines a normalized ORTHODIR process. Similar to the arguments given in Section 1, we apply this procedure to (1.3) with  $\hat{Z} = \hat{H}$ , the normalized ORTHODIR then reduces to normalized Lanczos/ORTHODIR. The formulas are given in Table 2. Note that

Table 3. Solving (2.1) by normalized Lanczos/ORTHODIR

D	h	Lanczos/ORTHODIR	Normalized Lanczos/ORTHODIR	
		Number of Iterations	Number of Iterations	Total Work
10 <sup>2</sup>	1/8	22*a	46	49,450
	1/16	28*	60	303,504
	1/24	31*	60	719,220
10 <sup>3</sup>	1/8	11*	49	52,675
	1/16	12*	151	763,909
	1/24	14*	188	2,253,556

a.n\* denotes floating overflow occurs at n<sup>th</sup> iteration.

they are similar to Lanczos/ORTHODIR in Table 1 except for  $b_n$  and the normalization.

We find that both Lanczos/ORTHODIR and normalized Lanczos/ORTHODIR require  $9N$  storage locations for  $u^{(n-1)}$ ,  $q^{(n-1)}$ ,  $q^{(n-2)}$ ,  $\tilde{q}^{(n-1)}$ ,  $\tilde{q}^{(n-2)}$ ,  $r^{(n-1)}$ ,  $\tilde{r}^{(n-1)}$ ,  $Aq^{(n-1)}$  and  $A^T \tilde{q}^{(n-1)}$  in order to compute  $u^{(n)}$ . The extra required computations include evaluating  $\|\hat{q}^{(n)}\|$  norm,  $2N$  multiplications for computing  $q^{(n)}$ ,  $\tilde{q}^{(n)}$ , and a multiplication for computing  $b_n$ . We solved (2.1) for  $D = 100$  and  $1000$  and list the numerical results in Table 3. We also solved the same problems by Lanczos/ORTHOMIN and Lanczos/ORTHOES for comparison, the results are given in Table 4.

Table 4. Solving (2.1) by Lanczos/ORTHOMIN and Lanczos/ORTHOES

D	h	Lanczos/ORTHOMIN		Lanczos/ORTHOES	
		Number of Iterations	Total Work	Number of Iterations	Total Work
10 <sup>2</sup>	1/8	46	35,834	46	45,034
	1/16	60	222,420	60	276,660
	1/24	60	528,660	60	655,860
10 <sup>3</sup>	1/8	49	38,171	49	47,971
	1/16	151	559,757	151	696,261
	1/24	199	1,753,389	188	2,055,028

### 3. CONCLUSION

Theoretically speaking, Lanczos/ORTHODIR is more reliable than Lanczos/ORTHOMIN and Lanczos/ORTHORES. But, practically, on a minicomputer or a microcomputer which does not have large range for real numbers, floating overflow always occurs when we applied Lanczos/ORTHODIR. Therefore, we proposed a new algorithm, named normalized Lanczos/ORTHODIR, which works in theory and in practice.

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# Lanczos 法解不可對稱化線性系統之應用

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## 摘 要

用理想的推廣共軛梯度 (IGCG) 法來解不可對稱化之大型線性系統  $Au=b$ ，常需要大量的電腦儲存空間和運算，我們加入一個假想系統而把 IGCG 法化簡導出 Lanczos 法之三種型態，在此三種程序中，Lanczos/ORTHODIR 最為可靠，可是却不適合用在迷你電腦或微電腦上，因為運算中往往發生浮點超限之現象，所以我們推導了正規化之 Lanczos/ORTHODIR 以達實際應用之目的。



# THE SOLUTION OF THE INITIAL VALUE PROBLEM FOR THE KORTEWEG-DE VRIES EQUATION

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## ABSTRACT

We use inverse scattering theory to find the solution of the initial value problem for the KdV equation  $u_t + 6uu_x + u_{xxx} = 0$ ,  $u = u(x, t)$ ,  $(-\infty < x, t < \infty)$ . This result was first proved by S. Tanaka; in this paper we give a different integration for deriving the Marchenko equations, from which the above result also can be obtained.

## I. INTRODUCTION

In this paper we will use inverse scattering theory to find the solution of the initial value problem for the Korteweg-de Vries (KdV) equation

$$u_t + 6uu_x + u_{xxx} = 0 \quad u = u(x, t) \quad (-\infty < x, t < \infty). \quad (1.1)$$

Gardner, Greene, Kruskal and Miura<sup>(3)</sup> have shown that the application of inverse scattering theory gives a guide to the explicit realization of the solution. Also, Tanaka<sup>(6)</sup> used inverse scattering theory, which was described in Faddeev's paper<sup>(2)</sup>, to construct general solutions of the initial value problem. Although we still use inverse scattering theory, we here give a different integration for deriving the Marchenko equations and many other types of equations. This alternative method was also used by Sattinger<sup>(5)</sup>.

In section 2, we describe results from the scattering theory of a one dimensional Schrödinger operator and derive the integral equations of inverse scattering theory. In section 3, we study the time dependence of scattering data and the existence of potential  $u(x, t)$ . Finally, we prove that  $u(x, t)$  satisfies the KdV equation.

## II. EVOLUTION OF THE SCATTERING DATA

The Schrödinger equation is given by

$$\psi_{xx} + (u + \lambda^2) \psi = 0 \quad -\infty < x < \infty \quad (2.1)$$

where  $\lambda$  is a complex number. We assume that the potential  $u(x)$  is a real differentiable function which satisfies the condition

$$\int_{-\infty}^{\infty} (1 + |x|) |u(x)| dx < \infty. \quad (2.2)$$

Let  $\psi_{\pm}(x, \lambda)$  be the unique solutions of equation (2.1) with the asymptotic behavior

$$\psi_{\pm}(x, \lambda) \sim e^{\pm i\lambda x} \quad \text{as } x \rightarrow \pm \infty.$$

For  $\lambda$  real we can write

$$\psi_- = a(\lambda) \bar{\psi}_+ + b(\lambda) \psi_+. \quad (2.3)$$

Moreover, we can solve for  $a(\lambda)$  and  $b(\lambda)$ , obtaining

$$a(\lambda) = \frac{W[\psi_-, \psi_+]}{W[\psi_+, \psi_+]}, \quad b(\lambda) = \frac{W[\psi_-, \bar{\psi}_+]}{W[\psi_+, \bar{\psi}_+]} \quad (2.4)$$

where  $W$  is the Wronskian,  $W[\psi_+, \bar{\psi}_+] = 2i\gamma$ , and

$$a(\lambda) = \frac{W[\psi_+, \psi_-]}{2i\lambda}, \quad b(\lambda) = \frac{W[\psi_-, \bar{\psi}_+]}{2i\lambda}.$$

Both of functions  $\psi_-$  and  $\psi_+$  have analytic continuations to the upper half plane, so  $a(\lambda)$  is analytic in  $\text{Im } \lambda > 0$ . At the zeros of  $a(\lambda)$ ,  $\psi_+$  and  $\psi_-$  are linearly dependent. Since  $\psi_+$  and  $\psi_-$  decay exponentially as  $x \rightarrow +\infty$  and  $x \rightarrow -\infty$ , the zeros of  $a(\lambda)$  are eigenvalues. At an eigenvalue  $\lambda = i\eta_j$ , we have

$$\psi_-(x, i\eta_j) = b_j \psi_+(x, i\eta_j), \quad j = 1, 2, \dots, N. \quad (2.5)$$

The constants  $b_j$  are parts of the scattering data needed to invert the scattering problem.

Now, we study the Fourier transform equations of  $\psi_{\pm}$  to obtain the Marchenko Integral equations of inverse scattering. See Sattin-ger<sup>(6)</sup>.

For real  $u$  we have  $\psi_-(x, \bar{\lambda}) = \bar{\psi}_-(x, \lambda)$ . Furthermore, for

real  $\lambda = \xi$ , we have  $\overline{\psi_+}(x, \xi) = \psi_+(x, -\xi)$ . Setting

$$\psi_+(x, \xi) = e^{i\xi x} \phi_+(x, \xi),$$

$\phi_+$  then satisfies

$$\phi_{+xx} + 2i\xi\phi_{+x} + u\phi_+ = 0, \quad \phi_+ \sim 1 \quad \text{as } x \rightarrow +\infty.$$

Similarly, let  $\overline{\psi_+} = e^{-i\xi x} \overline{\phi_+}(x, \xi)$  then  $\overline{\phi_+}$  satisfies

$$\overline{\phi_{+xx}} - 2i\xi\overline{\phi_{+x}} + u\overline{\phi_+} = 0, \quad \overline{\phi_+} \sim 1 \quad \text{as } x \rightarrow +\infty.$$

Hence  $\overline{\phi_+(x, \xi)} = \phi_+(x, -\xi)$ . By the uniqueness of the solutions, we obtain

$$\overline{\psi_+(x, \lambda)} = \psi_+(x, -\lambda).$$

Since  $e^{-i\lambda x} \psi_+(x, \lambda) - 1$  is an analytic function in  $\text{Im } \lambda > 0$  which tends to zero as  $\lambda \rightarrow \infty$ , its Fourier transform with respect to  $\lambda$  vanishes for  $s < 0$ . we thus obtain

$$e^{-i\lambda x} \psi_+ - 1 = \frac{1}{2\pi} \int_0^\infty e^{i\lambda s} K_+(x, s) ds. \quad (2.6)$$

For real  $\lambda = \xi$ , (2.6) becomes

$$\psi_+(x, \xi) = e^{i\xi x} + \frac{1}{2\pi} \int_0^\infty e^{i\xi(s+x)} K_+(x, s) ds.$$

If we replace  $s+x$  by  $s$ , we have

$$\psi_+(x, \xi) = e^{i\xi x} + \frac{1}{2\pi} \int_x^\infty e^{i\xi s} K_+(x, s-x) ds. \quad (2.7)$$

Setting

$$G_+(x, s) = \frac{1}{2\pi} K_+(x, s-x), \quad (2.8)$$

we obtain

$$\psi_+(x, \xi) = e^{i\xi x} + \int_x^\infty e^{i\xi s} G_+(x, s) ds \quad (2.9)$$

where  $G_+ = 0$  for  $s < x$ . It follows from  $\overline{\psi_+(x, \xi)} = \psi_+(x, -\xi)$  and  $\overline{\psi_+(x, \xi)} = e^{-i\xi x} + \int_x^\infty e^{-i\xi s} \overline{G_+(x, s)} ds$ , we have

$$\overline{G_+(x, s)} = G_+(x, s), \quad (2.10)$$

so

$$\overline{\psi_+(x, \xi)} = e^{-i\xi x} + \int_0^\infty e^{-i\xi s} G_+(x, s) ds.$$

If we replace  $s$  by  $-s$ , we obtain

$$\overline{\psi_+(x, \xi)} = e^{-i\xi x} + \int_{-\infty}^{-x} e^{i\xi s} G_+(x, -s) ds. \quad (2.11)$$

Since

$$\psi_-(x, \xi) = a(\xi) \overline{\psi_+(x, \xi)} + b(\xi) \psi_+(x, \xi)$$

and substitute (2.9) and (2.11) for  $\psi_+$  and  $\overline{\psi_+}$ ; we have

$$\begin{aligned} \frac{\psi_-(x, \xi)}{a(\xi)} - e^{-i\xi x} &= \int_{-\infty}^{-x} e^{i\xi s} G_+(x, -s) ds + \frac{b(\xi)}{a(\xi)} e^{i\xi x} \\ &\quad + \frac{b(\xi)}{a(\xi)} \int_0^\infty e^{i\xi s} G_+(x, s) ds. \end{aligned} \quad (2.12)$$

Taking Fourier transforms of (2.12), and letting

$$I_+(x, s) = \int_{-\infty}^\infty \left( \frac{\psi_-(x, \xi)}{a(\xi)} - e^{-i\xi x} \right) e^{-i\xi s} d\xi,$$

then by computing the residues at the poles  $\xi = i\eta_j$  and utilizing  $\psi_-(x, i\eta_j) = b_j \psi_+(x, i\eta_j)$ , we have

$$I_+(x, s) = 2\pi i \sum_{j=1}^N \frac{b_j(i\eta_j) e^{\eta_j s}}{a'(i\eta_j)} \psi_+(x, i\eta_j). \quad (2.13)$$

By applying (2.9) into the equation (2.13), we get

$$I_+(x, s) = B_+(s-x) + \int_0^\infty G_+(x, \tau) B_+(s-\tau) d\tau \quad s+x < 0 \quad (2.14)$$

where

$$B_+(y) = 2\pi i \sum_{j=1}^N \frac{b_j(i\eta_j)}{a'(i\eta_j)} e^{\eta_j y}. \quad (2.15)$$

The Fourier transform of  $(b(\xi)/a(\xi)) e^{i\xi x}$  is

$$C_+(s-x) = \int_{-\infty}^\infty \frac{b(\xi)}{a(\xi)} e^{-i\xi(s-x)} d\xi. \quad (2.16)$$

Also, the Fourier transform of  $\int_{-\infty}^{-x} e^{i\xi s} G_+(x, -s) ds$  becomes

$$\begin{cases} 0 & s+x > 0 \\ 2\pi G_+(x, -s) & s+x < 0. \end{cases} \quad (2.17)$$

Finally, the Fourier transform of  $b(\xi)/a(\xi) \int_{\omega}^{\infty} e^{i\xi s} G_+(x, s) ds$  is

$$\int_{\omega}^{\infty} C_+(s-\tau) G_+(x, \tau) d\tau. \quad (2.18)$$

Putting (2.14), (2.16), (2.17) and (2.18) together, we obtained

$$\begin{aligned} B_+(s-x) + \int_{\omega}^{\infty} G_+(x, \tau) B_+(s-\tau) d\tau \\ = 2H G_+(x, -s) + C_+(s-x) + \int_{\omega}^{\infty} C_+(s-\tau) G_+(x, \tau) d\tau \\ s+x < 0. \end{aligned}$$

If we replace  $s$  by  $-s$ , require  $s > x$ , and put

$$F_+(y) = \frac{1}{2\pi} [C_+(-y) - B_+(-y)],$$

then we can conclude that

$$G_+(x, s) + \int_{\omega}^{\infty} F_+(s+\tau) G_+(x, \tau) d\tau + F_+(s+x) = 0, \quad (2.19)$$

where

$$F_+(y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{b(\xi)}{a(\xi)} e^{i\xi y} d\xi - i \sum_{j=1}^N \frac{b_j(i\eta_j) e^{-\eta_j y}}{a'(i\eta_j)}.$$

Similarly, for the  $\psi_-(x, \xi)$ , we can obtain

$$\psi_-(x, \xi) = e^{-i\xi x} - \int_{\omega}^{-\infty} e^{i\xi s} G_-(x, s) ds,$$

and

$$G_-(x, s) - \int_{\omega}^{-\infty} F_-(s+\tau) G_-(x, \tau) d\tau + F_-(s+x) = 0$$

**Theorem 1.** Let  $G_{\pm}(x, s)$  be the kernel of the equation

$$\psi_{\pm}(x, \xi) = e^{\pm i\xi x} \pm \int_{\omega}^{\pm\infty} e^{i\xi s} G_{\pm}(x, s) ds. \quad (2.20)$$

Then  $G_{\pm}(x, s)$  satisfies the hyperbolic equation

$$G_{\pm xx}(x, s) - G_{\pm ss}(x, s) + u(x) G_{\pm}(x, s) = 0 \quad (2.21)$$

and

$$U_{\pm}(x) = 2 \frac{d}{dx} G_{\pm}(x, x). \quad (2.22)$$

**Proof.** We prove the equations (2.21) and (2.22) for  $G_+(x, s)$ . By substituting two times  $x$ -differentiations of (2.20) into the equation (2.1) for real  $\lambda = \xi$ , we then have

$$\begin{aligned} & \psi_{+xx} + (u + \xi^2) \psi_+ \\ &= \left[ -i\xi G_+(x, x) - \frac{d}{dx} G_+(x, x) - G_{+x}(x, x) + u(x) \right] e^{i\xi x} \\ & \quad + \int_{\infty}^{\infty} [G_{+xx}(x, s) + u G_+(x, s)] e^{i\xi s} ds \\ & \quad + \int_{\infty}^{\infty} \xi^2 G_+(x, s) e^{i\xi s} ds. \end{aligned} \quad (2.23)$$

Since

$$\int_{\infty}^{\infty} \xi^2 G_+(x, s) e^{i\xi s} ds = - \int_{\infty}^{\infty} \left( \frac{\partial^2}{\partial s^2} e^{i\xi s} \right) G_+(x, s) ds,$$

and utilizing integration by parts, we obtain

$$\begin{aligned} \int_{\infty}^{\infty} \xi^2 G_+(x, s) e^{i\xi s} ds &= i\xi G_+(x, x) e^{i\xi x} - G_{+s}(x, x) e^{i\xi x} \\ & \quad - \int_{\infty}^{\infty} G_{+ss}(x, s) e^{i\xi s} ds. \end{aligned} \quad (2.24)$$

Moreover, it follows from (2.23) and (2.24) that

$$\begin{aligned} 0 &= \psi_{+xx} + (u + \xi^2) \psi_+ \\ &= \left[ -2 \frac{d}{dx} G_+(x, x) + u(x) \right] e^{i\xi x} \\ & \quad + \int_{\infty}^{\infty} [G_{+xx}(x, s) - G_{+ss}(x, s) + u(x) G_+(x, s)] e^{i\xi s} ds. \end{aligned}$$

Since this must hold identically in  $\xi$ , the theorem thus follows.

### III. THE EXISTENCE OF POTENTIAL $u(x, t)$

The analytical properties of the reflection coefficient were studied by Tanaka<sup>(6)</sup>. We refer to <sup>(6)</sup> for details.

Set

$$F_{\pm}(x, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{b(\xi)}{a(\xi)} e^{\pm i\xi x \pm 8i\xi^3 t} d\xi - i \sum_{j=1}^N \frac{b_j(i\eta_j) e^{\mp \eta_j x \pm 8\eta_j^3 t}}{a'(i\eta_j)}, \quad (3.5)$$

then the Marchenko equation (2.19) is solvable for each  $t$ . Let  $G_{\pm}(x, s; t)$  be the solutions. Set

$$U_{\pm}(x, t) = 2 \frac{d}{dx} G_{\pm}(x, x; t). \quad (3.6)$$

It is easily to see that  $F_{\pm}$  satisfy the differential equations

$$\frac{\partial}{\partial t} F_{\pm}(x, t) + 8 \frac{\partial^3}{\partial x^3} F_{\pm}(x, t) = 0. \quad (3.7)$$

Differentiating the Marchenko equation (2.19) with respect to  $t$  and utilizing the differential equations (3.7), we get

$$G_{\pm t}(x, s; t) \pm \int_{\omega}^{\pm\infty} F_{\pm}(s + \tau, t) G_{\pm t}(x, \tau; t) d\tau + D_{\pm}(x, s; t) = 0 \quad (3.8)$$

where

$$D_{\pm}(x, s; t) = \mp \int_{\omega}^{\pm\infty} 8F_{\pm xxx}(s + \tau, t) G_{\pm}(x, \tau; t) d\tau - 8F_{\pm xxx}(s + x, t). \quad (3.9)$$

**Theorem 2.** The function  $u(x, t)$  in the formulas (3.6) satisfies the KdV equation.

**Proof.** Since

$$\frac{\partial L}{\partial t} = [B, L]$$

is equivalent to the KdV equation (1.1), if we can show that

$$(\partial_t - B) \psi_{\pm} = 4(\pm i\lambda)^3 \psi_{\pm}, \quad (3.4)$$

then differentiating  $L\psi_{\pm} = -\lambda^2 \psi_{\pm}$  with respect to  $t$  and applying (3.4), we obtain

$$\frac{\partial L}{\partial t} \psi_{\pm} = [B, L] \psi_{\pm},$$

in other words, we have

$$(u_t + 6uu_x + u_{xxx}) \psi_{\pm} = 0.$$

Let  $\psi = \psi_+$ , applying (2.21), (2.22) and integration by parts, (3.4) is equivalent to

$$\frac{d\psi}{dt} = \int_{-\infty}^{\infty} H(x, s; t) e^{i\lambda s} ds \quad (3.10)$$

where

$$\begin{aligned} H(x, s; t) = & -G_{xxx}(x, s; t) - 3G_{xss}(x, s; t) - 3G_{xss}(x, s; t) \\ & - G_{sss}(x, s; t) - 3u(x, t) G_x(x, s; t) \\ & - 3u(x, t) G_s(x, s; t). \end{aligned} \quad (3.11)$$

From (2.21), integration by parts, and differentiating the Marchenko equation (2.19), we can prove that  $H(x, s; t)$  satisfies the integral equation

$$H(x, s; t) + \int_{-\infty}^{\infty} F(s + \tau, t) H(x, \tau; t) d\tau + D(x, s; t) = 0. \quad (3.12)$$

The homogeneous equation associated with the Marchenko equation has only a trivial solution. Thus by (3.8) and (3.12), we can conclude that

$$G_t = H. \quad (3.13)$$

Differentiation of (2.9) with respect to  $t$  and (3.13) lead to equation (3.10).

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## KdV 方程式的初值問題之解

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### 摘 要

我們用反散佈理論找出 KdV 方程式  $u_t + 6uu_x + u_{xxx} = 0$  之初值問題的解。此為搭那卡 (Tanaka) 所得的結果。但在此文章中，我們採用相異的積分來求馬陳可 (Marchenko) 方程式，再由馬程可方程式來得到搭那卡的結果。



## NOTE ON CYLINDRICAL HELICES

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The fundamental theorem of space curves states that for 2 continuous functions  $f(s) \geq 0$  and  $g(s)$  in an interval  $I (\subseteq \mathbb{R})$  containing 0, and a given frame  $\{T_0, N_0, B_0\}$  at an arbitrary point  $p \in E^3$ , there exists a unique curve  $r(s)$  with  $f(s)$  as its curvature  $k$  and  $g(s)$  as its torsion  $\tau$  for every value of arc length  $s$  in  $(0 \in I' \subseteq) I$  with  $\{T_0, N_0 \in B_0\}$ ,  $\epsilon = 1$  or  $-1$ , as its Frenet frame at  $r(0) = p$ . But in practice, it is very complicated to solve such a problem, since it involves the solution of a Riccati differential equation.<sup>(1)</sup>

Here we give a simple form to treat such a problem for the curves of cylindrical helices by a 1st order homogeneous matrix DE with constant coefficients. Before discussing our theorem, we solve a matrix DE as follows<sup>(2)</sup>.

**Lemma.** Given a 1st order homogeneous matrix DE with constant coefficients,

$$\frac{dX}{dt} = AX, \quad X = \begin{pmatrix} X_1 \\ \vdots \\ X_n \end{pmatrix} \quad A = (a_{ij}), \quad 1 \leq i, j \leq n \quad (1)$$

with initial vector

$$X(0) = \begin{pmatrix} X_1(0) \\ \vdots \\ X_n(0) \end{pmatrix}, \quad t \in I \text{ \& } 0 \in I, \quad (2)$$

then there exists a unique solution  $X(t)$  of (1) satisfying (2) in an interval  $I' \subseteq I$  containing 0 such that

$$X(t) = R(X(0))f(t) \quad t \in I'. \quad (3)$$

where  $R$  is a constant matrix determined by  $X(0)$ , and  $f(t)$  is a column vector function consisting of  $n$  linearly independent particular solutions of a DE with character equation of  $A$ . In case

$X(t)$  takes the form

$$X(t) = \Phi(t)X(0) \quad t \in I, \quad (4)$$

then the fundamental matrix  $\Phi(t)$  of DE (1) has the expression

$$\Phi(t) = (R(e_1)f(t), \dots, R(e_n)f(t)), \quad (5)$$

$e_1, \dots, e_n$  being the natural coordinate column vectors and

$$R(e_i) = (e_i, Ae_i, \dots, A^{n-1}e_i)F^{-1}(0), \quad F = (f, f', \dots, f^{(n-1)}). \quad (6)$$

**Proof.** Since every  $x_i(t)$  ( $i = 1 \dots n$ ) in (1) can be expressed as the linear combination of  $n$  linearly independent particular solutions of a DE with characteristic equation of  $A^{(3)}$ , we have a solution of (1)  $\ni$  (2) as given in (3). By (1) we have

$$\frac{d^r X}{dt^r} = A^{r-1} X, \quad r = 1, 2, \dots, n-1. \quad (7)$$

Since  $R(X(0))f(t)$  satisfies (1), we get

$$R(X(0)) \frac{d^r f}{dt^r} = A^{r-1} R(X(0))f, \quad r = 1, 2, \dots, n. \quad (8)$$

or we may write (8) as

$$R(X(0))F(t) = (R(X(0))f(t), AR(X(0))f(t), \dots, A^{n-1}R(X(0))f(t)), \quad (9)$$

$$F(t) = (f(t), f'(t), \dots, f^{(n)}(t)).$$

It is known that  $R(X(0))f(0) = X(0)$ , hence we put  $t = 0$  in (9) to get

$$R(X(0)) = (X(0), AX(0), \dots, A^{n-1}X(0))F^{-1}(0). \quad (10)$$

(10) expresses that  $R(X(0))$  is a constant matrix determined by  $X(0)$ , ( $F$  being non-singular,  $F^{-1}(0)$  exists). Since  $X(t)$  has the expressions (3) and (4) with

$$R(X(0)) = R\left(\sum_{i=1}^n x_i(0) e_i\right) = \sum_{i=1}^n x_i(0) R(e_i), \quad (11)$$

hence

$$\begin{aligned}
 R(X(0))f(t) &= \sum_{i=1}^n x_i(0) R(e_i) f(t) \\
 &= (R(e_1) f(t), \dots, R(e_n) f(t)) \begin{pmatrix} x_1(0) \\ \vdots \\ x_n(0) \end{pmatrix} \\
 &= \Phi(t) X(0),
 \end{aligned} \tag{12}$$

which implies that

$$\Phi(t) = (R(e_1) f(t), \dots, R(e_n) f(t)),$$

as stated in (5), and

$$R(e_i) = (e_i, Ae_i, \dots, A^{n-1} e_i) F^{-1}(0).$$

obtained by replacing  $X(0)$  by  $e_i$  in (10).

**Theorem.** Given two continuous functions  $f(s) \geq 0$  and  $g(s)$  *s. t.*  $g(s)/f(s) = c$ , a constant,  $t \in I \subseteq \mathbb{R}$ , ( $0 \in I$ ), and a right handed frame  $\{T_0, N_0, B_0\}$  at  $P \in E^3$ . Then there exists a unique cylindrical helix  $r(s)$  with  $f(s)$  and  $g(s)$  as its curvature  $k$  and torsion  $\tau$  respectively, and  $s$  as its arc length with Frenet frames fitting  $\{T_0, N_0, B_0\}$  at  $p = r(0)$ ,  $s \in I' \subseteq I$ .

**Proof.** Let  $\{T, N, B\}$  be a the Frenet frame field fitting the initial frame at  $r(0) = P$ ,  $0 \in I$ . Consider a differentiable function  $t(s)$  satisfying

$$\frac{dt}{ds} = k(s) \quad s \in I, \tag{13}$$

or

$$t(s) = \int_0^s k(u) du, \quad s \in I' \subseteq I, \quad t \in I''. \tag{14}$$

By the Frenet formulae and (13),

$$\left. \begin{aligned}
 \frac{dT}{ds} &= kN = k \frac{dT}{dt} \\
 \frac{dN}{ds} &= -kT + \tau B = k \frac{dN}{dt} \\
 \frac{dB}{ds} &= -\tau N = k \frac{dB}{dt}
 \end{aligned} \right\} \tag{15}$$

i. e., since  $\tau/k = c$ , (15) becomes

$$\left. \begin{aligned} \frac{dT}{dt} &= N \\ \frac{dN}{dt} &= -T + cB \\ \frac{dB}{ds} &= -cN \end{aligned} \right\} \quad (16)$$

or

$$\frac{d}{dt} \begin{pmatrix} T \\ N \\ B \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & c \\ 0 & -c & 0 \end{pmatrix} \begin{pmatrix} T \\ N \\ B \end{pmatrix}, \quad t \in I'' \quad (17)$$

a homogeneous 1st order matrix DE with constant coefficients and the initial frame  $\{T_0, N_0, B_0\}$  at  $r(0) = p$ . Let

$$A = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & c \\ 0 & -c & 0 \end{pmatrix} \quad (18)$$

then the characteristic equation

$$\begin{aligned} f(\lambda) &= |A - \lambda I| = \begin{vmatrix} -\lambda & 1 & 0 \\ -1 & -\lambda & c \\ 0 & -c & -\lambda \end{vmatrix} \\ &= -\lambda(\lambda^2 + 1 + c^2) = 0 \end{aligned} \quad (19)$$

of  $A$  gives 3 characteristic roots  $0, bi$  and  $-bi$ ,  $b = \sqrt{1 + c^2}$ .

Thus, the solution of (17) satisfying the initial frame  $\{T_0, N_0, B_0\}$  at  $r(0) = p$ , obtained by applying the equation (4) of the above lemma 3 times to the 3 column DE of  $d/dt \begin{pmatrix} T \\ N \\ B \end{pmatrix}$ , can be written as

$$\begin{pmatrix} T \\ N \\ B \end{pmatrix} = \Phi(t) \begin{pmatrix} T_0 \\ N_0 \\ B_0 \end{pmatrix} \quad (20)$$

Since  $f(t) = \begin{pmatrix} 1 & & \\ & e^{bit} & \\ & & e^{-bit} \end{pmatrix}$  for matrix  $A$ , the Wronskian matrix  $F(t)$

of  $f(t)$  is

$$F(t) = \begin{pmatrix} 1 & 0 & 0 \\ e^{bit} & bie^{bit} & -b^2 e^{bit} \\ e^{-bit} & -bie^{-bit} & -b^2 e^{-bit} \end{pmatrix}, \text{ hence}$$

$$F(0) = \begin{pmatrix} 1 & 0 & 0 \\ 1 & bi & -b^2 \\ 1 & -bi & -b^2 \end{pmatrix}$$

and

$$F^{-1}(0) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{2bi} & -\frac{1}{2bi} \\ \frac{1}{b^2} & -\frac{1}{2b^2} & -\frac{1}{2b^2} \end{pmatrix}.$$

By computation,

$$\begin{aligned} R(e_1) f(t) &= \begin{pmatrix} \frac{c^2}{b^2} & \frac{1}{2b^2} & \frac{1}{2b^2} \\ 0 & -\frac{1}{2bi} & \frac{1}{2bi} \\ \frac{c}{b^2} & -\frac{c}{2b^2} & -\frac{c}{2b^2} \end{pmatrix} \begin{pmatrix} 1 \\ e^{bit} \\ e^{-bit} \end{pmatrix} \\ &= \begin{pmatrix} \frac{c^2}{b^2} + \frac{\cos bt}{b^2} \\ -\frac{\sin bt}{b} \\ \frac{c}{b^2} - \frac{c \cos bt}{b^2} \end{pmatrix}, \end{aligned} \tag{21}$$

$$\begin{aligned} R(e_2) f(t) &= \begin{pmatrix} 0 & \frac{1}{2bi} & -\frac{1}{2bi} \\ 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & -\frac{c}{2bi} & \frac{c}{2bi} \end{pmatrix} \begin{pmatrix} 1 \\ e^{bit} \\ e^{-bit} \end{pmatrix} \\ &= \begin{pmatrix} \frac{\sin bt}{b} \\ \cos bt \\ -\frac{c \sin bt}{b} \end{pmatrix}, \end{aligned} \tag{22}$$

$$\begin{aligned}
 R(e_3) f(t) &= \begin{pmatrix} \frac{c}{b^2} & -\frac{c}{2b^2} & -\frac{c}{2b^2} \\ 0 & \frac{c}{2bi} & -\frac{c}{2bi} \\ \frac{1}{b^2} & \frac{c^2}{2b^2} & \frac{c^2}{2b^2} \end{pmatrix} \begin{pmatrix} 1 \\ e^{bit} \\ e^{-bit} \end{pmatrix} \\
 &= \begin{pmatrix} \frac{c}{b^2} - \frac{c \cos bt}{b^2} \\ \frac{c}{b} \sin bt \\ \frac{1}{b^2} + \frac{c^2 \cos bt}{b^2} \end{pmatrix}, \tag{23}
 \end{aligned}$$

thus

$$\Phi(t) = \begin{pmatrix} \frac{c^2}{b^2} + \frac{\cos bt}{b^2} & \frac{\sin bt}{b} & \frac{c}{b^2} - \frac{c \cos bt}{b^2} \\ -\frac{\sin bt}{b} & \cos bt & \frac{c}{b} \sin bt \\ \frac{c}{b^2} - \frac{c \cos bt}{b^2} & -\frac{c \sin bt}{b} & \frac{1}{b^2} + \frac{c^2 \cos bt}{b^2} \end{pmatrix}. \tag{24}$$

(20) and (24) imply

$$\begin{aligned}
 \frac{dr}{ds} = T &= \left( \frac{c^2}{b^2} + \frac{\cos bt}{b^2} \right) T_0 + \frac{\sin bt}{b} N_0 \\
 &+ \left( \frac{c}{b^2} - \frac{c}{b^2} \cos bt \right) B_0, \quad b = \sqrt{1 + c^2}. \tag{25}
 \end{aligned}$$

Integrating, we have

$$\begin{aligned}
 r(s) &= \left( \frac{c^2}{1 + c^2} s + \frac{1}{1 + c^2} \int_0^s \cos \sqrt{1 + c^2} t \, du \right) T_0 \\
 &+ \left( \frac{1}{\sqrt{1 + c^2}} \int_0^s \sin \sqrt{1 + c^2} t \, du \right) N_0 \\
 &+ \left( \frac{cs}{1 + c^2} - \frac{c}{1 + c^2} \int_0^s \cos \sqrt{1 + c^2} t \, du \right) B_0, \\
 t &= \int_0^s f(u) \, du, \quad s \in I', \quad o \in I', \tag{26}
 \end{aligned}$$

which is the required unique cylindrical helix with the most general form.

In the case of plane curves, we may regard them as special

cases of (26) with  $c = 0$ , hence we easily get the known form as in the following.

**Corollary.** Given a continuous function  $k(s)$  in  $I$  with initial frame  $\{T_0, N_0\}$  at  $p$ , then the plane curve with  $k(s)$  as its curvature function and  $s$  as its arc length, fitting the initial frame at  $r(0) = p$ , can be given as

$$r(s) = \left( \int_0^s \cos t \, dt \right) T_0 + \left( \int_0^s \sin t \, dt \right) N_0,$$
$$\frac{dt}{ds} = k(s), \quad s \in I' \subseteq I, \quad 0 \in I'. \quad (27)$$

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# 一般螺線的求法

顏 一 清

## 摘 要

若一曲線的曲率  $k$  與撓率  $\tau$  成一定比  $c$ ，則我們可以用一階常數微分方程組解出這個曲線（稱為一般螺線或是定傾曲線）的一般式。

如果已知一階常數矩陣微分方程式的解法，則此篇可算是最簡易的求一般螺線的方法。

# 用電腦連線分析層析儀輸出之波形— 比較各種波峯偏離值之求法

化 學 系

陳 天 鐸      陳 壽 椿

## 前 言

管柱 (column) 的退化與否, 對色層分析 (chromatography) 實驗結果有很大的影響, 而判斷管柱的好壞可以用波峯 (peak) 的形狀來做判斷<sup>(1)</sup>。在相同條件下, 如果使用中的管柱所跑出來的波峯和新買時所跑的形狀不一樣, 則表示管柱有了問題, 表示分離管柱需要再生或換新管柱了。

判斷波峯的形狀的方法很多, 不過以往多用經驗或目視法來判斷, 無法論及客觀和精確度。以下列舉幾種計算方法, 並將儀器所輸出的類比資料經過類比/數值轉換 (A/D conversion) 輸入電腦, 並做資料的分析和處理, 提高了客觀性及精確度。

本文中利用金屬錯鹽作為波峯研究的對象, 是因為金屬錯鹽在 HPLC 管柱中, 尤其在管柱是金屬材質時, 常有分叉的現象<sup>(2)</sup>。尤其在管柱使用一段時間後, 很快就發生波峯有偏離正態之現象, 在實際分析工作上造很多問題。如果平常用電腦來作波形 (peak shape) 之分析就可作追蹤和評估。本文中之波形分析方法亦可推廣至其他色層分析系統。

## 理 論

### (一) 波峯的形狀

1. 對稱性 (symmetry): 如圖 1, 為一對稱的波峯 (高斯波峯 Gaussian peak)<sup>(3)</sup>, 其中  $\sigma_z$  標準差 (standard deviation)。

$$\sigma_z = \sqrt{\frac{\sum(X - M)^2}{N}}$$

X: 數列的值  
M: 數列的算術平均數  
N: 項數

$y = 0.607 h$  時的寬度

$e = 2.71828$  自然對數底

$w$ : 以兩反曲點作切線交於底線 (Base line) 之兩點的寬度

$h$ : 波峯的高度

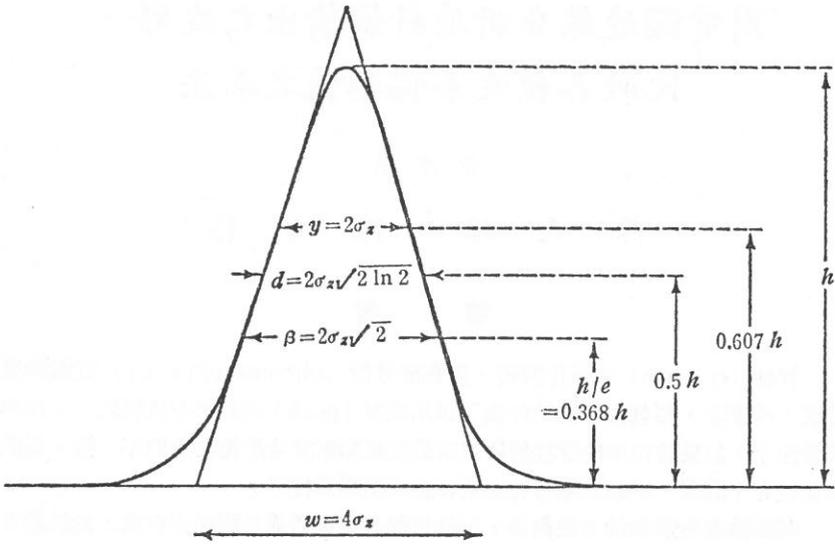


圖 1. 對稱的波峯， $\sigma_z$  為標準差。

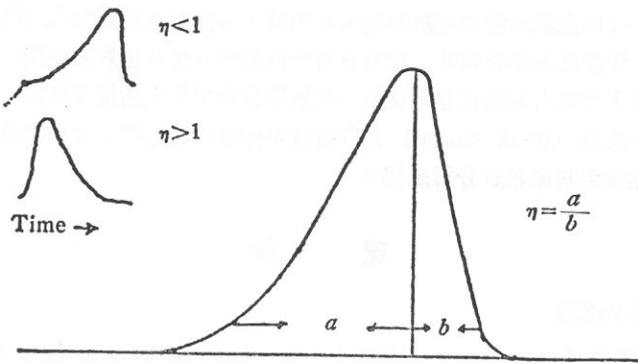


圖 2. 非對稱的波峯，偏態值為  $\eta = a/b$ 。

2. 非對稱性 (asymmetry)：如圖 2，為一非對稱的波峯，其中  $\eta$  為偏態值 (skewness)<sup>(4)</sup>。

$$\eta = a/b$$

$\eta > 1$  稱為前伸峯 (fronting peak)

$\eta < 1$  稱為拖尾峯 (tailing peak)

(二) 計算的方法

1.  $f/g$ :  $\langle i \rangle$  如圖 3 所示,  $f$  為波峯起點之切線到滯留時間 (retention time) 的距離。 $g$  為波峯終點之切線到滯留時間的距離。

$f/g = 1$  為對稱峯 (normal)

$f/g > 1$  為前伸峯 (fronting)

$f/g < 1$  為拖尾峯 (tailing)

此法用於不對稱的波峯為宜, 但必須底線的斜率趨近於零,  $f/g$  值才可靠, 否則如圖 3 所示, 當  $f/g=1$  時, 不一定是一個對稱的波峯。

$\langle ii \rangle$  如圖 3 所示, 亦可取  $f'/g'$  值, 當底線斜率趨近於零時,  $f'/g' = f/g$ , 故可簡化電腦的運算時間。

2. 偏態值 (skewness): 利用波峯不同高度的寬度比值  $\eta = a/b$ ,  $a$  為左半寬,  $b$  為右半寬 (如圖 2 所示)。

$\langle i \rangle$  半寬高度的比, 即  $0.607 h$  處的  $\eta$  值<sup>(4)</sup>。

$\eta = 1$  時為對稱峯 (normal)

$\eta > 1$  時為前伸峯 (fronting)

$\eta < 1$  時為拖尾峯 (tailing)

此法用於對稱波峯為宜, 若處理不對稱的波峯時, 取  $10\% h$  處的  $\eta$  值為宜。

$\langle ii \rangle$   $10\% h$ , 計算  $\eta = a/b$  值。當波峯的起點和終點不明確時用偏態值的方法為宜。

3. 第一動差法 (first moment):  $skew = (m_1 - t_r) / \sigma_z$ , 利用第一動差和滯留時間的差除以標準差<sup>(5)</sup>。

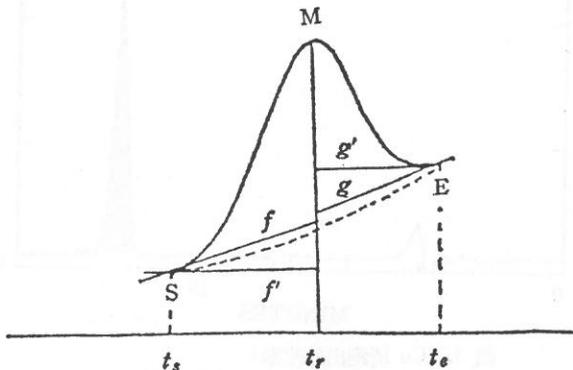


圖 3.  $f/g$  法的圖解。

$m_1$  : 第一動差 (first moment)

$$m_1 = \frac{\sum_{t=1}^n y_i t_i \Delta t}{\sum_{t=1}^n y_i \Delta t}$$

$y_i, t_i$  表點的高度和時間

$(y_i, t_i)$  表波峯的起點之高度和時間

$(y_n, t_n)$  表波峯的終點之高度和時間

$\Delta t$  表切割的時間

$t_r$  表波峯最高點的時間

$\sigma_z$  表標準差 (standard deviation)

此法不論對稱或不對稱的波峯皆可以使用，而偏態值通常在  $\pm 1$  之間。

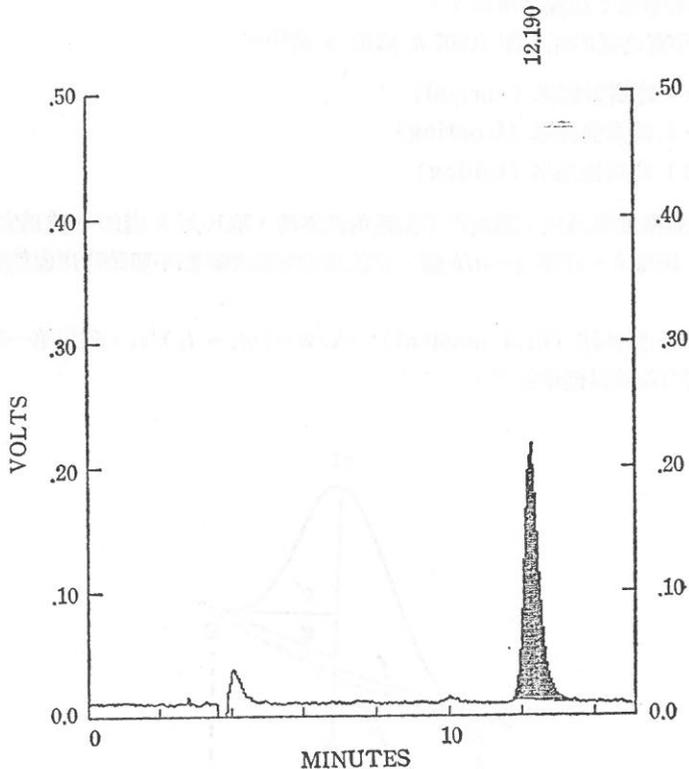


圖 4. Co 所跑出的波峯。

Solvent: 26% H<sub>2</sub>O in MeOH

Flow Rate: 1.0 ml/min

- skew = 0 為對稱峯 (normal)
- skew > 0 為拖尾峯 (tailing)
- skew < 0 為前伸峯 (fronting)

一般在統計學上，用愈高級的動差來表示波峯的偏態較靈敏而且正確。但若是偶數級的動差，無法表示出波峯的正負偏態，只能算出偏態的程度而已。如用四級動差計算波峯的偏態，雖比三級動差法靈敏，但却無法表示出波峯的正負偏態了。所以跳過二級動差法而介紹三級動差法。

4. 三級動差法 (third moment):  $\pi_3 = m_3/\sigma_z^3$  (1)

$m_3$  表三級動差， 
$$m_3 = \frac{\sum_{i=1}^n y_i (t_i - m_1)^3 \Delta t}{\sum_{i=1}^n y_i \Delta t}$$

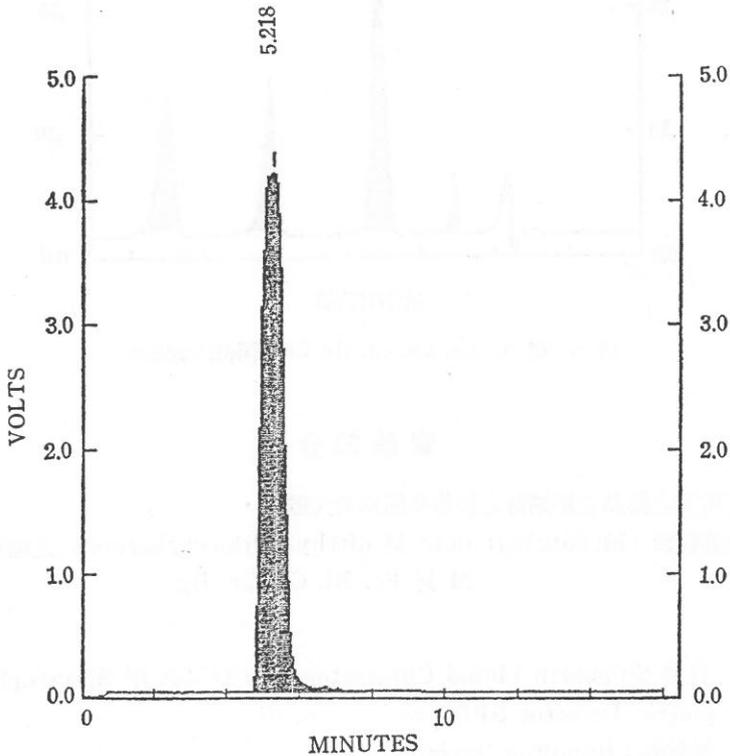


圖 5. Benzene 所跑出的波峯。  
 Solvent: H<sub>2</sub>O/CH<sub>3</sub>OH/CH<sub>3</sub>CN  
 33:37:30  
 Volume: 10  $\mu$ l

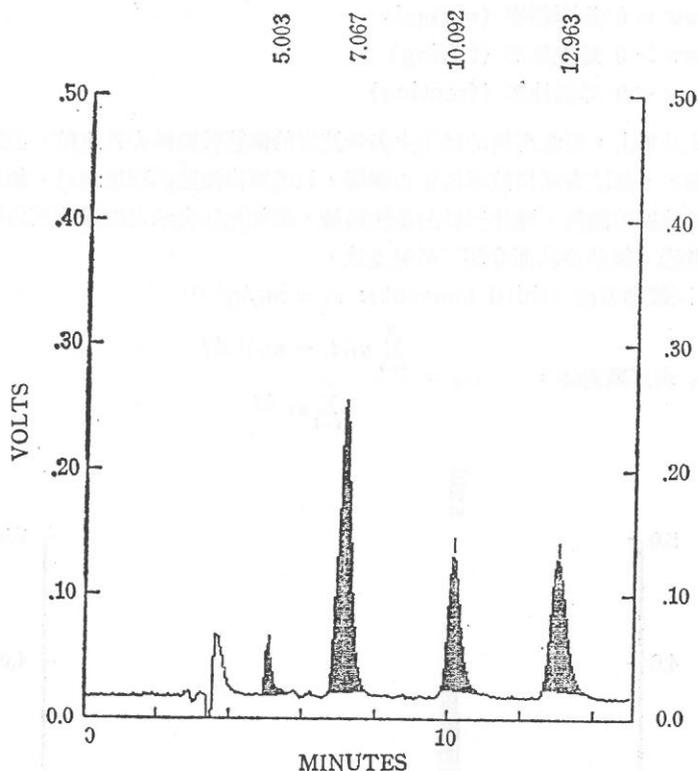


圖 6. 為 Ni, Co, Cu, Cr, Hg Cd 所跑出的波峯。

### 實驗部分

藥品：所需之樣品金屬錯鹽之製備參照參考文獻<sup>(2)</sup>，

金屬錯鹽 (M(ddtc)*n*)：ddtc 為 diethyl dithiocarbamate 之縮寫。

M 為 Fe, Ni, Co, Cr, Hg。

儀器：

1. 日製 Shimadzu Liquid Chromatograph LC-3A 附 Spectrophotometric Detector SPD-1。
2. 注射器：Hamilton Syringe 50  $\mu$ l。
3. 8 位元電腦：CPU 6502, 192K RAM

16 頻道 12 位元類比/數值轉換器。

Appligratation II 色層分析資料處理套裝軟體。

表 1. Peak Detection Results

PK #	ID #	Stirt Time (Min)	End Time (Min)	Ret Time (Min)	$f/g$	Peak Area (Volts-Min)	Area %	Peak Hght (Volts)	SKEWMT1 (BL/4)	SKEWMT2 (60.7%)	Peak Type	Peak Name	SKEWab1 10%	SKEWab2 60.7%
1	1	11.703	13.310	12.190	0.435	0.0936	100.000	0.1962	00.5665	00.5169	B B		00.69	01.03 TN
Totals						0.0936	100.000	0.196						

Note: Offscale peaks not included in percent calculations.

表 2. Peak Detection Results

PK #	ID #	Stirt Time (Min)	End Time (Min)	Ret Time (Min)	$f/g$	Peak Area (Volts-Min)	Area %	Peak Hght (Volts)	SKEWMT1 (BL/4)	SKEWMT2 (60.7%)	Peak Type	Peak Name	SKEWab1 10%	SKEWab2 60.7%
1	1	4.668	9.147	5.218	0.140	2.8140	100.000	4.1554	00.6388	00.4573	B B		00.99	01.52 HF
Totals						2.8140	100.000	4.155						

Note: Offscale peaks not included in percent calculations.

表 3. Peak Detection Results

PK #	ID #	Stirt Time (Min)	End Time (Min)	Ret Time (Min)	$f/g$	Peak Area (Volts-Min)	Area %	Peak Hght (Volts)	SKEWMT1 (BL/4)	SKEWMT2 (60.7%)	Peak Type	Peak Name	SKEWab1 10%	SKEWab2 60.7%
1	1	4.830	5.508	5.003	0.343	0.0097	5.284	0.0418	01.5784	01.4059	B B		00.48	01.20 TF
2	2	6.663	7.638	7.067	0.706	0.0847	45.904	0.2306	00.1806	00.1873	B B		00.90	01.00 TN
3	3	9.763	10.750	10.092	0.499	0.0414	22.424	0.1085	00.5848	00.5330	B B		00.70	01.02 TN
4	4	12.572	13.702	12.963	0.530	0.0487	26.389	0.1058	00.5606	00.4726	B B		00.67	01.00 TN
Totals						0.1845	100.000	0.487						

Note: Offscale peaks not included in percent calculations.

### 實驗步驟

金屬錯鹽之製備參照游朝晴論文中之方法。取金屬錯鹽 0.02~0.1  $\mu\text{g}$  溶於氯仿中配成錯鹽氯仿溶液打入液相層析儀中，經 HPLC 之分離後，由紫外光檢出器傳出信號透過 A/D 轉換器直接與上述電腦連線，然後由電腦的 Appligran II 軟體處理基本資料，再由本文中所提之波峰偏離程式計算。

### 結果與討論

由表 3 和表 4 可看出用 SKEWMT1 所求出的偏態值較其他方法的靈敏度為高，表 4 是實驗三以第二個波峯為標準，所求得的百分誤差值(%)。此處我們較有興趣的是 SKEWMT1 和 SKEWMT2 的  $\sigma_z$  值取法：

$\sigma_B$ ：SKEWMT1 的標準差，如圖 1 所示， $\sigma_B$  為波峯的兩反曲點作切線，交於底線寬度的四分之一。

$\sigma_h$ ：SKEWMT2 的標準差，如圖 1 所示， $\sigma_h$  為 0.607  $h$  處的寬度的一半<sup>(6)</sup>，若無法正確的找出底線，則用  $\sigma_h$  較好。

表 5 為實驗三所用的  $\sigma_B$  和  $\sigma_h$ ，取第二個波峯為標準，所求的百分誤差(%)。從表 4 和表 5 可以看出以上所用的方法，以 SKEWMT1 較為靈敏精確，這一點在以前就為科學家所承認，但是當時電腦昂貴，無法普及一般實驗室<sup>(3,7)</sup>，

表 4. 以實驗三(圖六)的第二個波峯為標準，求各法的百分誤差

PK	$f/g$	SKEWMT1	SKEWMT2	SKEWab1	SKEWab2
01	-21.306%	1,206.028%	1,017.804%	-51.724%	17%
02	—	—	—	—	—
03	10.398%	22.167%	8.404%	-21.839%	3%
04	-61.300%	65.880%	35.808%	-26.437%	-1%

表 5. 實驗三中  $\sigma_B$ ,  $\sigma_h$  的百分誤差

PK	SKEWMT1	SKEWMT2
01	-46.507%	-37.500%
02	—	—
03	0.381%	13.125%
04	12.066%	36.875%

另外用此法計算時，電腦需時較長，所以許多儀器製造商都用  $a/b$  法或  $f/g$  法速度較快。但是絕大多數的儀器之電腦不具備這種功能。

### 結 語

實驗室自動化已是潮流所趨了，利用電腦的快速運算，不但可提高儀器的功能，而且可得到更可靠的實驗結果。本次的實驗正是一個很好例子，把以往只是用理論來作的研究，付諸於電腦來實現理論的真實性，故實驗室自動化將是今後的一大趨向。

### 誌 謝

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## On-line Microcomputer Analysis of Chromatographic Peak Shape—A Comparison of Several Popular Calculation Methods

TIAN-DOW CHEN and SHOW-CHUEN CHEN

### ABSTRACT

Several popular methods to determine chromatographic peak asymmetry—often a good indicator of chromatographic column performance—were compared using an on-line 8-bit microcomputer. The shew ratio calculated based on the first statistical moment provided the most sensitive indicator, while the widely practiced calculation based on  $f/g$  ratio, with moderate sensitivity to peak asymmetry, had the advantage of fast computing speed.

# STEREOSELECTIVE SYNTHESIS OF THE SEX PHEROMONE OF *HELIOTHIS ARMIGERA*

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Department of Chemistry

## ABSTRACT

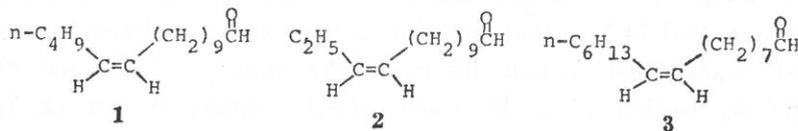
The three most probable components of the sex pheromone of *Heliothis armigera*, (*Z*)-11-hexadecenal (1), (*Z*)-11-tetradecenal (2) and (*Z*)-9-hexadecenal (3), have been stereoselectively synthesized from readily available starting materials.

## INTRODUCTION

*Heliothis armigera* (Hübner) is a polyphagous insect widespread in Asia, Africa, Europe, America and Australia<sup>(10)</sup>. The moths are among the most devastating pest insects infesting a wide range of crops such as cotton, corn, tomatoes, peanuts, soybeans, sorghum, tobacco, cabbage and lettuce<sup>(12)</sup>. The excessive use of insecticides for pest control has caused severe pollutions to the environment. Thus, the sex pheromones have in recent years found use not only in monitoring the insect populations in fields, but also in techniques such as mass trapping and mating disruption<sup>(7)</sup>. A component of the sex pheromone of *Heliothis armigera* was first identified by Piccardi *et al* in 1977 as (*Z*)-11-hexadecenal. This aldehyde was also found attractive to the male moths in the fields in Sudan<sup>(19)</sup>. Rothschild reported in 1978 that addition of 2% (*Z*)-9-tetradecenal to the (*Z*)-11-hexadecenal further increased the efficacy of the lure<sup>(20)</sup>. However, Gothilf *et al* identified (*Z*)-11-hexadecenal and (*Z*)-11-tetradecenal as the sex attractants, but these two compounds had no synergistic effect<sup>(8)</sup>. The effectiveness of (*Z*)-11-hexadecenal and (*Z*)-11-tetradecenal in attracting the male moths has been tested with two types of releasing devices-rubber dispensers and dental rolls. It has also been shown that (*Z*)-9-tetradecenal did not increase

the luring efficacy<sup>(9)</sup>. Nesbitt *et al* reported in 1979 that besides (*Z*)-11-hexadecenal and (*Z*)-11-hexadecen-1-ol there was a third component, (*Z*)-9-hexadecenal, which was found only in some of the moths of Malawi origin<sup>(16)</sup>. Kehat *et al* demonstrated that (*Z*)-11-hexadecenal and (*Z*)-9-hexadecenal in a ratio of 9:1 was more attractive to males than the virgin females, but this effect was observed only when rubber dispensers were used to release the lure<sup>(13)</sup>. Nesbitt *et al* subsequently confirmed the presence of (*Z*)-9-hexadecenal as a minor component of the female sex pheromone<sup>(17)</sup>. Sattar-Zade *et al* reported in 1980 that a mixture of (*Z*)-11-hexadecenal and (*Z*)-11-tetradecenal in a ratio of 3:1 was more effective than the virgin females in luring the male moths<sup>(21)</sup>.

From the above results it can be seen that the sex pheromones of *Heliothis armigera* may vary with the regions where these species are found, but that the three most probable components are (*Z*)-11-hexadecenal (**1**), (*Z*)-11-tetradecenal (**2**) and (*Z*)-9-hexadecenal (**3**). We decided to synthesize these three compounds so that their luring efficacy could be tested in the laboratory and in fields. (*Z*)-9-Hexadecenal (**3**) has been synthesized from methyl palmitoleate which was very expensive<sup>(12)</sup>. Piccardi's synthesis of (*Z*)-11-hexadecenal (**1**) also required a very special starting material<sup>(19)</sup>. Bestmann *et al* synthesized both (*Z*)-11-hexadecenal (**1**) and (*Z*)-11-tetradecenal (**2**) from vaccenyl acetate, but this starting material was, unfortunately, rather difficult to obtain<sup>(5)</sup>. Here we report our stereoselective synthesis of these three compounds from readily available starting materials. Compounds **1** and **2** have a common intermediate.

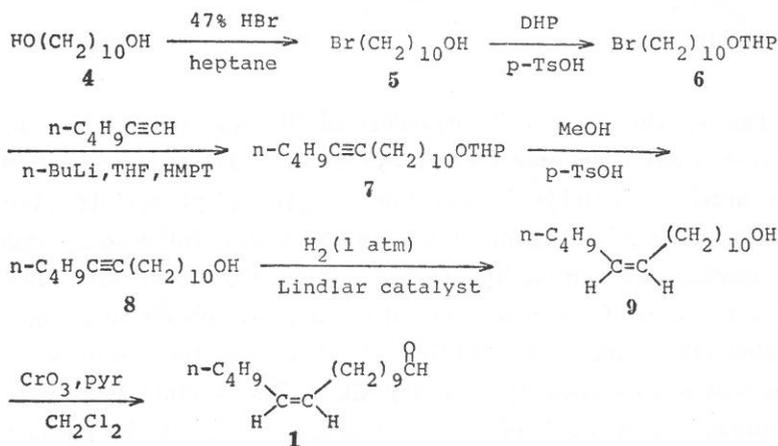


## RESULTS AND DISCUSSION

The synthesis of (*Z*)-11-hexadecenal (**1**) is shown in **Scheme I**. Treatment of 1,10-decanediol (**4**) with 47% aqueous hydrobromic

acid in hot heptane in a continuous extractor gave the monobrominated product, 10-bromo-1-decanol (**5**)<sup>(6)</sup>. The alcohol functional group was then protected as its tetrahydropyranyl ether **6** using dihydropyran and a catalytic amount of *p*-toluenesulfonic acid<sup>(2)</sup>. Further reaction of compound **6** with 1-hexynyllithium generated *in situ* from 1-hexyne and *n*-butyllithium gave the substitution product **7**<sup>(22)</sup>. The alcohol protective group was then removed by acid-catalyzed solvolysis to give 11-hexadecyn-1-ol (**8**)<sup>(2)</sup>. Selective *cis*-hydrogenation of alkyne **8** in a Parr apparatus using Lindlar catalyst<sup>(15)</sup> poisoned with synthetic quinoline gave (*Z*)-11-hexadecen-1-ol (**9**)<sup>(6)</sup>. The stereoselectivity of this reaction was >99% as shown by GC/MS. However, if quinoline was omitted in this reaction the product **9** was contaminated with some fully saturated alcohol. Finally, alcohol **9** was oxidized by Collins' reagent to give the desired product, (*Z*)-11-hexadecenal (**1**)<sup>(6)</sup>. The purity of this compound was confirmed by comparing the GC/MS data with an authentic sample from Zoecon Corporation.

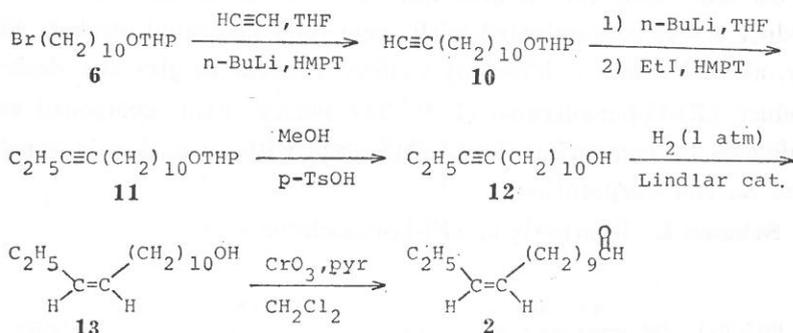
**Scheme I.** Synthesis of (*Z*)-11-hexadecenal (**1**)



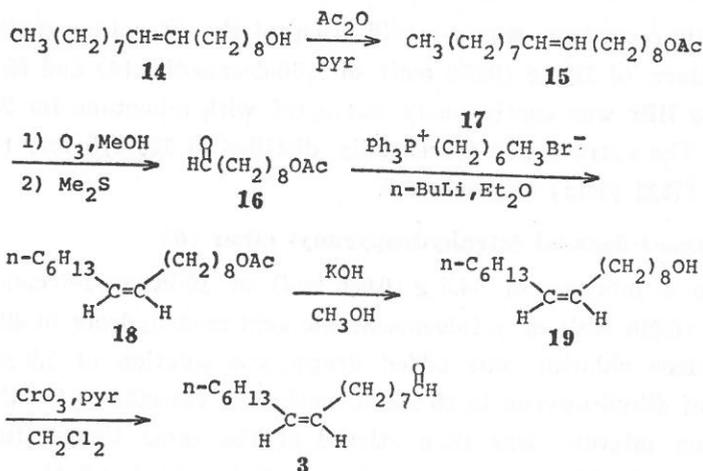
The synthesis of (*Z*)-11-tetradecenal (**2**) (**Scheme II**) utilized the same intermediate, 10-bromo-1-decanol tetrahydropyranyl ether (**6**), as that for (*Z*)-11-hexadecenal (**1**). Treatment of compound **6**

with lithium acetylide generated *in situ* from acetylene and *n*-butyllithium gave the substitution product **10**<sup>(1)</sup>. Further reaction with *n*-butyllithium and then with ethyl iodide gave the disubstituted alkyne **11**<sup>(22)</sup>. Acid-catalyzed solvolysis of compound **11** removed the alcohol protective group to give 11-tetradecyn-1-ol (**12**)<sup>(2)</sup>. Catalytic hydrogenation under conditions stated above yielded (*Z*)-11-tetradecen-1-ol (**13**)<sup>(44)</sup>. Selective oxidation with Collins' reagent then provided the desired product, (*Z*)-11-tetradecenal (**2**)<sup>(5)</sup>. The purity of compound **2** was confirmed by comparing its GC/MS spectrum with that of an authentic sample from Zoecon Corporation.

**Scheme II.** Synthesis of (*Z*)-11-tetradecenal (**2**)



The synthesis of (*Z*)-9-hexadecenal (**3**) was carried out by a different route (**Scheme III**). Oleyl alcohol (**14**) was first reacted with acetic anhydride in pyridine to give oleyl acetate (**15**)<sup>(8)</sup>. Ozonolysis<sup>(18)</sup> in methanol at low temperatures followed by reductive workup with dimethyl sulfide gave 9-acetoxynonanal (**16**)<sup>(9)</sup>. Wittig reaction of compound **16** with *n*-heptyltriphenylphosphonium bromide (**17**)<sup>(4)</sup> and *n*-butyllithium in ether gave the alkene **18** (*cis*:*trans* = 94:6 as shown by capillary GC). The acetate **18** was then hydrolyzed to alcohol **19**<sup>(4)</sup> by potassium hydroxide in methanol. Finally, oxidation of **19** with Collins' reagent gave (*Z*)-9-hexadecenal (**3**)<sup>(13)</sup> which was purified by silver nitrate-impregnated preparative TLC. Its purity was confirmed by comparing the GC/MS spectrum with that of an authentic sample from Zoecon Corporation.

**Scheme III.** Synthesis of (*Z*)-9-hexadecenal (**3**)

In summary, we have synthesized (*Z*)-11-hexadecenal (**1**), (*Z*)-11-tetradecenal (**2**) and (*Z*)-9-hexadecenal (**3**), which are the three most probable components of the sex pheromone of *Heliothis armigera*, from readily available starting materials. These three compounds have also been subjected to simple bioassay. The male moths showed strong response to (*Z*)-11-hexadecenal (**1**) and weaker response to (*Z*)-11-tetradecenal (**2**) and (*Z*)-9-hexadecenal (**3**), individually. Different combinations of these compounds will also be tested both in the laboratory and in the field for their luring efficiency.

**EXPERIMENTAL**

Infrared spectra were recorded on a Beckmann Acculab TM 1 grating spectrometer. The proton NMR spectra were recorded on a Varian EM 360 L spectrometer. Tetramethylsilane (TMS) was used as an internal standard. The NMR absorptions are recorded as  $\delta$  values in *ppm*. Multiplicities are indicated by *s*=singlet, *d*=doublet, *t*=triplet, *q*=quartet, and *m*=multiplet. Oleyl alcohol (**14**) and 1,10-decanediol (**4**) were obtained from E. Merck AG., and were used without purification. Tetrahydrofuran and diethyl ether were purified by first refluxing with lithium aluminum hydride for four hours and then distilled under nitrogen.

**10-Bromo-1-decanol (5)**

This procedure was a modification of the literature method<sup>(6)</sup>. A mixture of 13.9 g (0.079 mol) of 1,10-decanediol (4) and 80 ml of 47% aq HBr was continuously extracted with *n*-heptane for 24 h at 65°C. The extract was fractionally distilled at 110°C/5 torr to give 15.1 g (79% yield) of product 5.

**10-Bromo-1-decanol tetrahydropyranyl ether (6)**

To a mixture of 14.5 g (0.066 mol) of 10-bromo-1-decanol and 0.02 g (0.010 mol) of *p*-toluenesulfonic acid monohydrate in 40 ml of methylene chloride was added dropwise a solution of 1.5 g (0.017 mol) of dihydropyran in 20 ml of methylene chloride at 5–7°C. This reaction mixture was then stirred at the same temperature for another 3 h. The solvent was removed *in vacuo* and the residue then taken up in 150 ml of ether. The ethereal solution was washed with saturated sodium bicarbonate solution and brine, and was then dried. Evaporation of the solvent yielded 4.4 g of a crude product which was chromatographed on silica gel using hexane-ethyl acetate (19:1) as the eluent to give 4.33 g of compound 6 (98% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.58 (*m*, 1H), 3.49 (*m*, 6H), 1.30 (*m*, 22H).

**11-Hexadecyn-1-ol tetrahydropyranyl ether (7)**

To a solution of 0.33 g (4.0 mmol) of 1-hexyne in 10 ml of dry THF was added under nitrogen 2.35 ml (3.7 mmol) of *n*-butyllithium while keeping the temperature at –10°C for 30 min. The slurry of 1-lithio-1-hexyne was added with a syringe to a solution of compound 6 (0.55 g, 1.7 mmol) in 13 ml of HMPT. The reaction mixture was kept at 0°C for 3 h and was then poured into a large volume of ice water. After extraction twice with hexane, the organic layer was washed with water and brine, and was dried. Evaporation of the solvent gave 0.60 g of a crude product. A flash chromatography afforded 0.51 g of compound 7 (93% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.56 (*m*, 1H), 3.49 (*m*, 4H), 2.08 (*m*, 4H), 1.30 (*m*, 26H), 0.89 (*t*, 3H).

**11-Hexadecyn-1-ol (8)**

A mixture of 2.30 g (7.14 mmol) of compound 7 and 0.13 g (0.68

*mmol*) of *p*-toluenesulfonic acid monohydrate in 80 ml of methanol was stirred at room temperature for 1 h. Evaporation of the solvent gave 0.68 g of a crude product. A flash chromatography gave 1.46 g (85% yield) of the desired product 8.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.62 (*t*, 2H), 2.13 (*t*, 4H), 1.33 (*m*, 20H), 0.89 (*t*, 3H).

#### (*Z*)-11-Hexadecen-1-ol (9)

A mixture of 0.89 g (3.7 *mmol*) of compound 8, 0.1 g of Lindlar catalyst (Aldrich Chemical Co.), 0.1 ml of synthetic quinoline and 20 ml of hexane was reacted with hydrogen (1 atm) in a Parr shaker. After filtration, extraction and column chromatography, 0.67 g (75% yield) of compound 9 was obtained.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  5.40 (*m*, 2H), 3.59 (*t*, 2H), 2.10 (*m*, 4H), 1.30 (*m*, 21H), 0.89 (*t*, 3H); mass spectrum *m/e* 222 ( $\text{M}^+ - 18$ ).

#### (*Z*)-11-Hexadecenal (1)

To a mixture of 0.79 g (9.8 *mmol*) of pyridine and 10 ml of methylene chloride was added under nitrogen 0.49 g (4.9 *mmol*) of chromium trioxide. After stirring at *rt* for 15 min, a solution of 0.2 g (0.83 *mmol*) of compound 9 in 2 ml of methylene chloride was added in one portion. The mixture was stirred at *rt* for 30 min and the solution was decanted. The residue was washed with 100 ml of ether. The combined organic solution was washed with 50 ml (three times) of 5% *aq* sodium hydroxide, 100 ml of 5% *aq* hydrochloric acid, 100 ml of 5% sodium bicarbonate solution, 100 ml of brine, and was dried over *anh* magnesium sulfate. Evaporation of the solvent yielded 0.17 g of a crude product. After a flash column chromatography and a silver nitrate-impregnated preparative TLC, 0.13 g (70% yield) of compound 1 was obtained.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) 9.78 (*t*, 1H), 5.29 (*m*, 2H), 2.18 (*m*, 4H), 1.18 (*m*, 20H), 0.89 (*t*, 3H); mass spectrum, *m/e* 238 ( $\text{M}^+$ ), 220 ( $\text{M}^+ - 18$ ); IR (neat) 2,740, 1,730  $\text{cm}^{-1}$ .

#### 11-Dodecyn-1-ol tetrahydropyranyl ether (10)

A stream of purified acetylene was passed through a solution of 2.4 ml (3.8 *mmol*) of *n*-butyllithium (1.6 N in hexane) in 10 ml of dry THF while keeping the temperature at 0°C. After the reaction

was completed the lithium acetylde generated was added with a syringe to a solution of 0.57 g (1.7 mmol) of compound **6** in 10 ml of HMPT at 0°C. The reaction mixture was stirred at 0°C for 3 h and was worked up as the procedure for compound **7**. The crude product was chromatographed to give 0.36 g (76% yield) of compound **10**. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.59 (m, 1H), 3.51 (m, 4H), 2.1 (m, 2H), 1.88 (t, 1H), 1.28 (m, 22H).

#### **11-Tetradecyn-1-ol tetrahydropyranyl ether (11)**

To a solution of 1.33 g (5.0 mmol) of compound **10** in 10 ml of THF was added 3.75 ml (12.8 mmol) of *n*-butyllithium (1.6 N in hexane) while keeping the temperature at -10°C. After 30 min a solution of 1 ml (12 mmol) of ethyl iodide in 10 ml of HMPT was added to the reaction mixture. The solution was stirred at 0°C for 3 h and was then worked up as before to give 1.3 g (88% yield) of compound **11**. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.59 (m, 1H), 3.51 (m, 4H), 3.09 (m, 4H), 1.28 (m, 22H), 0.88 (t, 3H).

#### **11-Tetradecyn-1-ol (12)**

In a procedure similar to that for the preparation of compound **8**, 0.3 g (1 mmol) of compound **11** was hydrolyzed to give 0.22 g (85% yield) of product **12**. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.59 (t, 2H), 2.03 (m, 4H), 1.26 (s, 17H), 0.86 (t, 3H).

#### **(Z)-11-Tetradecen-1-ol (13)**

In a procedure similar to that for the preparation of compound **9**, 0.2 g (0.9 mmol) of compound **12** was hydrogenated to give 0.15 g (75% yield) of product **13**. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 5.31 (m, 2H), 3.62 (t, 2H), 2.01 (m, 4H), 1.30 (m, 17H), 0.95 (t, 3H).

#### **(Z)-11-Tetradecenal (2)**

In a procedure similar to that for the preparation of compound **1**, 0.17 g (0.83 mmol) of compound **13** was oxidized to give 0.11 g (54% yield) of product **2**. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 9.78 (t, 1H), 5.30 (m, 2H), 2.38 (m, 4H), 1.29 (m, 16H), 0.91 (t, 3H); mass spectrum *m/e* 210 (M<sup>+</sup>), 192 (M<sup>+</sup>-18); IR (neat) 2,740, 1,733 cm<sup>-1</sup>.

**Oleyl acetate (15)**

A mixture of 4.8 ml (50 mmol) of acetic anhydride, 13.4 g (50 mmol) of oleyl alcohol (14) and 3.4 ml (60 mmol) of pyridine was refluxed for one hour. After cooling the reaction mixture was poured into 40 ml of 2 N sulfuric acid. The solution was extracted with ether, and the combined organic solution was washed with cold saturated sodium bicarbonate, water and brine, and was dried. Distillation, after evaporation of the solvent, afforded 12.4 g (80% yield) of oleyl acetate (15) (b. p. 158°C/0.15 torr). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 5.23 (m, 2H), 3.93 (t, 2H), 1.93 (s, 3H), 1.26 (m, 28H), 0.89 (t, 3H); IR (neat) 1,740, 1,240 cm<sup>-1</sup>.

**9-Acetoxynonanal (16)**

A solution of 23.0 g (74.1 mmol) of oleyl acetate (15) in 150 ml of methanol was cooled to 0°C. When the reaction was complete, 8 ml (0.11 mol) of dimethyl sulfide was added at -60°C. The solution was then stirred at -10°C for 1 h, then at ice bath temperature for another hour and finally at *rt* for one more hour. The solvent was removed and the residue was extracted with ether. The ether solution was washed with water, dried, and evaporated. The residue was distilled at 120°C/0.15 torr to afford 9.0 g (60% yield) of the desired product 16. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 9.74 (t, 1H), 4.0 (t, 2H), 2.0 (s, 3H), 1.3 (m, 12H); IR (neat) 2,735, 1,725, 1,240 cm<sup>-1</sup>.

***n*-Heptyltriphenylphosphonium bromide (17)**

A solution of 9.16 g (35 mmol) of triphenylphosphine and 6.26 g (35 mmol) of 1-bromoheptane in 50 ml of xylene was heated at reflux for 8 h. The mixture was cooled at *rt* and the supernatant was decanted off. The residual oil was mixed with 50 ml of ether, whereupon the resulting pasty mass solidified after standing for several hours at *rt*. The solid was triturated several times with ether and dried *in vacuo* over phosphorus pentoxide to afford 9.08 g (59% yield) of product 17, m. p. 170-171°C.

**(*Z*)-9-Hexadecenyl acetate (18)**

To a solution of 4.41 g (10 mmol) of compound 17 in 20 ml of

dry ether under nitrogen was added 7 ml (11.2 mmol) of *n*-butyllithium (1.6 N in hexane). This mixture was stirred at 10°C for 1 h, and a solution of 1.7 g (8.5 mmol) of compound **16** in 3 ml of dry ether was then added at 10°C over a period of 10 min. After stirring for additional 20 min the reaction mixture was poured into 100 ml of water. The aqueous layer was extracted with ether. The ether layers were combined and washed with brine, dried with anhydrous sodium sulfate. After evaporation of the solvent 1.8 g of a crude product was obtained. A flash chromatography afforded 1.6 g (70% yield) of compound **18**. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 5.31 (*m*, 2H), 4.0 (*t*, 2H), 2.0 (*s*, 3H), 1.28 (*m*, 20H), 0.88 (*t*, 3H).

#### **(Z)-9-Hexadecen-1-ol (19)**

A mixture of 0.05 g of potassium hydroxide and 0.17 g (0.6 mmol) of compound **18** in 10 ml of methanol was heated at reflux for 3 h. This was poured into water, and the aqueous layer was extracted with ether. The combined organic solution was washed with water and brine, and was dried. After evaporation of the solvent 0.17 g of a crude product was obtained. A flash column chromatography afforded 0.09 g (63% yield) of product **19**. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 5.3 (*m*, 2H), 3.59 (*t*, 2H), 2.0 (*m*, 4H), 1.28 (*m*, 20H), 0.88 (*t*, 3H); mass spectrum *m/e* 222 (M<sup>+</sup>-18).

#### **(Z)-9-Hexadecenal (3)**

In a procedure similar to that for the preparation of compound **1**, 0.2 g (0.83 mmol) of compound **19** was oxidized to give 0.12 g (60% yield) of compound **3**. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 9.8 (*t*, 1H), 5.3 (*t*, 2H), 2.3 (*m*, 4H), 1.29 (*m*, 20H), 0.89 (*t*, 3H); mass spectrum *m/e* 238 (M<sup>+</sup>), 220 (M<sup>+</sup>-18); IR (neat) 2,725, 1,730 cm<sup>-1</sup>.

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## 蕃茄夜蛾性費洛蒙之合成

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### 摘 要

蕃茄夜蛾性費洛蒙最可能的三種成份，(順)-11-十六烯醛 (1)，(順)-11-十四烯醛 (2) 與 (順)-9-十六烯醛 (3)，已成功地在此實驗室合成。

**Key words:** *Heliothis armigera*, sex pheromone, synthesis, (Z)-11-hexadecenal, (Z)-11-tetradecenal, (Z)-9-hexadecenal.

# 輔仁大學空氣懸浮粒子之分析與鑑定

化學系

李偉平 朱謙嵩 溫馥華 賴劍書

## 甲、序 言

輔仁大學位居新莊各型工廠林立之處，大學校門前交通頻繁，且附近亦有不少農田施放驅蟲及殺蟲劑，加上數處私用垃圾焚燒場地，致使輔大人深受空氣污染之害。

本計劃由收集空氣中之懸浮粒子開始，分成重金屬及有機碳氫化合物兩部份進行分析。重金屬部份是利用原子吸收光譜儀去測定，所測出的數種重金屬中，以鉛之含量較高，多由汽油而來。碳氫化合物部份則利用液體管路層析法 (Liquid Column Chromatography), HPLC, GC 及 GC/MS 去鑑定。其中酞酸酯類之化合物含量最多，此類物質多由垃圾焚燒爐而來。樣品之純化及分離亦在討論的範圍內。

## 乙、實驗過程

### 1. 採樣

空氣中之懸浮粒子係以高速空氣集塵器 (Hi-vel sampler, General Metal Work, GMWL-2000)，放置 8"×10" 之玻璃纖維濾紙 (Research Appliance Company)，以 40 C.F.M. (Cubic feet per minute) 的流量所抽取的，採樣時間為 24~48 小時。採樣地點見圖 1。純屬隨意採樣。濾紙在採樣前後均須乾燥一天，以除去水份。乾燥後樣品之分析流程圖見圖 2。所收集的懸浮粒子重量在 0.3955 克至 0.6638 克之間。

### 2. 重金屬之分析

剪取整張濾紙之  $\frac{1}{6}$ ，放入蒸發皿中，加 20 ml 的  $\text{HClO}_4 / \text{HNO}_3$  混合液 (10 ml  $\text{HClO}_4 + 90$  ml  $\text{HNO}_3$ )，加熱消化至生成白煙。當皿中溶液僅剩 5 ml 時，再加入 20 ml  $\text{HNO}_3$  作二度消化，繼續加熱至溶液僅剩 5 ml 為止，即可把熱源移開，使溶液冷卻。然後以去離子水稀釋至 250 ml<sup>(1)</sup>。利用原子吸收光譜儀 (Atomic Absorption Spectroscopy, AA) 在 217.0 nm 測鉛的吸光度，228.8 nm 測鎘的吸光度，248.3 nm 測鐵的吸光度，324.7 nm 測銅的吸光度。表 1 為這四種金屬之標準溶液的空白試驗結果。表 2 則為這四種重金屬在不同樣品溶液中之吸光度，可由此換算出溶液中重金屬的濃度。

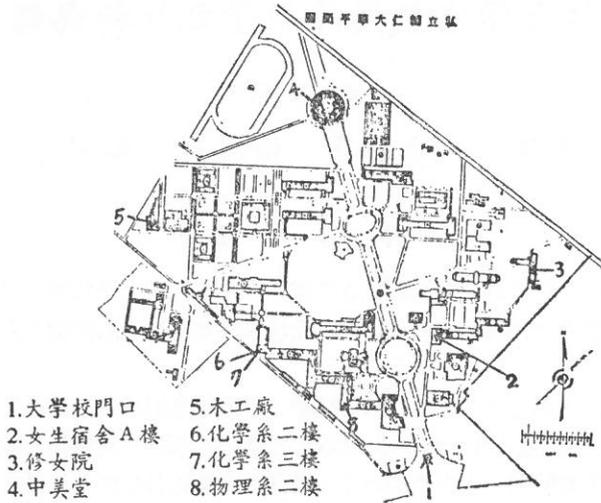


圖 1. 採樣地點圖

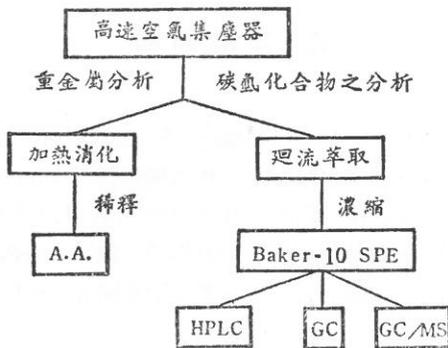


圖 2. 樣品分析流程圖

表 1. 重金屬標準溶液之吸光度

	Pb	Cd	Cu	Fe
濃度 (ppm)	20	2	5	5
吸光度	0.180	0.333	0.225	0.138
波長 (nm)	217.0	228.8	324.7	248.3

表 2. 樣品溶液中重金屬之吸光度

採樣地點	日期	天氣	吸光度			
			Pb	Cd	Cu	Fe
化學系二樓	84.12.4	雨	0.19	0.04	0.01	3.04
	85.3.25	晴	6.36	0.04	0.31	11.96
	85.7.12	晴	0.110	0.325	0.020	0.194
化學系三樓	84.11.28	晴	1.28	0.01	0.041	5.54
	85.5.11	晴	2.15	0.02	0.011	6.24
校門口	85.3.20	雨	0.69	0.00	0.011	4.35
	85.7.15	晴	0.105	0.328	0.022	0.261
中美堂	85.4.30	晴	1.64	0.01	0.021	14.29
	85.7.17	晴	0.106	0.324	0.037	0.327
修院	84.12.14	晴	1.82	0.01	0.021	7.05
	85.7.19	陰	0.100	0.329	0.015	0.244
木工廠	85.4.30	晴	0.79	0.00	0.001	4.19
	85.7.23	雨	0.101	0.326	0.052	0.253
物理系二樓	84.12.12	晴	0.48	0.03	0.011	4.47
女生宿舍	84.12.19	陰	0.08	0.01	0.001	1.55

### 3. 碳氫化合物之分析

(1)前處理：另取  $\frac{1}{8}$  的濾紙，剪成片狀，放入圓底磨口瓶內，以 80 ml 環己烷 (Merck, HPLC Grade) 為溶劑，迴流 6~8 小時後，在室溫下，以真空旋轉蒸發器 (EYELA, N-1) 濃縮至 5 ml。把濃縮後之萃取液置入 'Baker'-10 SPE (J. T. Baker Chemical Co.) 系統中的矽膠可廢棄管 (Silica gel disposable column) 內，以環己烷當沖提液，在減壓的密閉系統內使之達到分離與純化的效果。分離出來的物質可直接應用在 HPLC, GC 及 GC/MS 上，不需再經過其它過濾的手續。若溶液之濃度太低，可以氮氣濃縮後再注射入各分析儀器內。

(2)標準化合物：分為直鍊碳氫化合物及多苯環碳氫化合物 (Polynuclear Aromatic Hydrocarbon, PAH) 兩種，前者為  $C_7-C_{26}$  (TCI, Tokyo, Japan) 而 PAH 則為行政院衛生署環境保護局所提供。這些化合物各以甲苯或環己烷為溶劑，配製成 40-44 ppm 的溶液。所有的標準化合物及樣品萃取液均分別放入深棕色及有 Teflon 瓶蓋的瓶子內，並保存於 4°C 的冰箱內。

(3) HPLC: 經過 'Baker'-10 SPE 處理後之樣品萃取液, 可直接注射入島津 (Shimadzu) LC-3A 型的 HPLC 內, 所用之分光光譜檢示器 (Spectrophotometric Detector) 為島津 SPD-1 型。波長調在 254 nm。Du Pont 製之 Zorbax-ODS 管 (25 cm × 4.6 mm i. d.) 作析離用。其動相之組成為氟甲烷/水(80/20), 各溶劑均需事先過濾及去氣。沖提條件為等容系統 (isocratic mode); 沖提時間為 35 分鐘, 沖提速率為 0.9 ml/min; 圖表速率為 2.5 mm/min; 壓力為 200 kg/cm<sup>2</sup>; 注射體積為 10  $\mu$ l。

(4) GC: 在本實驗中所採用的 GC 為 Varian 3700 型, 外接 HP 3390 A 之積分器 (Integrator), 作為處理數據之用。檢示器為 FID (Flame Ionization Detector)。所用之管柱為長八呎, 外徑為 1/8 吋的不銹鋼管。充填物質為 3% Dexsil 300 GC on Chromosorb W-AW, 100/120 Mesh, MAOT = 400°C。攜帶氣體為氮氣, 其流速為 30 ml/min。每次分析的操作條件如下: 起始溫度 140°C, 四分鐘後以 8°C/min 的速率增溫直到 300°C 為止, 在 300°C 停留半小時以便趕出管內雜質。注射口之溫度為 230°C; 檢示器則為 300°C。範圍 (Range) 為  $1 \times 10^{-10}$  Amp/MV; 減弱調整刻度 (Attenuator) 為 1。所用之注射器屬氣閉式 (Gas-Tight Syringe, Hamilton, Australia); 注射體積為 1  $\mu$ l。

(5) GC/MS: 此部份係委託清華大學貴重分析儀器中心代為操作。其質譜儀為 Jeol, JMS-D-100 型。採電子游離法 (Electron Ionization, EI)。Vacuum 為  $2 \times 10^{-7}$  torr, 而樣品壓力 (Sample pressure) 則為  $6 \times 10^{-6}$  torr。游離電流為 300  $\mu$ A; 游離能 12 eV。Scanning 的範圍由  $m/e=50$  至  $m/e=400$ 。

## 丙、結果與討論

### 1. 重金屬

因限於不同波長之光源種類, 故只測定了樣品中之鉛、鎘、銅與鐵四種重金屬之吸光度而已。由於吸光度與離子濃度成正比例, 故可由此關係換算出溶液中離子的濃度。

一般而言, 大氣中之鉛微粒來自含鉛之汽油, 而鎘、銅與鐵則來自電鍍廠, 合金, 電池及油漆工廠等。此類物質吸入人體後, 容易造成對呼吸道之傷害<sup>(1)</sup>。由表 2 的結果可以看出在同一地點所採取之樣品會因採樣時間之不同及氣候之改變而影響其中重金屬含量之多寡。特別是在七月期間 (暑假) 所採的樣品中各物質之量均有顯著下降的情形, 因為在此段時間內, 往來學生數目大大減少, 交通量亦因而降低之故。

## 2. 碳氫化合物

### (1) HPLC :

①標準物質：多苯環碳氫化合物之標準物共計十種（表3），其中 Naphthalene（萘）及 Anthracene（蒽）之溶劑為環己烷，而其它則以甲苯為溶劑，各自配製成 40-44 ppm 之溶液，後再稀釋為 10 ppm。先測定每一標準物質之滯留時間（retention time），再將彼等混合，以相同條件注入 HPLC 內，得出結果如圖3。B[a]P (O=C1C=CC(=O)C=C1)；B[e]P (O=C1C=CC(=O)C=C1) 及 Perylene (O=C1C=CC(=O)C=C1) 三者為五苯環類；若比較這些化合物之單獨及混合溶液的HPLC圖，則可知 B[e]P 及 Perylene 無法互相析離。對四苯環類中之 Chrysene

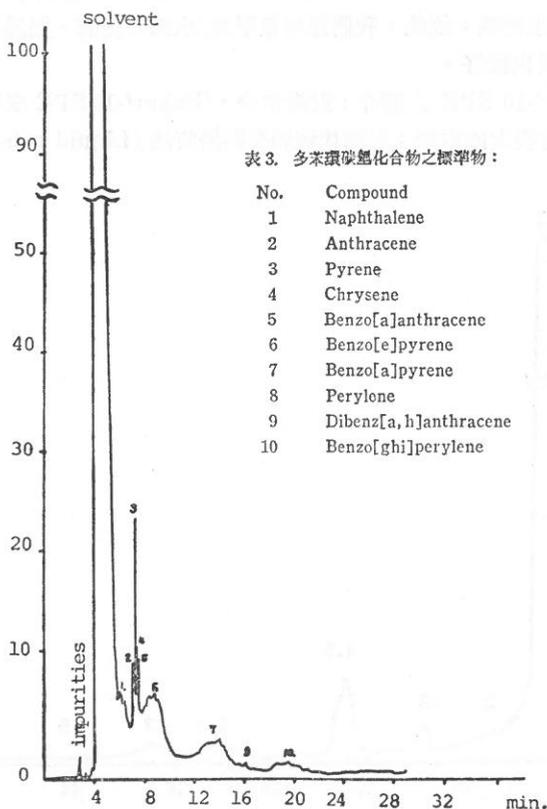


圖 3. 多苯環碳氫化合物混合標準液之 HPLC 圖（氫甲烷 / 水為沖提液），圖中號碼所代表之化合物如表(三)。

(O=C1OC2OC3OC4OC5OC6OC7OC8OC9OC10OC23456789, 蒽) 及 Benzo[a]anthracene (O=C1OC2OC3OC4OC5OC6OC7OC8OC9OC10OC2345678) 而言, 亦有同樣的情形發生。因此在十個標準物的混合溶液中, 只出現了八個尖峯; Benzo[ghi]Perylene (O=C1OC2OC3OC4OC5OC6OC7OC8OC9OC10OC11OC12OC13OC14OC15OC16OC17OC18OC19OC20OC12345678910111213141516171819) 是最後出來的一個化合物。Das 與 Thomas 亦提出某些多苯環碳氫化合物在 HPLC 上會有尖峯重疊而不能互相析離的結果<sup>(2)</sup>。他們使用氟甲烷/水 (82/18) 為沖提系統, 所用的是紫外光檢示器。

②沖提液的選擇: 以相同的沖提條件 (沖提速率 0.9 ml/min, 壓力 200 kg/cm<sup>2</sup>), 把沖提液由氟甲烷改為甲醇, 結果發現沖提時間增長許多 (比較圖 4 與圖 3)。Benzo[ghi]perylene 在以氟甲烷/水為沖提液時, 只需 18 分鐘即可析離出來; 但在使用甲醇/水的沖提系統中, 則需 50 分鐘。此外, 蒽的尖峯超過最大的刻度; Chrysene 及 Benzo[a]anthracene, Benzo[e]pyrene 及 Perylene 亦不能互相析離。故此, 我們採用氟甲烷/水為沖提液, 因為不單沖提時間縮短, 析離效果也較好。

③ 'Baker'-10 SPE 之簡介: 近幾年來, 'Baker'-10 SPE 在微量樣品的分離及純化方面有很大的貢獻; 可取代液體管路層析法 (Liquid column chroma-

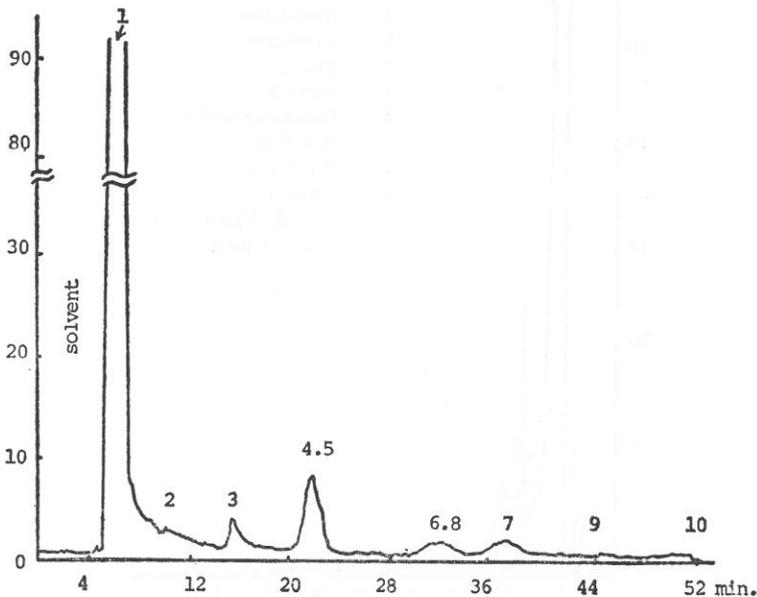


圖 4. 多苯環碳氫化合物混合標準液之 HPLC 圖 (甲醇 / 水為沖提液), 圖中號碼所代表之化合物如表(三)。

tography)。整個過程是以類似抽氣過濾的方法做快速的分離。管子內之靜相物質可依分離物質之不同性質而作適當的選擇<sup>(3)</sup>。它在生化及環境污染上有很大的用處。

在本實驗中，曾以同一樣品分別利用液體管路層析法及 'Baker'-10 SPE 分離法作一比較，由 HPLC 的結果可以看出在前者的洗出液中，混合物之分離效果沒有 'Baker'-10 SPE 的高。故全部分離過程均採 'Baker'-10 SPE 法。

④樣品的鑑定：圖 5 所示為七月所採樣品之 HPLC 圖。在圖 5(a) 中加了 10 ppm 之萘及 10 ppm 之蔥。

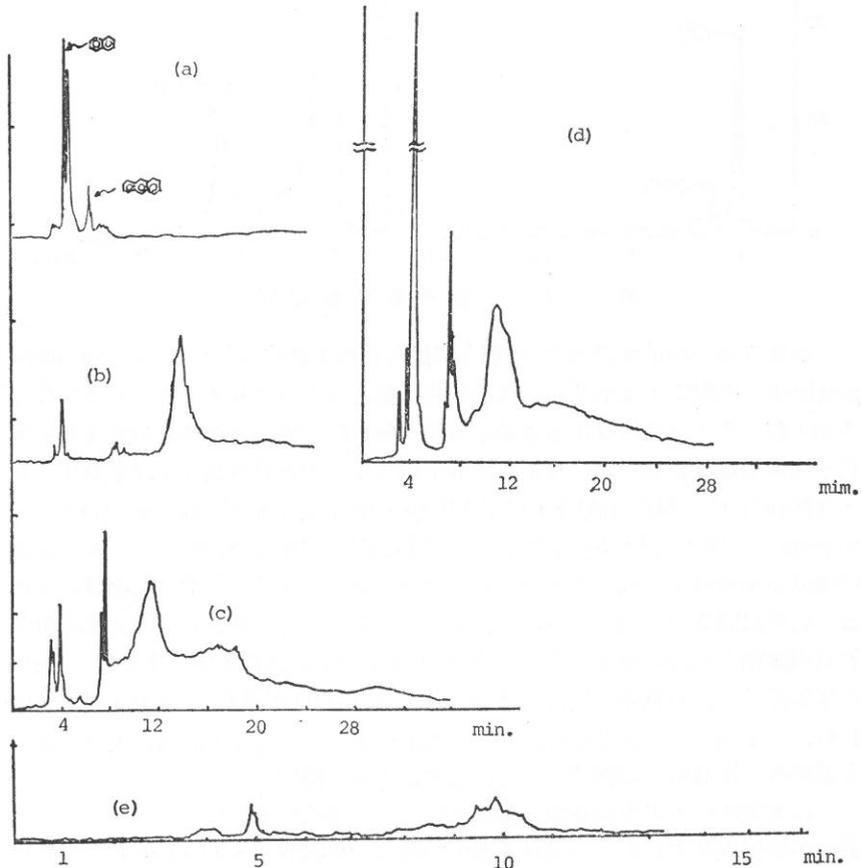


圖 5. 不同地點樣品之 HPLC 圖，依序為：(a) 木工廠，(b) 修女院，(c) 化學系系館二樓，(d) 校門口及 (e) 中美堂。

(a)~(d) 之圖表速率為 2.5 mm/min，(e) 圖則為 10 mm/min。

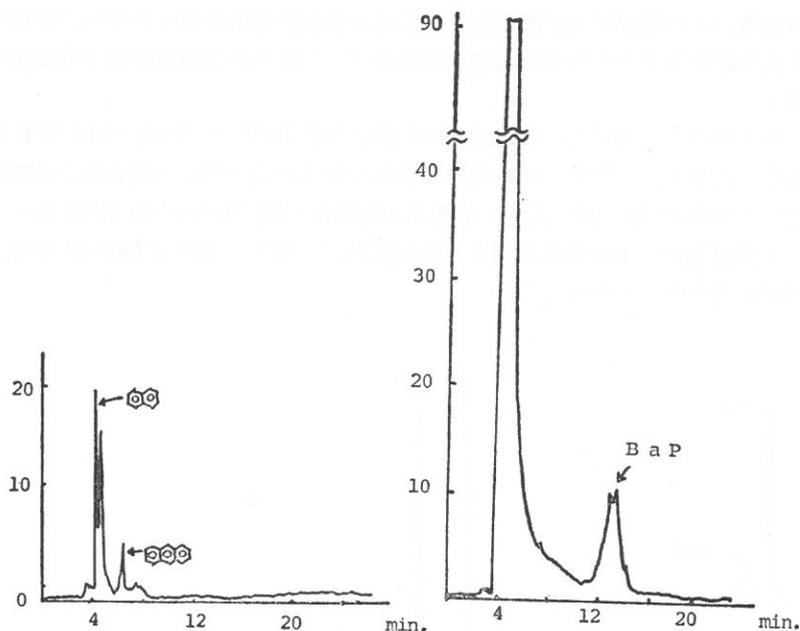


圖 6. 以內在標準物法鑑定樣品

對這五個不同的樣品而言，曾分別以內在標準物法 (Internal Standard method) 去鑑定，見圖 6。發現在收集的樣品中，可能有相當成份的多苯環化合物，但它們不是屬於純的多苯環碳氫化合物，極可能是已被其它的官能基所取代了的多苯環化合物。為了更進一步的去鑑定這些物質是否為多苯環碳氫化合物，我們利用 GC/MS 來配合，在 PAH 中，Benzo[a]anthracene, Benzo[a]pyrene 及 Dibenz[a, h]anthracene 等均已被 EPA 公佈為致毒物。在所收集的樣品中未能直接找到這些物質的存在。校門口及化學系二樓的空氣品質比較複雜。這可以圖 5 中之 (c) 及 (d) 兩圖來說明。若與其它三處比較，則此兩處空氣在質與量兩方面均有顯著之不同。原因可能是化學系因常年做化學實驗。致使化學藥品暴露於空氣中的機會增多。而校門口則因面對省道，交通流量大，因 PAH 主要來源之一即為燃料之不完全燃燒而產生的。此外，因輔仁大學位居工業區附近，燒油的工廠很多，亦是污染物之主要來源<sup>(4)</sup>。

在本實驗中，也發現氣溫之變化是空氣中污染物組成改變之因素之一。這可從春冬季節與夏季在同一地點所採集的樣品做一比較說明。圖 7(a) 為三月廿日在校門口採集樣品之 HPLC 圖，而圖 7(b) 則為七月十五日在同一地點之 HPLC 圖。兩者在質與量上均有顯著之不同。可能是因為溫度的升高，對物質之揮發性會有相當性增加之故。

(2) GC, GC/MS :

①所用管柱：本實驗中所使用的管柱都是自己填充的，我們曾分別使用 3% SE-30 及 3% Dexsil 300 GC 兩種不同的管柱，結果顯示後者之效果較好，所

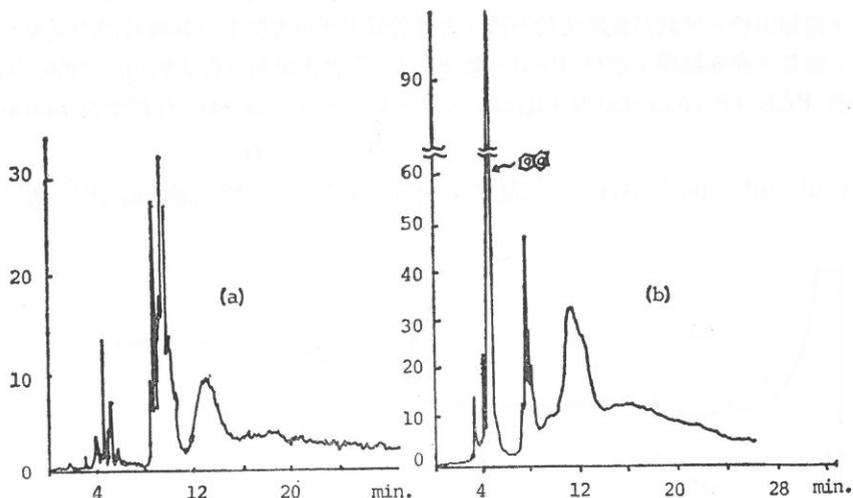


圖 7. (a) 三月廿日輔大校門口空氣樣品之 HPLC 圖  
(b) 七月十五日輔大校門口空氣樣品之 HPLC 圖

表 4. 標準物質之滯留時間

No.	Compound	RT (min.)
1	Naphthalene	1.78
2	n-heptadecane	8.66
3	n-octadecane	10.18
4	Anthracene	11.60
5	n-eicosane	13.01
6	Pyrene	16.10
7	Benzo[a]anthracene	19.31
8	Chrysene	19.61
9	Benzo[e]pyrene	23.34
10	Perylene	23.68
11	Benzo[a]pyrene	23.94
12	Dibenz[a, h]anthracene	26.50
13	Benzo[ghi]perylene	27.60

以採用 3% Dexsil 300 GC 管柱。

②標準物質：各溶液配製方法如前。表 4 所列為各物質之滯留時間。

③樣品之鑑定：由一年採樣的分析結果，知道樣品會隨着氣溫之高低，風向之改變及地點之各異而在質與量上均有顯著之不同。此外，亦由許多參考文獻中，得知由於各物質蒸氣壓力的不同，有些物質甚至會在較長之採樣時間內損失<sup>(5)</sup>。而且，在採樣時，有些 PAH，如 B[a]P 等會在濾紙上與大氣中之 NO<sub>2</sub>, O<sub>3</sub> 及 PAN (Peroxyacetyl nitrate,  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\overset{\text{O}}{\parallel}{\text{N}}-\text{O}$ ) 作用生成 mutagenic nitro-derivatives，只要有 1 ppm 的 NO<sub>2</sub>，反應立刻會進行<sup>(6)</sup>。所以

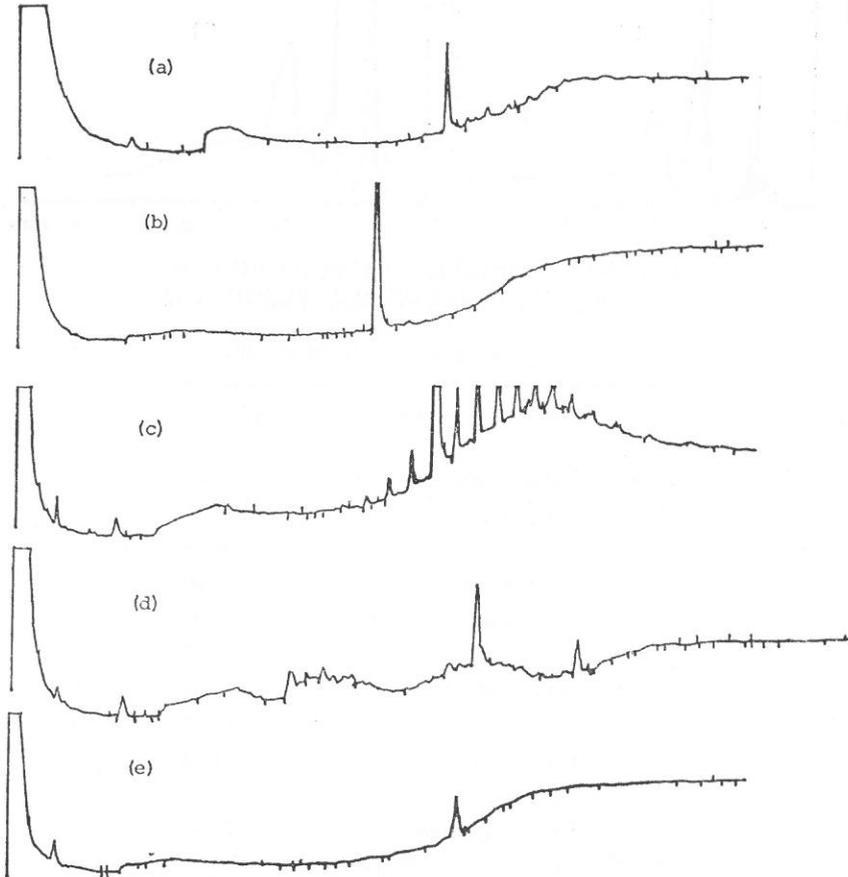


圖 8. 不同地點樣品之 GC 圖

，純化分離後之萃取液盡量在48小時內完成分析。

圖 8 為與前述相同之五處地點樣品之 GC 圖，與 HPLC 的結果相同的是：(c) 與 (d) 兩圖較其它的複雜，表示在質與量方面均與其它的不同。

圖 9，圖10及圖11為三個不同樣品之 GC 及 GC/MS 圖。三圖中之 (a) 為

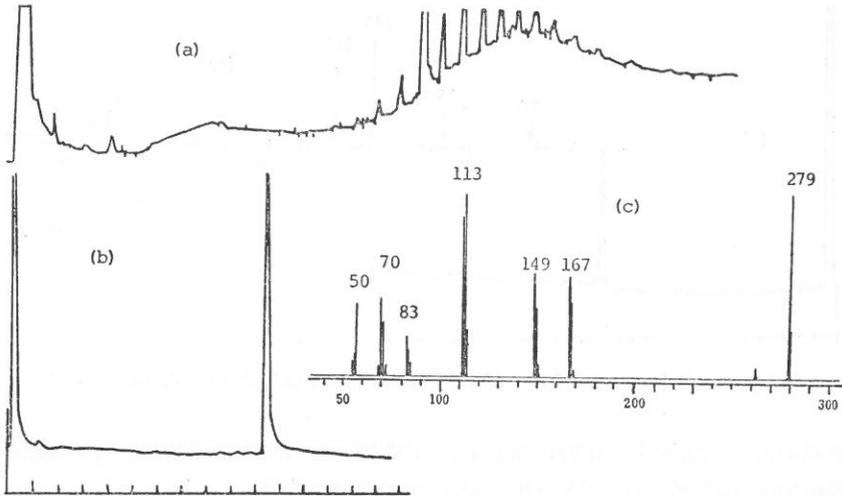


圖 9. 七月十二日 (化學系系館二樓) 樣品之 (a) GC 圖, (b) 及 (c) 為 GC/MS 圖

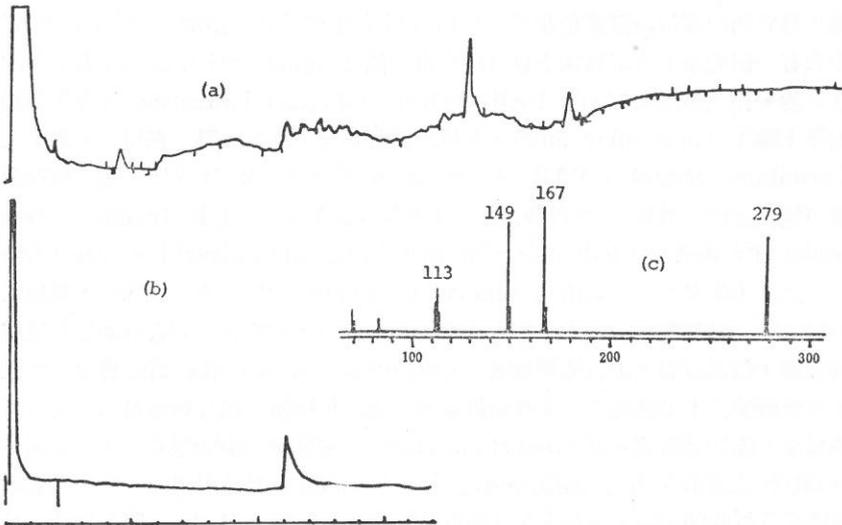


圖 10. 七月十五日 (輔仁大學校門口) 樣品之 (a) GC 圖, (b) 及 (c) 為 GC/MS 圖

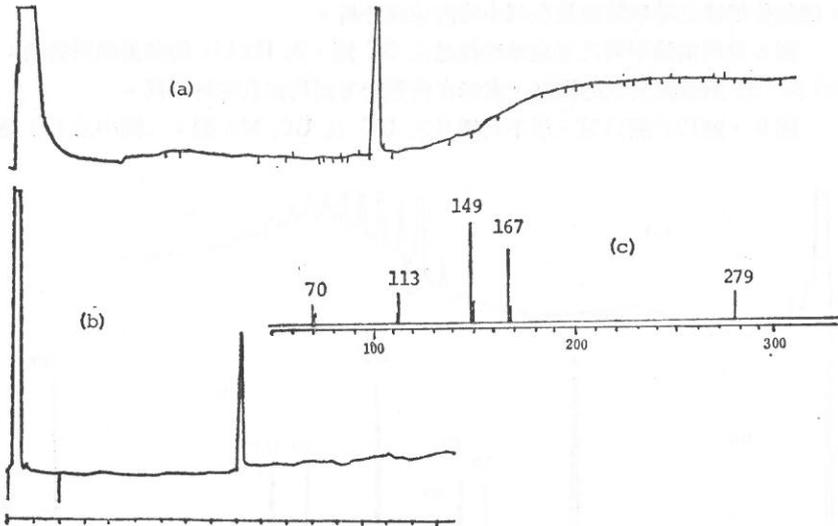


圖 11. 七月十七日(修女院)樣品之 (a) GC 圖, (b) 及 (c) 為 GC/MS 圖

樣品處理完畢後四十八小時內所得到的 GC 圖。而(b)則為相隔三至四個星期後所得到的 GC 圖；(c) 為與 (b) 一起使用所得出之質譜。

在這三個圖中，可以馬上看出對同一個樣品而言，(a) 與 (b) 有相當大的不同。這三個不同的樣品，其(a)圖有很明顯的差異；但其(b)圖則只出現一個尖峯，且它們的滯留時間都很相近。在(a)圖上的其它尖峯均偵測不出來。由於(b)中只有一個尖峯，所以質譜上也只鑑定出一個 fragmentation peaks 並不多的化合物。由文獻上可以知道 PAH 對 electron-impact ionization 會現出明顯的分子離子 (molecular ions)，足以提供計算分子量的資料，在同一文獻上，Choudhury 亦曾提出 PAH 之 fragmentation peaks 不多<sup>(7)</sup>。這三個質譜極可能代表同一物質，因彼等之分子量相同，都是 279，而其 fragmentation peaks 亦大致相同。其中  $m/e=149$  所代表的是 phthalic acid esters (酞酸酯) 之基本尖峯<sup>(8)</sup>。已知的是 dibutyl phthalate 的分子量為 278.34，為油質物質，乃一驅蟲劑。輔仁大學附近亦有不少的農田，故空氣中若含有驅蟲劑雖尚稱合理，但需政府大力的協助改善。Cautreels 及 Cauwenberghé 曾提及酞酸酯為焚燒爐之主要產品<sup>(9)</sup>。大學附近雖無正式之焚燒爐，但有數處私用之露天焚燒場地。此物是否真正為 dibutyl phthalate 則需更進一步的鑑定。至於三圖中 (a) 與 (b) 之差異可能是因兩部不同之 GC 的靈敏度各異而引起的，另一可能之原因為分析時間與樣品處理完畢之時間相隔太久(三至四個星期)，導致物質之揮發，此外，在本次的實驗分析中，沒有發現空氣中含有直鍊碳氫化合物之存在。

## 丁、誌 謝

本實驗乃賴、朱、溫三位同學修習“專題研究”之合作作品，一學年的時間稍嫌短促，故未能完成定量方面之分析。暑假期間，莊慧玲，黃世杰及吳維東三位同學亦加入工作行列。此實驗中之重金屬分析部份得蒙行政院衛生署環境保護局第六組多位人士提供資料協助，在此一併致謝。

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**Analysis and Identification of Complex Mixtures  
on Airborne Particulate Matter at  
Fu Jen University**

W. P. LEE, C. S. CHU, F. H. WEN and J. S. LAI

**ABSTRACT**

Fu Jen University has been disturbed by air pollution for a long time. The neighborhood factories, the heavy traffic on the street in the front, the spreading of insect repellants and insecticides in the nearby fields and several private open-air garbage burning grounds contribute to the pollutants which certainly constitute a serious threat to health and environment.

In the research conducted during the past year, the air particulate matter was collected by a high-volume sampler with glass fiber filters. Heavy metals were determined by the Atomic Absorption Spectrometer. Several heavy metals were identified. Lead, the most predominant one, most probably comes from gasoline. The organic extract was purified and separated by the Baker-10 SPE method and reverse-phase high performance liquid chromatography. Self packed column gas chromatography and gas chromatography/Mass Spectrometry were used for the identification of sample components. Results indicate that one family, phthalic acid esters, is present in higher concentration than all the others. This type of compounds comes mostly from garbage incinerators. Seasonal variation of compounds found was observed and discussed.

# 離子選擇電極之製備與評估

## 銅離子電極與氯離子電極

化學系

劉正宇 陳佳珍 陳壽椿

### 前 言

離子選擇電極在近年來受到各行各業的重視，有關論文也是非常多。因為製備離子選擇電極雖然需要特殊的方法及配方，但是一旦製造的程序確定，並不需要昂貴的設備，所以一支電極之市價也不高，約在臺幣壹仟伍至壹萬元之間。尤其在使用時僅需一較精密的毫伏電位計 (mV-Voltmeter)，所費有限，約在臺幣陸仟至兩萬元之間。如果是可與電腦介面之機種，即價錢可高到臺幣肆萬至拾萬元之間。離子選擇電極在近年來備受重視之另一原因是工業界流行自動化，需要更多的化學感測器 (chemical sensors) 來作程序與控制分析<sup>(1)</sup>。事實上，根據統計，離子選擇電極的成長率在化學分析儀器的市場上已可進入前三名。

一般離子電極可分為玻璃電極，固態電極，液膜電極，和酵素電極。尤其以前二者發展較早，使用較普遍，通常使用在測金屬離子和 pH 上，因為我們對於銅與氯離子在水溶液中或有機溶劑中，如甲醇，之含量有很大的興趣，所以以銅離子及氯離子電極作為以後一系列研究的開端。

### 理 論

在離子選擇電極的實驗中，所測得的電位是和溶液中的活性有關，而不是和濃度有直接的關係<sup>(2)</sup>，其表示法為：

$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}} + E_{ij}$$

其中  $E_{\text{ind}}$  是指示電極的電位， $E_{\text{ref}}$  是參考電極的電位， $E_{ij}$  是液面界面電位。在一般情形下， $E_{\text{ref}}$  為常數，而  $E_{ij}$  可以省略，用能氏方程式表示為

$$E_{\text{cell}} = E_{\text{constant}} + \frac{RT}{nF} \ln a_j \quad (1)$$

其中  $a_j$  為金屬離子在水中的活性度

可以求出水溶液中的金屬離子  $M^+$  的濃度。

當我們以  $\text{AgX}$  作為電極時

$$E = E_{0,Ag} + \frac{RT}{nF} \ln a_{Ag^+}$$

因

$$a_{Ag^+} \cdot a_{X^-} = K_{AgX}$$

故

$$E = E_{0,Ag} + \frac{RT}{nF} \ln K_{AgX} - \frac{RT}{nF} \ln a_{X^-}$$

在 25°C 下

$$E = E_{0,Ag} - 59.1 \text{ P}K_{AgX} + 59.1 \text{ P}a_{X^-} \quad (2)$$

由上式可知，使用不同的鹵化銀時，溶解度愈大，其所對應的電位就愈大<sup>(3)</sup>。

我們用沉澱物作為薄膜時，通常此電極可以測到相對應於正、負離子，電位對  $-\log$  濃度的關係圖，所得的斜率符號相反。如圖 1：

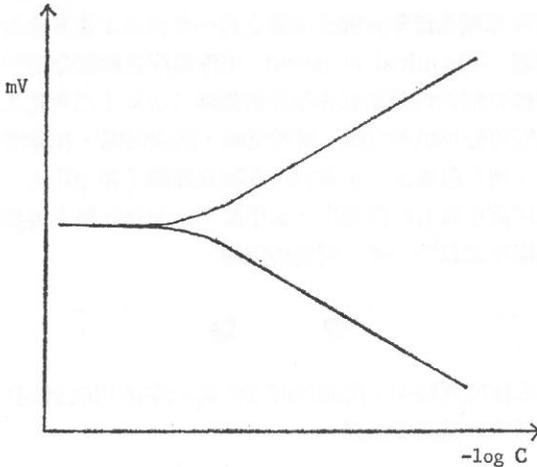


圖 1. 氯化銀電極，電位 vs.  $-\log$  濃度的關係圖。

可由下式中證明：

$$E = E_{0,Ag} + \frac{RT}{nF} \ln a_{Ag^+}$$

故  $E$  對  $-\log a_{Ag^+}$  作圖，其斜率為  $-RT/nF$

$$a_{Ag^+} \cdot a_{X^-} = K_{sp,AgX} \Rightarrow a_{Ag^+} = \frac{K_{sp}}{a_{X^-}}$$

$$E = E_{0.Ag} + \frac{RT}{nF} \ln \frac{K_{sp}}{a_{x-}}$$

$$E = E_{0.Ag} + \frac{RT}{nF} \ln K_{sp} - \frac{RT}{nF} \ln a_{x-}$$

故 E 對  $-\log a_{x-}$  作圖，其斜率  $RT/nF$ 。

## 實驗部份

### 第一部份 銅離子電極

#### 1. 藥品及器材：

碳棒 (電池 A A 號)	濃鹽酸
硫化鈉 (Merck)	硫酸銅 (Merck)
無水甲醇	去離子水
PVC 管	汞
強力接着劑 (市售)	鋁箔
喇叭線	細碳纖維束
碳粉	蠟 (市售)
玻璃管	單隔離電線
氯化鉀 (Merck)	二苯駢伍圈 (fluorene)
香蕉接頭	
環氧樹脂 [(K-poxy K-20)	MCKIM GROUP WALTHAM MA 02254 U. S. A]

#### 2. 儀器：

電位計 (Radio pH meter 22 Type PHM 22 No. 70731)

#### 3. 電極的製備：

電極 A 將電池中的碳棒浸入濃鹽酸中 1 天，然後依次移入飽和硫化鈉溶液及飽和硫酸銅溶液中各 1 小時，再用 50% 的甲醇水溶液洗碳棒，套入 PVC 管中，灌入汞作導體，用強力接着劑封口，電極之外導線為市售之喇叭線。

電極 B 方法和電極 A 同，僅飽和硫化鈉溶液和飽和硫酸銅溶液，兩者浸泡次序相反。

電極 C 將碳棒換成細碳纖維束，其他方法和電極 A 相同。

電極 D 將碳棒長度減小，其他方法和電極 A 相同。

電極 E 將電池中的碳棒換成碳粉，浸入濃鹽酸中 1 天，再移入飽和硫化鈉溶液及飽和硫酸銅溶液中各 1 小時，用 50% 的甲醇水溶液洗碳棒，乾燥，取 15% 此粉末及 85% 的蠟加熱混合均勻，做成薄膜，

套入玻璃管中，灌入飽和氯化鉀液，以鋁箔封口，插入單隔離電線作為導線。

- 電極 F 方法和電極 E 同，僅改變配製的比例，取55%的蠟和45%的粉末做成兩支電極，分別裝入不同的內導液，飽和氯化鉀液及汞液。
- 電極 G 將55%的 K-poxy (two-component) 混合均勻，加上45%的粉末，其他方法和電極 F 相同。
- 電極 H 方法和電極 G 相同，僅將55%的 K-poxy 換成55%的二苯駢伍圈。

## 第二部份 氯離子電極

### 1. 藥品及器材：

- |             |        |
|-------------|--------|
| 硝酸銀 (Merck) | 碘化鉀    |
| 濃硝酸 (Merck) | PP 管   |
| 銀線          | BNC 接頭 |
- 其他，請參照第一部份。

### 2. 儀器：

- 貝克曼 IR 光譜儀之 KBR 壓片模具 (IR Pellet die)。
- 其他，請參照第一部份。

### 3. 電極的製備：

- 電極 A 碘化銀與硫化銀以等摩爾比例混合，經過濾、乾燥，用瑪瑙磨成細粉，以 KBR 壓片模具，壓力控制在10 噸/cm<sup>2</sup>，壓成 2mm 厚的薄膜。將此薄膜套入 PP 管中，管內裝約三分之二滿的10<sup>-3</sup>M 硝酸銀溶液，BNC 接頭焊接銀線，插入管中，作為導線。碘化銀中，加入硫化銀，主要是為了減少電極表面對光之靈敏度<sup>(3)</sup>。因為碘化銀有高電阻及相當大的光電電位，加入硫化銀就可避免這些缺點<sup>(4)</sup>。
- 電極 B 將電池中之碳棒浸入濃硝酸中一天，然後依次移入飽和硝酸銀溶液，飽和氯化鉀溶液，飽和硫化鈉溶液及飽和氯化鉀溶液中各一小時，再用50%的甲醇水溶液洗碳棒，套入 PVC 管中，灌入汞作導體，用強力接着劑封口，電極之外導線為單隔離線。
- 電極 C 將電池中之碳棒浸入濃鹽酸中一天，然後依次移入飽和硝酸銀溶液，0.1 M 硫化鈉溶液及飽和氯化鉀溶液中各一小時，其餘作法與電極 B 相同。
- 電極 D 除了將濃鹽酸換成濃硝酸外，其餘作法與電極 C 相同。
- 電極 E 先將碳粉浸於濃鹽酸中一天，經過濾、乾燥備用。將氯化銀與硫

化銀以等摩爾比例混合，經過濾、乾燥，用瑪瑙磨成細粉備用。取85%的二苯駢伍圓，10%的碳粉及5%的  $\text{Ag}_2\text{S}/\text{AgCl}$  粉末，加熱混合均勻，做成薄膜套入玻璃管中，灌入汞，以鋁箔封口，插入單隔離線作為導線。

電極 F 除了將二苯駢伍圓換成蠟以外，其餘作法與電極 E 相同。

電極 G 除了將薄膜的材料換成 55% 的 K-poxy，30% 的碳粉及 15% 的  $\text{Ag}_2\text{S}/\text{AgCl}$  粉末外，其餘作法與電極 E 相同。

電極 H 除了將電極 G 之 K-poxy 換成蠟以外，其餘方法與電極 G 相同。

## 結果與討論

### 第一部份 銅離子部份

浸泡溶液的次序會影響電極的線性範圍

電極 A 是根據參考文獻<sup>(5)</sup>所製備的結果，由圖 2、圖 3 的實驗數據來看，線性範圍較一般情況為差，尤其以硫離子為甚，所以推測可能是在製備過程中，最後吸附上去的離子扮演重要的角色，因為它對溶液中的待測離子的吸引或拒斥會有不同，因此考慮製備電極 B。由圖 6、圖 7 可以顯示電極 B 對於離子的可測下限有所幫助，所以認為改變製備程序中浸泡的程序，可以改變電極的特性，但是真正的感應機構 (response mechanism) 還尚待研究。

電極長短的影響

一般在製備電極時可能會偏好大電極，大概基於表面積大較為有利，但是由圖 2 和圖 11 及圖 3 和圖 12、圖 13 顯示出相反的結果，短電極無論在感應時間，線性範圍或靈敏度上 (離子的可測下限) 都優於長電極，所以引發用細碳纖維束來作電極的動機。由電極 C 中的圖 9、圖 10 可以合理的說明，愈小、愈短的電極對於線性範圍和靈敏度上有很大的改善。

浸泡時間對電極的影響

電極 A 測銅離子 線性範圍  $1 \times 10^{-1} \sim 1 \times 10^{-8}$   
 $1 \times 10^{-4} \sim 5 \times 10^{-7}$  (一個月後)

電極 B 測硫離子 線性範圍  $1 \times 10^{-2} \sim 5 \times 10^{-6}$   
 $5 \times 10^{-2} \sim 5 \times 10^{-6}$  (十八天後)

由電極 A 中的圖 4、圖 5 及電極 B 中的圖 6、圖 8 可以看出，電極置於水中浸泡時間愈長，其靈敏度愈好。因為電極平衡需要很長的時間，否則會有不理想的結果，但是浸泡的時間對於硫離子並沒有什麼大影響。是否與其分子的本性有關，還不能很確定。此外離子的感應時間 (response time) 和離子的吸附平衡有關<sup>(6)</sup>，可以知道在濃度高時，因所含離子較多，容易吸附在電極表面，所以感應時間較短，符合實際情形。

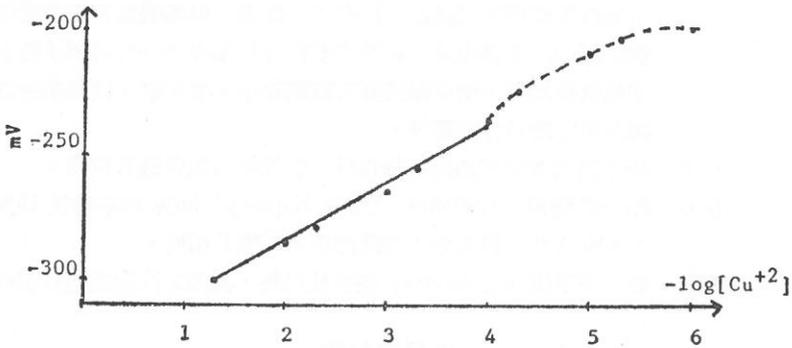


圖 2. 電極 A, 線性範圍  $1 \times 10^{-1} \sim 1 \times 10^{-4} \text{M}$ , 斜率 23.06。

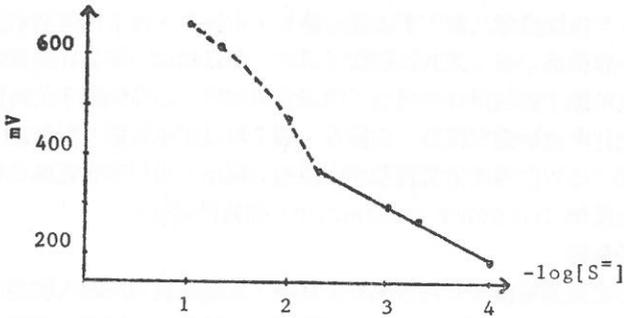


圖 3. 電極 A, 線性範圍  $5 \times 10^{-8} \sim 1 \times 10^{-4} \text{M}$ , 斜率 -103。

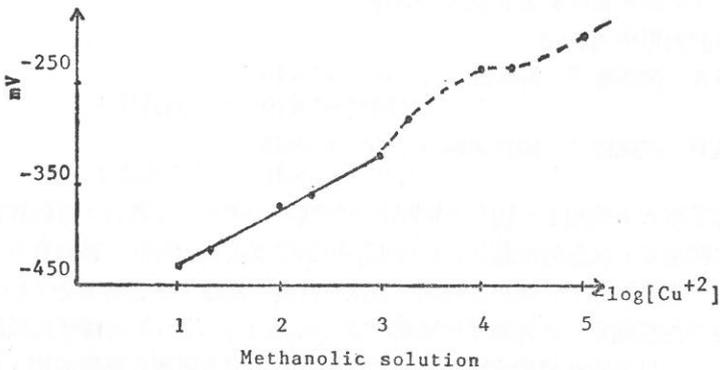


圖 4. 電極 A, 線性範圍  $1 \times 10^{-1} \sim 1 \times 10^{-8} \text{M}$ , 斜率 55。

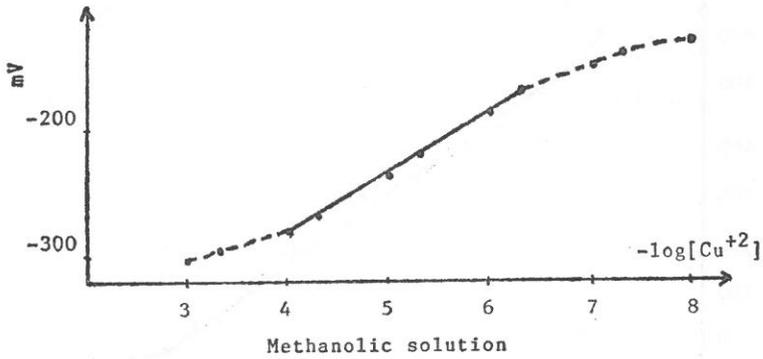


圖 5. 電極A, 線性範圍  $1 \times 10^{-4} \sim 5 \times 10^{-7} M$ , 斜率 46.5°

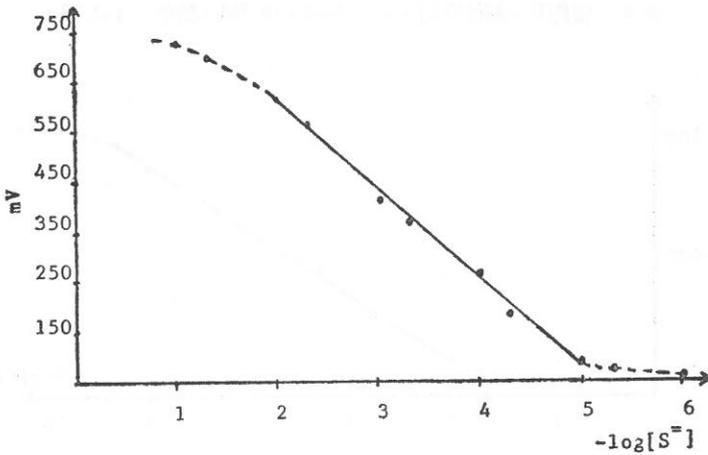


圖 6. 電極B, 線性範圍  $1 \times 10^{-2} \sim 5 \times 10^{-6} M$ , 斜率  $-175.67^\circ$

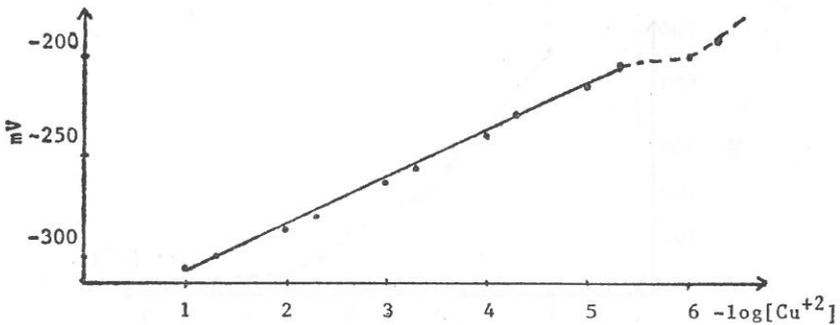


圖 7. 電極B, 線性範圍  $1 \times 10^{-1} \sim 5 \times 10^{-6} M$ , 斜率 23.33°

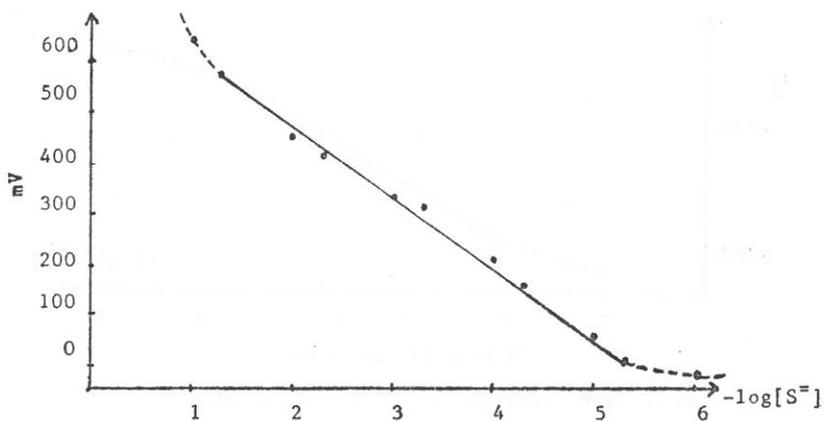


圖 8. 電極 B, 線性範圍  $5 \times 10^{-2} \sim 5 \times 10^{-6} M$ , 斜率  $-143.28^\circ$ .

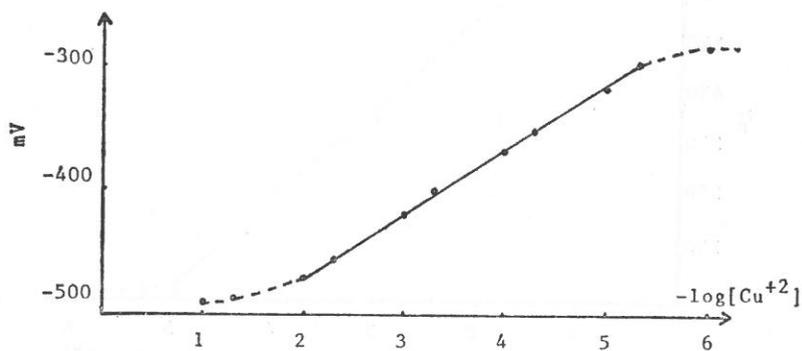


圖 9. 電極 C, 線性範圍  $1 \times 10^{-2} \sim 5 \times 10^{-6} M$ , 斜率  $51.50^\circ$ .

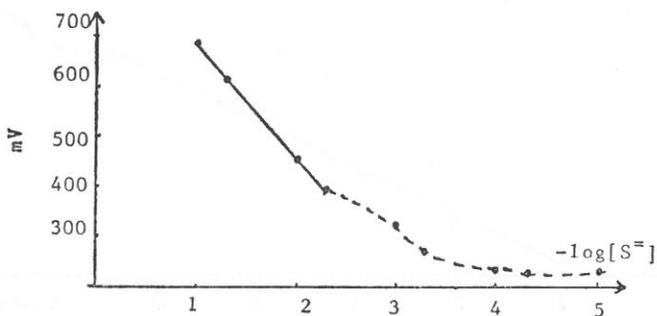


圖 10. 電極 C, 線性範圍  $1 \times 10^{-1} \sim 5 \times 10^{-8} M$ , 斜率  $-226.75^\circ$ .

內導液對於電極的影響

電極 F 圖15 線性範圍  $1 \times 10^{-1} \sim 5 \times 10^{-6}$  (灌入飽和氯化鉀液)

圖16 線性範圍  $1 \times 10^{-2} \sim 5 \times 10^{-6}$  (灌入汞)

由結果來看，線性範圍和靈敏度是很出乎意料之外的，一般說來用作為導體要比飽和氯化鉀液來得好（金屬間傳導比離子間移動來得快），這種結果可能是汞的表面張力大，使金屬導線在電極的管中常會移向管壁，而導致接觸不良。

固着劑 (hydrophobizing agent) 對電極的影響

電極 E、電極 F、電極 G、電極 H 是分別用不同的固着劑做成的電極。此種方法的優點是容易更新，而且可以使用很多次<sup>(7)</sup>，由結果可知碳粉和硫化銅粉末的混合比例愈多，其靈敏度愈好，而不同的固着劑、蠟、二苯駢伍圖及環氧樹脂

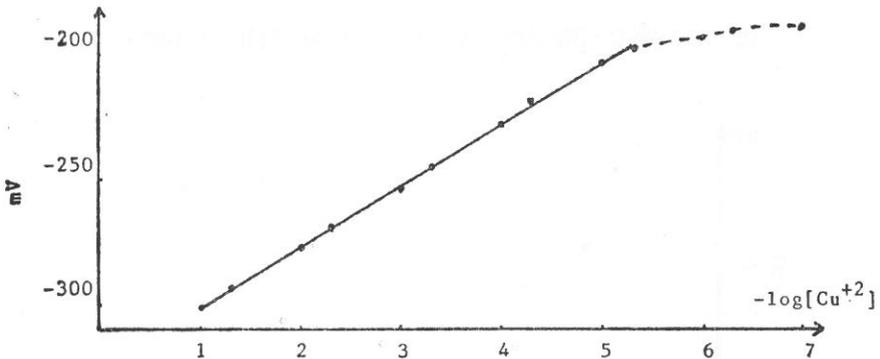


圖 11. 電極 D, 線性範圍  $1 \times 10^{-1} \sim 5 \times 10^{-6} \text{M}$ , 斜率  $24.33^\circ$

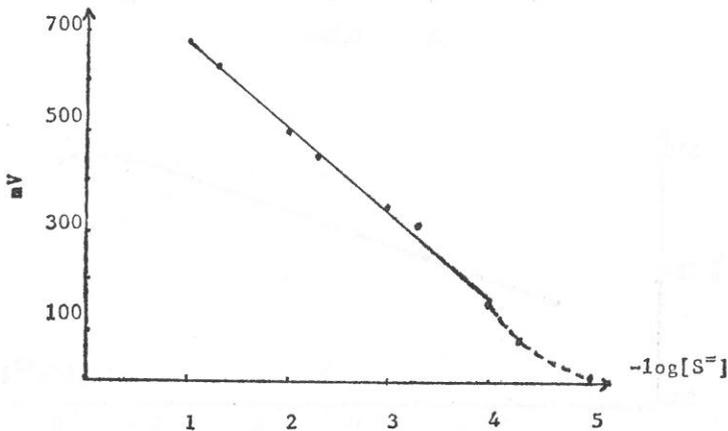


圖 12. 電極 D, 線性範圍  $1 \times 10^{-1} \sim 1 \times 10^{-4} \text{M}$ , 斜率  $-169.44^\circ$

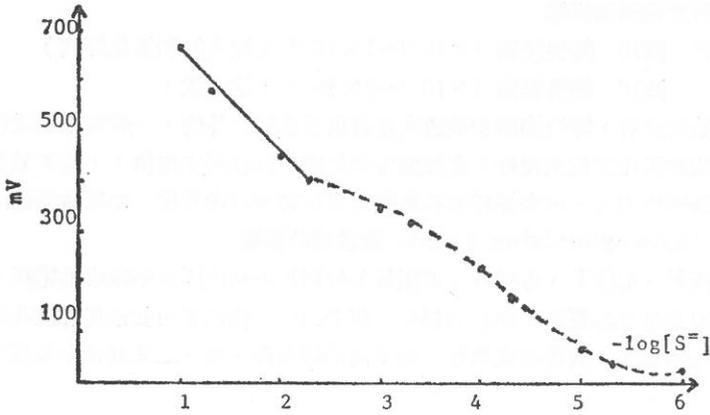


圖 13. 電極D, 線性範圍  $1 \times 10^{-1} \sim 5 \times 10^{-3} M$ , 斜率  $-203.69^\circ$

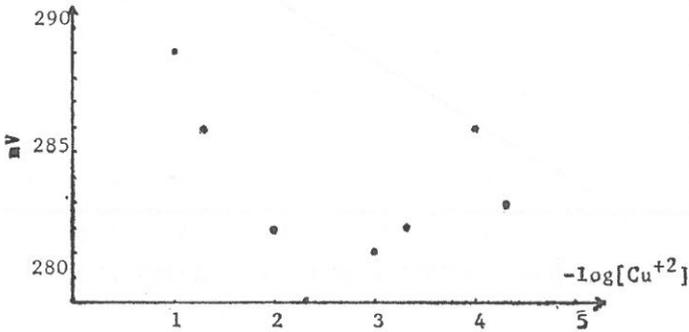


圖 14. 電極E。

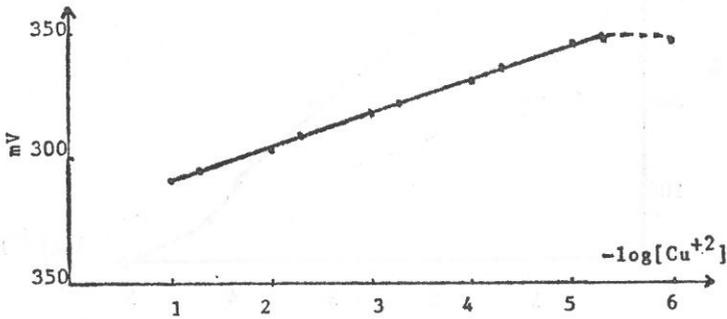


圖 15. 電極F, 線性範圍  $1 \times 10^{-1} \sim 5 \times 10^{-6} M$ , 斜率  $13.33^\circ$

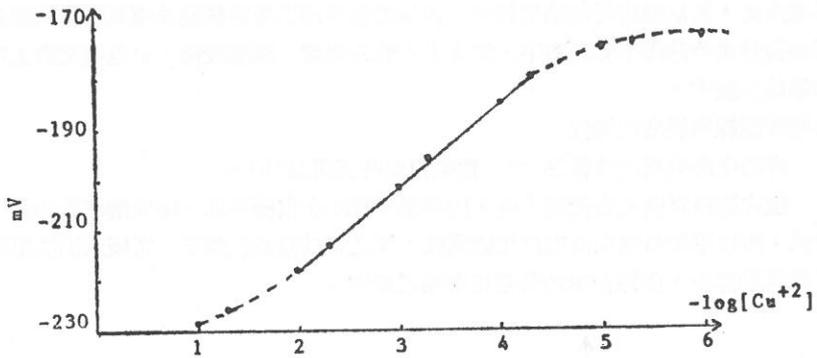


圖 16. 電極F，線性範圍  $1 \times 10^{-2} \sim 5 \times 10^{-5} \text{M}$ ，斜率 16.05。

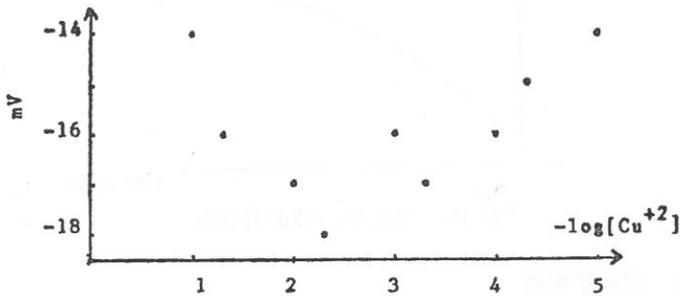


圖 17. 電極G。

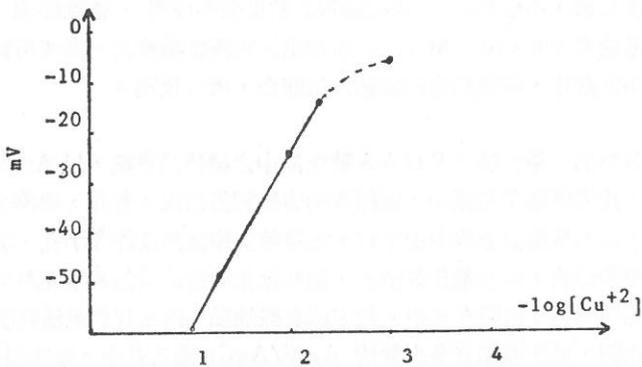


圖 18. 電極H，線性範圍  $1 \times 10^{-1} \sim 5 \times 10^{-3} \text{M}$ ，斜率 34。

三者來比，又以蠟所得的結果較好。因為熔化後的二苯聯伍圖及環氧樹脂與硫化銅磺粉形成的薄膜不容易磨平，造成表面較為粗糙，感應較慢，這也與文獻上所報導的一致<sup>(8)</sup>。

#### 感應時間線與濃度的關係

高濃度所表現的曲線為(a)，而低濃度時表現為(b)。

造成這種原因是在低濃度時，因為離子吸附在電極表面，造成溶液內的濃度降低，所以平衡曲線由高電位至低電位，反之對於高濃度離子，電極表面吸附離子對其影響小，曲線表示由低電位至高電位<sup>(9)</sup>。

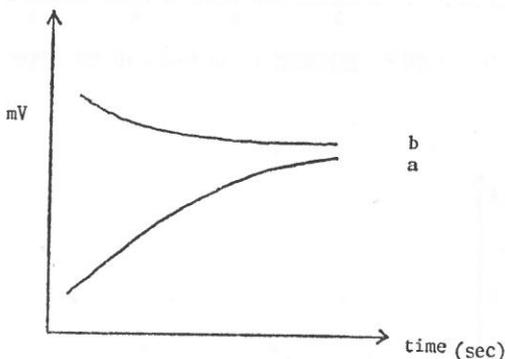


圖 19. 電位 vs. 時間的關係圖。

## 第二部份 氯離子電極

### 固態式電極

電極 A 是參考文獻<sup>(10)</sup>的方法，碘化銀與硫化銀以等摩爾比例混合成感應材料製備而成。因為所用的壓片機壓力雖為 10 噸 / 平方公分，但不穩定，使得壓成的薄膜不夠緊密，不夠均勻，所以測得之結果並不理想，線性範圍  $3 \times 10^{-2} \sim 10^{-3} M$ ，靈敏度  $2.5 \times 10^{-4} M$ 。此法所作出之電極體積較大。因使用較高之壓力及壓製較小之薄片，在實驗室內設備無法配合，所以放棄。

### 碳棒電極

電極 B 為另一種作法，是以 A A 號電池中之碳棒為電極，以  $Ag_2S/AgCl$  為感應材料，比照銅離子電極中，電極 A 的方法製備而成。首先，碳棒須以濃硝酸浸泡一天，目的是洗去碳棒中的雜質，並侵蝕碳棒使形成許多小孔，接着依次浸泡飽和硝酸銀溶液，飽和氯化鉀溶液，飽和硫化鈉溶液及飽和氯化鉀溶液各一小時，使  $Ag_2S/AgCl$  吸附在孔中。此方法有些缺點，例如我們無法控制硫化銀與氯化銀的比例，無法控制有多少量的  $Ag_2S/AgCl$  滲入孔中，無法得知  $Ag_2S/AgCl$  在整個碳棒中是否分佈均勻，及可以改變的因素太多。基於這些原因，

我們能做的就是一次同時做二個（或多個）電極，只改變其中一項因素，其他因素儘可能完全一樣，如此比較，才能從這種方法中，找出一個最好的方法來測待測物。電極B僅為其中的一種方法，所測之氯離子，線性範圍  $10^{-1} \sim 5 \times 10^{-3} M$ ，靈敏度  $5 \times 10^{-6} M$ 。銀離子之線性範圍  $10^{-2} \sim 10^{-4} M$ ，靈敏度  $10^{-7} M$ 。電極C, D為改變其中的一個變因。再接下來之電極則為另一製備方法。

濃酸浸泡對電極性質的影響

電極C與D，為一對照組，研究以濃鹽酸和濃硝酸之浸泡效果，所以除了電極C之碳棒以濃鹽酸浸泡，電極D之碳棒以濃硝酸浸泡以外，其他條件都一樣。測得之結果，電極C之線性範圍  $10^{-1} \sim 5 \times 10^{-4} M$ ，靈敏度  $5 \times 10^{-6} M$ 。電極D所畫之圖則無規律性，故我們確定以濃鹽酸浸泡較好。

固着材料對電極之影響

電極E所用之二苯駢伍圖，電極F和H所用之蠟及電極G所用之環氧樹脂為

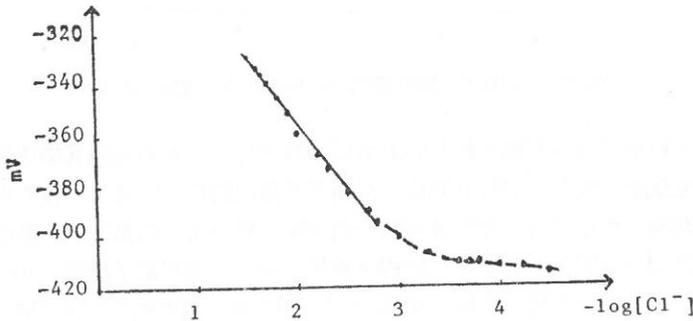


圖 20. 電極A，線性範圍  $3 \times 10^{-2} \sim 10^{-3} M$ ，斜率  $-52$ 。

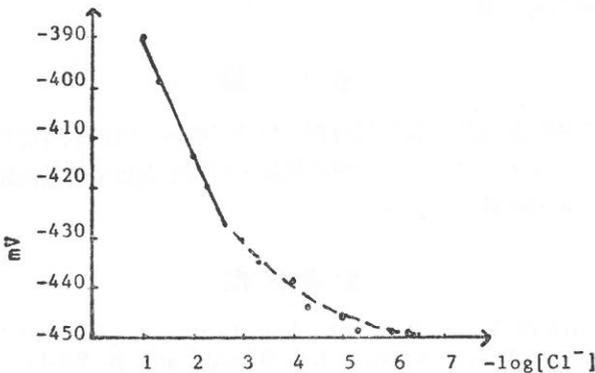


圖 21. 電極B，線性範圍  $10^{-1} \sim 5 \times 10^{-3} M$ ，斜率  $-22.5$ 。

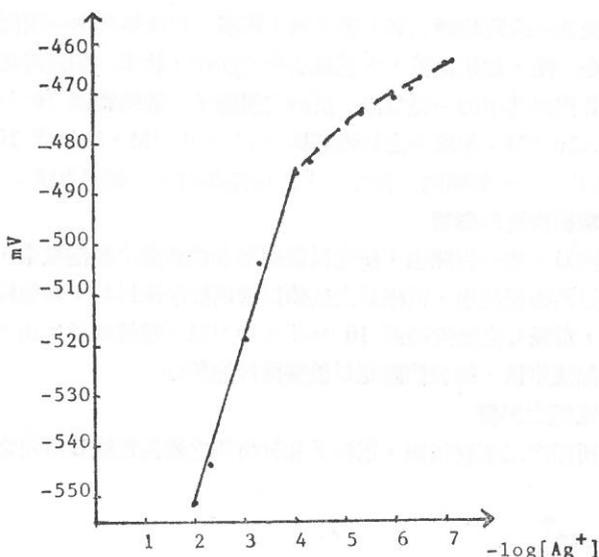


圖 22. 電極 B, 線性範圍  $10^{-2} \sim 10^{-4} M$ , 斜率 32.5。

固着劑，而前二者使用疏水性材料有抑制干擾之作用。使用電極 E 測電位時，因指針任意跳動，故無法記錄其電位。電極 F 所得之圖形，即圖 7，找不出一適當的線性範圍。圖中“×”是代表測某一濃度時，關機後，搖晃溶液，開機，再測電位，所測得之電位。其與第一次測之結果不同，可能與離子擴散 (diffusion) 或導電性差有關。電極 G 之線性範圍  $10^{-1} \sim 10^{-4} M$ ，靈敏度  $5 \times 10^{-6} M$ 。電極 H 之線性範圍  $10^{-1} \sim 5 \times 10^{-4} M$ ，靈敏度  $10^{-4} M$ 。結果顯示電極 G, H 比 E, F 好，故碳粉對固着劑之比例不能太低，否則導致導電不良。另外，電極 G 之靈敏度及感應速率略優於電極 H。

## 結 論

銅離子電極以碳纖維束做電極材料，無論是靈敏度或感應時間均比較好。氯離子電極則以環氧樹脂當固着劑之電極較好，但其中碳粉對環氧樹脂之比例不能太低，否則，會造成導電不良。

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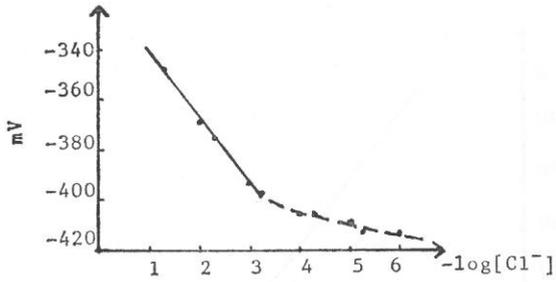


圖 23. 電極C, 線性範圍  $10^{-1} \sim 5 \times 10^{-4}M$ , 斜率  $-26^\circ$

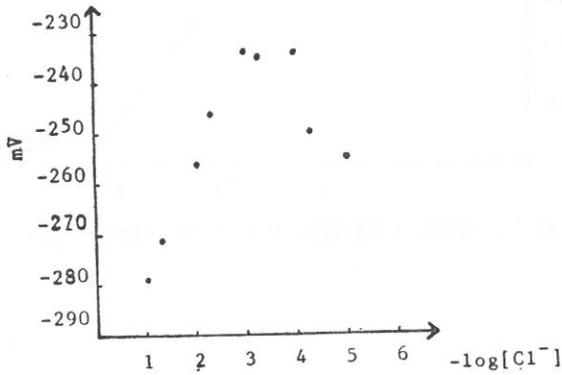


圖 24. 電極D。

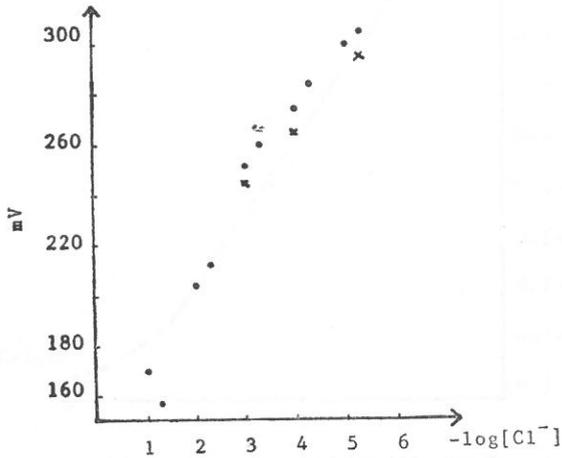


圖 25. 電極F。

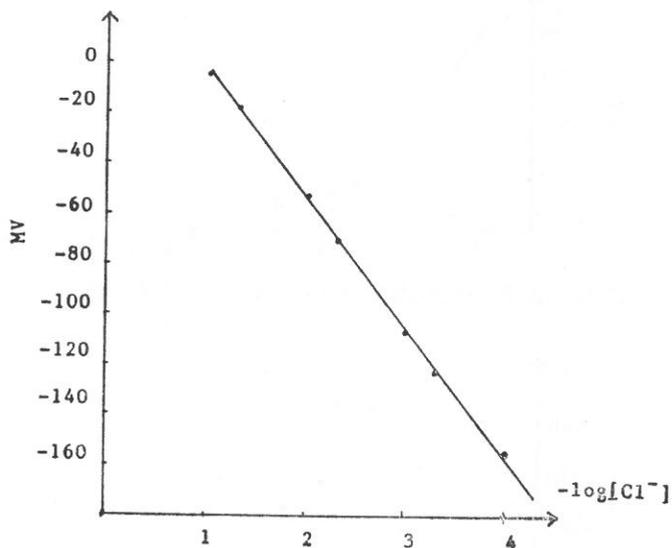


圖 26. 電極G，線性範圍  $10^{-1} \sim 10^{-4} M$ ，斜率  $-52^\circ$ 。

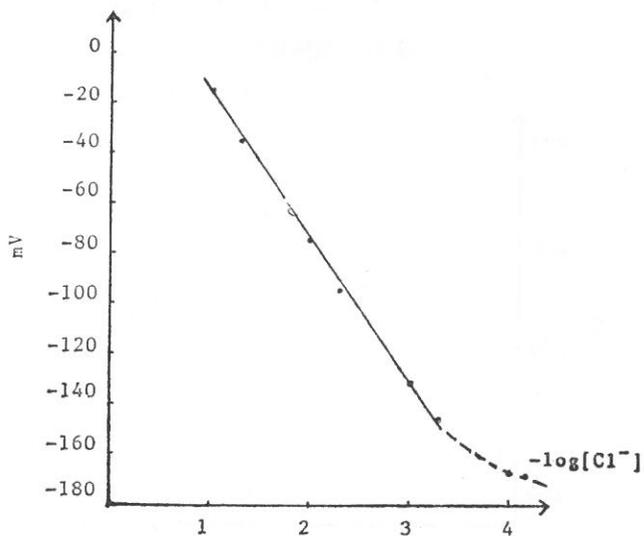


圖 27. 電極H，線性範圍  $10^{-1} \sim 5 \times 10^{-4} M$ ，斜率  $-58.25^\circ$ 。

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## The Fabrication and Evaluation of Copper Ion and Chloride Ion Selective Electrodes

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and SHOW-CHUEN CHEN

### ABSTRACT

The various fabrication methods for copper ion selective electrodes and chloride ion selective electrodes of carbon related materials were studied. Factors under investigation were the size of electrode, the soaking order of sensing elements, the type of carbon matrix and the dosage of sensing elements. Results indicated that electrodes prepared from carbon rods or carbon fiber bundles gave favorable responses compared to those from pressed pellets at low pressure or that from doped-graphite in polymer matrix.



# 榨汁前之碎果處理溫度及貯藏條件對 康歌葡萄果汁品質的影響

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陳 雪 娥

## 摘 要

本實驗以康歌 (Concord) 葡萄為材料，配合化學成分分析及感官品評方法，討論碎果加熱溫度對康歌葡萄果汁品質的影響，以找出最適當的加工方法。更進一步將果汁貯藏於不同環境條件下，探討其品質變化情形。

## 引 言

康歌 (Concord) 葡萄學名為 *Vitis labrusca* cv. Concord，因果汁酸度高，不適鮮食，是果汁專用品種 (Neubeck 1975)。康歌葡萄果實外觀呈紫紅色，顆粒小，色素主要成分為 delphinidine-3-glucoside，大部分於果皮上<sup>(3)</sup>。葡萄果汁色素的多寡和葡萄採收期、成熟度、碎果處理方法及貯藏條件都有關係。香氣的主要成分為 Methylanthranilate 是所有葡萄中含有 anthranil ester 最多的品種<sup>(6,8)</sup>。碎果經加熱處理的主要目的是提高榨汁率，萃取紅色色素以及抑制多酚類氧化酶 (polyphenoloxidase) 的褐變作用<sup>(4,6)</sup>。榨汁率因溫度的升高及壓榨時間的增長有增加的趨勢<sup>(7,12)</sup>，且加熱有助於果皮中之花青素 (anthocyanin) 被萃取出來，使果汁之紅色度增加。但若加熱榨汁處理不當，對果汁有反面的影響：如香味散失，色素被破壞，以及由醣類焦化形成糠醛 (furfural) 等褐化物質的前驅物的產生影響色澤，且因果膠質溶解出來將不利於果汁過濾<sup>(6)</sup>。多年以來利用果膠酶處理葡萄及其他含果膠量多的水果，以提高榨汁率、紅色素抽出率，增加風味以及降低榨汁的時間，增進果汁的澄清度、過濾性等，已有許多的文獻及實際利用的例子<sup>(9,13,14)</sup>。

本實驗擬找出最適當的碎果加熱溫度配合果膠分解酶的利用，並以此溫度所作的果汁於不同的貯藏條件下，探討對康歌葡萄果汁品質的影響。

## 材料與方法

民國72年7月採自臺灣土地銀行南澳分場之康歌葡萄 (植株年齡三年)，除梗洗淨，於  $-20^{\circ}\text{C}$  冷凍貯藏備用。

### 一、葡萄果汁之製造

取1公斤冷凍葡萄於室溫下自來水流解凍，經破碎後分別加熱至 $50\pm 1^{\circ}\text{C}$ 、 $60\pm 1^{\circ}\text{C}$ 、 $70\pm 1^{\circ}\text{C}$ 及 $80\pm 1^{\circ}\text{C}$ ，維持5分鐘後，迅速降溫至 $40\sim 50^{\circ}\text{C}$ ，加入0.1%果膠分解酶(pectinol，西德 Röh m 公司出品)處理1小時；另外以不加果膠酶而在室溫處理者為對照用。每種處理兩次重覆。五種處理分別壓榨取汁，將汁液迅速冷凍於 $-20^{\circ}\text{C}$ ，經1星期後於 $4^{\circ}\text{C}$ 冷藏庫解凍，虹吸取出上層液，加矽藻土過濾去除酒石及其他沈澱。過濾果汁裝於250毫升的玻璃瓶，以中心溫度達 $75^{\circ}\text{C}$ 熱水殺菌15分鐘。流水冷卻至室溫，於 $0^{\circ}\text{C}$ 貯藏作為化學成分分析及品評用。

### 二、官能品評

將果汁稀釋一倍，調糖至 $12^{\circ}\text{Brix}$ ，由未經品評訓練之人員10名，分別以果汁的顏色、香氣、風味及總體感覺等項目做品評，採用七分制為品評標準之嗜好性(Hedonic)品評方法，再以變方分析法統計，得一最佳溫度處理組。

### 三、果汁之貯藏試驗

以成分分析及官能品評所得之最佳溫度處理組為參考，取10公斤冷凍葡萄同上法處理，用油壓機壓榨、澄清、殺菌、裝瓶，所製得之果汁分別於 $-20^{\circ}\text{C}$ 、 $0^{\circ}\text{C}$ 、室溫不照光、室溫照光及 $35^{\circ}\text{C}$ 貯藏，每隔一段時間取四瓶供分析品評用。

### 四、果汁成分分析

1. 顏色：以色差儀(Tru-Color™, Neotec Instruments, INC™出品)作透光測定，所用標準白板為 $L=95.9$ ， $a=-1.2$ ， $b=2.2$ 。

2. 色素(TAcy)之定量：取果汁稀釋10倍，pH調至3.2，以光電比色計(Spectro 20)於520 nm波長下測其吸收值，以Malvin chloride(Sigma公司出品)為標品，作標準曲線(calibration curve)，定總色素量。

3. 可滴定酸之定量：取25 ml果汁加熱沸騰後，加50 ml蒸餾水冷卻至室溫，以N/3 NaOH滴定至pH=7，換算成酒石酸表示之。

4. 糖度：以Abbe Refractometer測之，校正至 $20^{\circ}\text{C}$ 的值以 $^{\circ}\text{Brix}$ 表示之。

5. pH：以pH meter測定之。

6. Hydroxymethylfurfural(HMF)含量之測定：取果汁1 ml，分別加入10% (M/V)之p-toluidin(溶於冰醋酸及異丙醇溶液)作用後，其中一組加1 ml  $\text{H}_2\text{O}$ 及1 ml 0.5% (M/V) barbituric acid，另外一組加2 ml  $\text{H}_2\text{O}$ 為對照，在550 nm波長下測其吸收值。另以hydroxymethylfurfural(Sigma公司出品)為標品作標準曲線。

## 五、榨汁率

以 1 公斤葡萄為原料，經加熱及酵素處理後，先以雙層紗布包裹，在不加外力情況下，至 15 秒內不滴汁為止，將流出量稱重即為自流汁量，再以手絞榨至不再滴流，所得第二部分之流出量是為壓榨汁。

$$\text{榨汁率}\% = \frac{\text{自流汁重} + \text{壓榨汁重}}{\text{原料重}} \times 100\%$$

## 結果與討論

### 一、不同碎果處理溫度對康歌葡萄果汁品質影響

葡萄果汁製造之實驗結果如表 1 顯示，碎果經 70°C 處理的榨汁率最高，根據 Tischer<sup>(12)</sup> 及 Sastry 與 Tischer<sup>(7)</sup> 指出，榨汁率隨着處理溫度升高及時間增長而增加。但 80°C 的榨汁率反而比 70°C 小，可能是部分水分蒸發較多之故。自流汁的量隨加熱溫度之上升有增高的趨勢。隨着碎果溫度的上升，可滴定酸及糖度均有增加的現象，而 pH 值沒有顯著改變，約在 3.2 左右。顏色、色素含量及 HMF 量則無明顯規則變化，但可以確定的是加熱有促進色素之抽取，同時 HMF 的量也會提高，80°C 處理的果汁比 50°C 處理的果汁 HMF 增加 10 ppm，亦即褐變的程度較嚴重。

Table 1. Effect of crushing temperature of mash on characteristics of concord grape juice

Characteristics		Temperature				
		Room temp.	50°C	60°C	70°C	80°C
Juice yield (%)	Free run	38.8	43.8	47.8	47.8	58.5
	Press	30.9	33.8	29.6	32.4	19.6
	Total	69.7	77.6	77.4	80.2	78.1
pH		3.20	3.22	3.26	3.16	3.20
°Brix		14.1	14.9	14.8	15.3	15.9
Titrable acid (g/l)		6.7	8.3	9.5	9.6	9.8
Color (dilute 10×)	L	75.4	73.1	74.5	72.0	72.5
	a	13.5	18.4	15.5	20.5	19.3
TAcy (mg/l)		795	1,540	1,262	2,651	2,154
HMF (mg/l)		3.96	13.84	22.42	18.46	23.50

Table 2. Effect of crushing temperature of mash on sensory value of concord grape juice

Temperature Item	Room temp.	50°C	60°C	70°C	80°C	F value
Color	2.5	5.4	5.0	5.3	6.2	111.09**
Aroma	4.1	5.1	4.2	4.6	3.9	12.55*
Flavor	4.2	4.6	4.2	4.1	4.2	0.33
Overall impression	3.6	5.2	4.8	4.7	5.0	8.4 *

\*\* 1% significant level

\* 5% significant level

不同碎果處理溫度所得之葡萄汁經品評結果如表 2，顏色隨溫度上升有愈被喜愛的情形，其中以 80°C 處理的果汁評分最高，以室溫不加酵素之對照組最差。而香氣、風味及總體感覺以 50°C 處理的評分最高；不加酵素的對照組，因粘度大，不易壓榨，許多成份物質沒有溶流出來，故色澤和總體感覺分數均很低。由此可知康歌葡萄非經酵素處理不可，否則很難得到滿意的榨汁效果。

由品評結果可知，不同碎果處理溫度所得之果汁在色澤及香氣上有顯著差異，而味道的差異不明顯。綜合而言，以總體感覺平均值最高的 50°C 處理，進行果汁貯藏試驗。

## 二、不同貯藏條件對康歌葡萄果汁品質的影響

1. pH 值：在各種貯藏條件，隨貯藏時間的增長，果汁之 pH 值有略微趨高的現象（見圖 1），Sistrunk 及 Cash<sup>(10)</sup> 也發現貯藏中的葡萄汁 pH 值會增加而酒石酸會減少。此由於葡萄果汁中的酒石酸或蘋果酸在貯藏過程中形成鉀鹽或鈣鹽而沈澱。

2. 可滴定酸度：貯藏時間及照光與否對果汁酸度影響不大，但都比原貯藏於 -20°C 的果汁酸度高（見表 3），可見在 -20°C 下酒石酸易形成酒石酸沈澱，高溫下較不易產生。

3. 糖度：貯藏愈久，果汁糖度有減少的趨勢（見表 4），其中置 35°C 及室溫下的樣品糖度下降較多，可能是糖和葡萄汁的其他成分如花青素作用而減少<sup>(1, 11)</sup>，或者葡萄果汁中的氨基酸和糖起梅納反應（maillard reaction），以及糖（尤其是果糖）變成 HFM<sup>(2)</sup> 而使糖度下降。

4. HMF：葡萄汁在貯藏過程中隨着貯藏時間之增加，HMF 之產量也增加（見圖 2）。在 35°C 貯藏者比其他貯藏條件下的樣品 HMF 形成量多，經 40 天貯藏後 HMF 增加 6.7 ppm。室溫照光者與室溫不照光者產生之 HMF 量差異

不大，可見光不會促進 HMF 的形成，而溫度對果汁貯藏過程中 HMF 之產生量影響很大。

5. 色素 (TAcy)：隨着貯藏時間的增加葡萄汁的色素量有減少的趨勢（見圖 3），貯藏溫度愈高色素量減少愈多，在 35°C 貯藏之果汁貯藏 1 個月後色素量減少約 50%，但即使在 0°C 貯藏之果汁經兩個月貯藏後，色素量約減少三分之一，且有沈澱產生，可能是部分的色素與其他的成分沈澱下來，故色素量減少。室溫下貯藏，照光與否對果汁色素的變化影響不大。由於康歌葡萄果汁中最主要色素成分是 delphinidin-3-glucoside，根據前人研究，此種色素相當不穩定

Table 3. Effect of storage conditions on titrable acid (g/l) of concord grape juice

Storage conditions Time (day)	H	RL	R	O
0	4.95	4.95	4.95	4.95
15	5.00	—	—	—
26	5.00	5.00	5.05	5.00
40	5.05	5.00	5.05	5.00
71	5.00	5.00	5.00	5.00
125	—	5.00	5.10	5.00

H: 35°C

RL: room temp. + day-light

R: room temp. + dark room

O: 0°C

Table 4. Effect of storage conditions on °Brix of concord grape juice

Storage conditions Time (day)	H	RL	R	O
0	9.0	9.0	9.0	9.0
15	9.2	—	—	—
26	9.2	9.3	9.4	9.1
40	9.0	9.3	9.1	9.4
71	9.0	9.0	9.0	9.0
125	—	8.4	8.0	8.7

H: 35°C

RL: room temp. + day-light

R: room temp. + dark room

O: 0°C

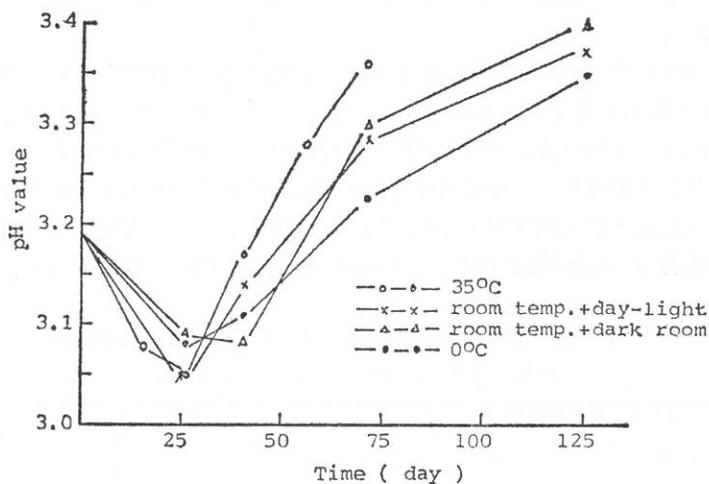


Fig. 1. Effect of storage conditions on pH of concord grape juice.

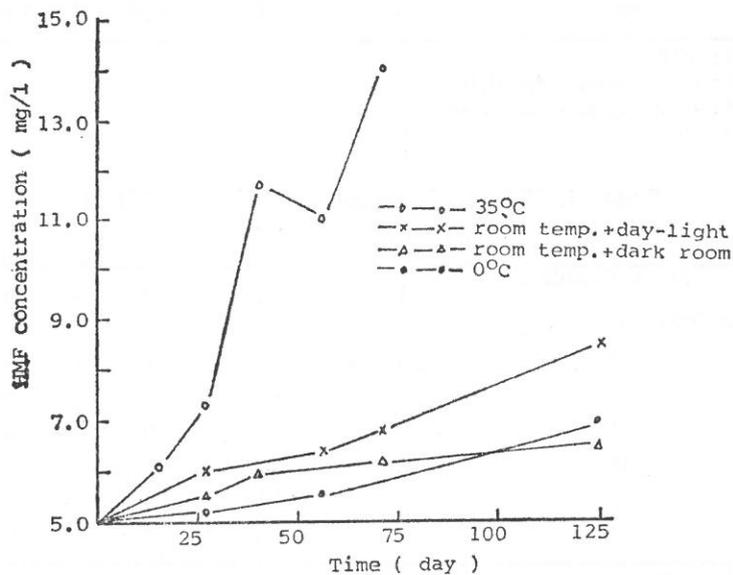


Fig. 2. Effect of storage conditions on HMF content of concord grape juice.

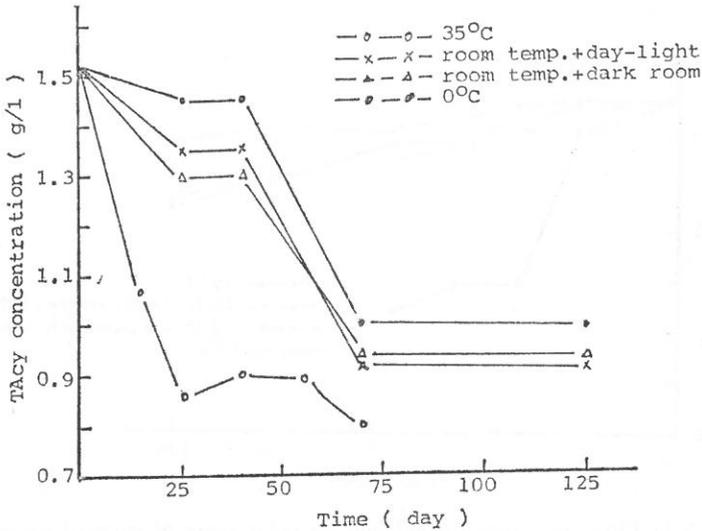


Fig. 3. Effect of storage conditions on TACY content of concord grape juice.

，而促進葡萄果汁色素量減少最大的因素是加工與貯存時的高溫度<sup>(7)</sup>；糖及糖的分解產物 furfural 及 5-hydroxymethylfurfural 亦有增加色素分解的效果<sup>(1,2)</sup>。一般來說，即使在很低的溫度，康歌葡萄汁的色素均有減低的現象，因此可知康歌葡萄汁並不是很耐貯存，只能貯放於低溫下儘量減緩色素降低的趨勢。

6. 官能品評：不同貯藏條件下康歌葡萄汁每隔一段時間取出所作的品評結果如圖4、圖5及圖6。可知在 0°C 貯藏的果汁經四個月後顏色、香味、總體感覺在統計上並無顯著的差異，而且平均值都在5~6之間，此表示品質保存尚好，隨貯藏之時間變化甚少。同樣地，高溫貯藏的果汁香氣、味道、總體感覺隨時間之增加亦無明顯地差異，只是總體感覺的平均值相當低，表示從第三個星期起，品質已有明顯劣變的情形。

各種貯藏條件，隨時間的增加顏色均有明顯的差異，即分數往低的趨勢。香味的變化，在室溫下照光與否其品評結果則為不規則性，此可能與品評人員有關，也可能光照對香味的變化並無明顯的作用，而高溫(35°C)下的果汁，品評人員給予香味評分却相當高，可能是具有特殊風味受到品評人員的喜愛。

總合化學成分分析與品評的結果，我們可以得知要獲得高品質的康歌葡萄汁，必須加工與貯藏的條件互相配合，適當的碎果加熱溫度配合酵素處理，可以獲得品質優良的葡萄汁，而為了顏色穩定性的關係，若要其保持品質穩定低劣變應以低溫貯藏為佳。

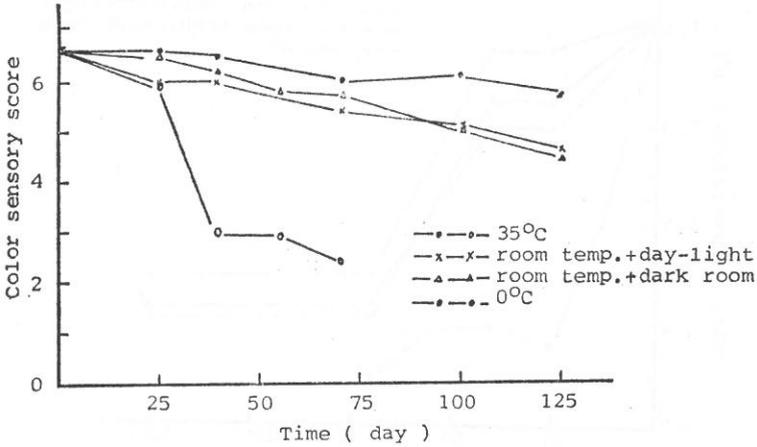


Fig. 4. Effect of storage conditions on color score of concord grape juice.

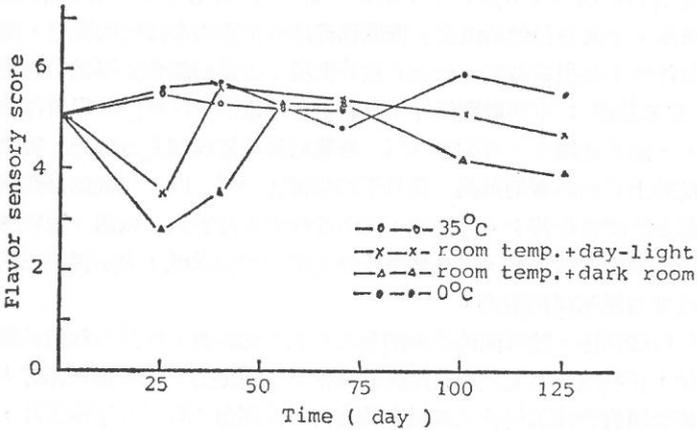


Fig. 5. Effect of storage conditions on flavor score of concord grape juice.

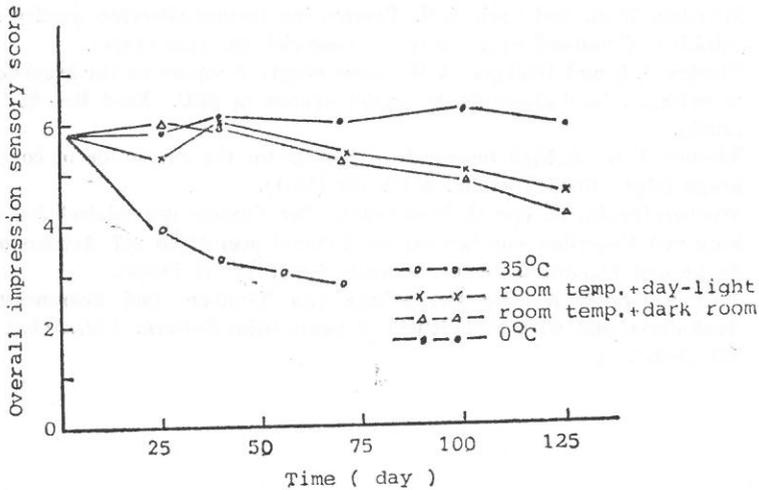


Fig. 6. Effect of storage conditions on overall impression score of concord grape juice.

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## **Effects of Crushing Temperature of Mash and Storage Conditions on the Quality of Concord Grape Juice**

HSUEH-ERR CHEN

### **ABSTRACT**

The chemical analysis and sensory evaluation techniques were used to investigate the effects of heat treatment on the quality of concord grape juice. The influences of different storage conditions on the juice quality were also studied.

# CARBAMATE INSECTICIDE REMOVAL IN LAUNDERING FROM COTTON AND POLYESTER FABRICS

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## ABSTRACT

Previous laundering studies have focused primarily on the organophosphate and organochlorine insecticides. Few studies have evaluated laundering procedures that are effective in removing carbamate insecticides from contaminated textile items. Because of the potential toxicity of carbofuran and methomyl, and their popular use to control field crop insect problems in Kansas, the purpose of this study was to evaluate the effectiveness of various laundering procedures [i.e., three detergents (All, Tide, and Wisk), and two laundering temperatures (60°C wash/49°C rinse, and 49°C wash/40°C rinse)] in removing carbofuran and methomyl contaminants from the contaminated cotton and polyester fabrics. Percentages of insecticides residue remaining on fabrics after laundering were analyzed by using high performance liquid chromatography (HPLC) with a fluorescence detector. The relative toxicity of the insecticide residues left on fabric after laundering was investigated by using a bioassay test method with *Drosophila melanogaster* Meigen.

The carbofuran contaminants could be readily removed by all laundering procedures investigated from the contaminated cotton and polyester fabrics. The methomyl contaminated cotton fabric could also be cleaned easily by the laundering procedures investigated in this study. However the interaction among polyester, methomyl and warm (or hot) laundering temperatures resulted in the highest percentages of insecticide residue remaining on laundered fabric. After 72 hours of bioassay test, mortality of fruit flies occurred on the methomyl-treated polyester fabric laundered in warm water. No fruit fly mortality was detected for the other fabric, insecticide and laundering temperature combinations. Consistent findings were obtained from the HPLC analysis and bioassay tests. Additionally, no significant differences were found among the three detergents investigated in this study.

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## INTRODUCTION

Pesticides provide a fast and efficient method of controlling pests in our environment to increase agricultural production and protect people from diseases; however, many pesticidal chemicals are toxic, persistent and polluting. The potential danger of pesticide products varies, depending on the chemical class, concentration, and formulation. Agricultural workers, commercial pesticide formulators and applicators as well as consumers who use these products in and about the home need to exert precautionary measures to reduce exposure to pesticides. Generally, the probability of exposure increases with the frequency of handling pesticides.<sup>(2,24)</sup>

Clothing worn by individuals who work with pesticides can be contaminated during the preparation, transference, and application of pesticides.<sup>(8-9,25-28)</sup> If the contaminated clothing is not laundered properly, pesticide residues on clothing may be absorbed through the skin, resulting in chronic exposure, illness, and even death. The most effective methods should be used in laundering contaminated clothing, thereby reducing the possibility of dermal exposure and absorption as well as cross-contamination of other clothing items in the wash. Current research has shown that effective removal of pesticide contaminants from textiles is dependent on numerous factors such as the chemical structure and class of the pesticidal chemical; product formulation, additives, and concentration; fiber type, fabric construction characteristics, and finishes; laundering procedures, detergent type, water temperature, additives, etc.<sup>(4-12, 14, 16-23)</sup>

Previous laundry studies have focused primarily on the organophosphate and organochlorine insecticides.<sup>(4-7,9-12,16-23)</sup> Few studies<sup>(16,21-23)</sup> have evaluated laundering procedures that are effective in removing carbamate insecticides from textiles. The carbamate insecticides were developed primarily in the 1960s. In general, carbamates tend to be more biodegradable, and some are considerably less toxic to nontarget species than other classes of insecticides. Governmental bans and restrictions on the use of organochlorine

compounds and the organophosphorus resistant strains of insects have resulted in an increase in the use of carbamate insecticides. The carbamates act in mammals as autonomic drugs, stimulating structures innervated by cholinergic nerves. This parasympathomimetic action results from the inhibition of acetylcholinesterase to allow local accumulation of acetylcholine. Because of the frequency of use, toxicity, and potential hazards associated with carbamate pesticides, this study examined the efficiency of various laundering conditions in removing selected carbamate pesticides (carbofuran and methomyl) from cotton and polyester fabrics which were similar in weight and construction characteristics to those commonly used in apparel items. Fabric samples were contaminated with specified concentrations and amounts of carbofuran or methomyl, laundered under controlled conditions, and then quantitatively evaluated to determine the biological activity and amount of insecticide residue remaining on the contaminated fabric after laundering.

## EXPERIMENTAL METHODS

### Fabric Selection and Preparation

The fabrics used in this study were a 100% bleached mercerized cotton (Style 419A) and 100% Dacron 54 polyester (Style 767) which were purchased from Testfabrics, Inc. These fabrics were similar in weight and construction and did not contain any finishes or dyestuffs, thereby minimizing potential problems in the extraction and identification of the insecticide residues.

Specimens measuring  $7.6 \times 7.6 \text{ cm}^2$  ( $3.0 \times 3.0 \text{ in}^2$ ) were cut from each fabric which had been conditioned for 24 hours in a standard atmosphere for testing ( $20 \pm 1^\circ\text{C}$  and  $65 \pm 2\%$  relative humidity). The lengthwise and widthwise directions were parallel to the warp and filling yarns. The specimens were taken no nearer to the selvage of the fabric than one tenth of the width of the fabric. In order to prevent yarn ravelling during laundering, the edges of specimens were serged by using sewing thread with the same fiber

content as the specimens.

Specimens were subjected to three prewashings to remove impurities. An adaptation of the procedures outlined in AATCC Test Method 135-78, Dimensional Changes in Automatic Home Laundering of Woven and Knit Fabrics, were used for prewashing.<sup>(1)</sup> Within these procedures, the specimens were washed in a Sears Kenmore automatic washing machine on a normal setting using a full water level, a 14 minute hot water ( $60 \pm 2^\circ\text{C}$ ) wash, 90 grams of AATCC detergent WOB, a 1.8 kg load, and a warm water ( $40 \pm 2^\circ\text{C}$ ) rinse. During the second and third cycles, the specimens were washed without detergent. After prewashing, the specimens were air dried and stored in clean plastic bags for future use.

#### **Preparation and Application of Insecticide Formulations**

The commercial pesticide formulations selected for this study were Furadan® 4F (i.e., carbouran produced by the FMC Corporation) and Lannate® L (i.e., methomyl produced by E.I. du Pont de Nemours & Company). According to the field crop insect management recommendations by the Kansas Agricultural Experiment Station and insecticide manufacturer's publications,<sup>(3,13,15)</sup> the highest concentration of these carbamates commonly used in field is a 4.0% (w/w) aqueous formulatjōn. Hence, this concentration was selected for fabric specimen contamination using deionized distilled water as the diluent. Additionally, these 4.0% (w/w) carbamate formulations provided an effective dosage level (100% kill) to the fruit flies used in the bioassay tests. A portion of diluted formulation of each carbamate pesticide was freshly prepared before every experimental replication and stored in a refrigerator at  $5^\circ\text{C}$  to keep consistant properties.

The fabric specimens measuring  $7.6 \times 7.6 \text{ cm}^2$  were suspended horizontally over polystyrene boards ( $10 \times 10 \times 1 \text{ cm}^3$ ) with stick pins so that there was approximately a 1.5 centimeter distance between the back of the specimen and the face of the polystyrene board. The boards were covered with aluminum foil which was replaced

after each subsequent insecticide treatment.

Since the weight of a polyester specimen was 1.1 times the weight of a cotton specimen, the amounts of various chemical solutions and solvents (i. e., diluted carbamate formulations used for specimen contamination, wash and rinse liquors used in laundering and methanol used for insecticide residue extraction) were adjusted to maintain the 1.1 to 1.0 fabric weight ratio. For example, each cotton specimen was treated with 1.50 ml of the diluted carbamate formulation, therefore, a 1.65 ml of the same formulation was used to treat a polyester specimen.

A 10 ml burette, mounted on a burette stand and housed in a fume hood, was used to apply the carbamate formulations to the cotton and polyester specimens. The tip of the burette was approximately two centimeters from the surface of the specimen during application. The polystyrene board with the suspended specimen mounted above was moved back and forth at a constant rate during treatment to ensure even application of the insecticide formulation. Pesticide respirator, goggle, lab coat and plastic gloves were worn to minimize exposure to the insecticides. After applying the carbamate formulations, the specimens were air dried in a fume hood for 48 hours before laundering or extraction (i. e., for the blanks).

For each fabric type, carbamate insecticide, detergent, and laundering temperature, two sets of specimens were treated, one set for the high performance liquid chromatography analysis and the other set for the bioassay test. In addition, two sets of specimens of each fabric type which served as "blanks" were contaminated with the carbamate formulations, extracted with methanol, and then analyzed by using high performance liquid chromatography and the bioassay test.

### **Laundering**

AATCC Test Method 61-75: Colorfastness to Washing, Domestic; and Laundering, Commercial: Accelerated<sup>(1)</sup> was modified to establish the laundering procedures to simulate one laundering

cycle. All volumes used were initially calculated from a 12 gallon wash load to duplicate the home laundering situation. The use of deionized distilled water was necessary to reduce water impurities (i.e., metallic hard water ions) and to facilitate accurate residue analyses after laundering. An Atlas Launder-Ometer (Model LHT) equipped with stainless steel canisters was used as the laundering equipment. The canister lids lined with rubber gaskets provided efficient laundering without leakage. In addition, teflon liners were used in the lids to prevent retention of carbamate residues by the rubber gaskets. Twenty-five steel balls (0.64 cm diam.) were placed in each canister to simulate the abrasion action which occurs in laundering.

Three detergents, All (nonionic), Tide (anionic) and Wisk (nonionic-anionic) were selected for this study on the basis of consumer use and ionic properties of the surfactant. For each detergent type plus the controls (i.e., deionized distilled water only without the detergent), the following wash and rinse cycles were investigated: (a) a 12 minute hot wash at  $60 \pm 1^\circ\text{C}$ , followed by two five-minute warm rinses at  $49 \pm 1^\circ\text{C}$ , and (b) a 12 minute warm wash at  $49 \pm 1^\circ\text{C}$  followed by two five-minute warm rinses at  $40 \pm 1^\circ\text{C}$ . Freshly prepared 0.2% (w/w) detergent solutions were used for each laundering (i.e., 0.30 g of detergent per 150 ml detergent solution per cotton specimen and 0.33 g of detergent per 165 ml detergent solution per polyester specimen). The pH value of wash liquors was determined before laundering by using a Beckman Zeromatic pH meter.

After washing and rinsing, the fabric specimens were dried for eight hours by hanging them on a clothes line under atmospheric conditions ( $25 \pm 2^\circ\text{C}$  and  $60 \pm 5\%$  relative humidity). Then half of the dried laundered specimens were placed individually by using tweezers in labeled 500 ml Erlenmyer flasks and capped tightly for later extraction (i.e., wrapped with one layer of aluminum foil underneath and two layers of parafilm on top). The rest of the dried specimens were stored individually in labeled sample vials (10 dram each) for future bioassay tests. The glasswares containing

the dried specimens were placed in a refrigerator at 5°C until needed.

### **High Performance Liquid Chromatography (HPLC) Analyses**

#### *Extraction*

Before extraction, the refrigerated specimens were placed in atmospheric conditions until reaching room temperature. The specimens were extracted three times for 40 minutes with 50 ml of distilled in glass grade methanol (Burdick and Jackson Laboratories, Inc.) each time by using a mechanical shaker (i.e., Burrell Wrist-Action Shaker Model BB). Following completion of the third shaking, an additional 50 ml of methanol was used to rinse the stopper, specimen, and flask. This final rinse was combined with the three methanol extracts in a 500 ml round-bottomed flask for future concentration. For extracting polyester specimens, the volume of methanol was adjusted to 55 ml.

#### *Concentration*

A rotary evaporator (i.e., Buchi Rotavapor-R) connected to a water aspirator was used to concentrate the methanol extracts. The concentrated extract was transferred to a sample vial with aluminum lined cap. Three methanol rinses were used to dissolve any carbamate residue remaining in the flask and then combined with the concentrated extract in the sample vial to bring the total volume to 10 mls (i.e., 15 mls for blanks). These concentrated methanol extracts were stored in refrigerators at 5°C until HPLC analyses.

#### *HPLC Analyses*

The carbamate residues in the methanol extracts were analyzed by using an HPLC postcolumn fluorometric labeling technique. The analytical column (Du Pont Co.) used was 25 cm × 4.6 mm i.d. packed with 6 mm Zorbax C-8 spherical particles. Additionally, a guard column (Whatman Inc.) 7 cm × 2.1 mm i.d. packed with 25-37 μm Co-Pell ODS was used to remove impurities from the injected samples. The mobile phase was a 40% Acetonitrile-H<sub>2</sub>O solution with a flow rate 1 ml/minute and  $1.2 \times 10^4$  KPa pressure. After 20 μl of the carbamate methanol extract was injected into

and separated by HPLC, the carbamate residues were hydrolyzed by reacting with 0.05N NaOH at a 0.05 ml/min flow rate under 100°C in a hydrolysis chamber (RFL Industries, Inc.). Following the hydrolysis step, the N-methyl groups of carbamate residues were labeled by reacting with a special reactant (i.e., 0-phthalaldehyde + 2-mercaptoethanol in 0.05 M sodium tetraborate) and detected by a Perkin-Elmer 650-105 Fluorescence Spectrophotometer with a scan speed of 120 nm/min., an emission wavelength of 455 nm, and an excitation wavelength of 340 n.m. The peak height and retention time of sample peaks were measured and compared to the EPA standard peaks to determine the amount of carbamate residue remaining left on the specimens after laundering.

#### **Bioassay Tests**

The bioassay tests were used to determine if carbamate residues remaining left on the fabric specimens after laundering were biologically active. *Drosophila melanogaster* Meigen (Canton "S", a wild normal strain), commonly known as the fruit fly, was selected for this study due to its extreme sensitivity to insecticides. The specimens placed in sample vials originally stored in a refrigerator were allowed to reach test conditions ( $25 \pm 2^\circ\text{C}$  and  $60 \pm 5\%$  relative humidity) before conducting the bioassay tests. Twenty fruit flies, 24- to 30-hour-old, were transferred into each specimen vial. Then, the specimen vials were stoppered with black cotton balls (i.e., white cotton dyed with 5% o.w.f. C.I. Direct Black 38 using a 30 to 1 liquid to goods ratio) which were barely wetted out with 30% sugar water to provide enough food, moisture, and ventilation during the test period. The vials containing the test specimens and fruit flies were stored at room temperature. The mortality of fruit flies was counted and recorded after 24, 48, and 72 hours.

#### **Statistical Analyses**

This study was designed as a factorial experiment with four factors: fabrics, carbamates, detergents, and wash and rinse bath water temperatures. Two complete replications were conducted of the entire experimental procedures. The percent carbamate residue

Table 1. Mean Insecticide Remaining on Laundered Fabrics

Insecticide	Fabric	Laundering Temperature	Detergent	Insecticide Remaining	
				Weight of Insecticide* 10 <sup>-3</sup> mg	Percent 10 <sup>-3</sup> %
Carbofuran	Cotton	Warm	All	ND	0
			Tide	ND	0
			Wisk	0.37	0.60
			Water only	0.34	0.55
		Hot	All	ND	0
			Tide	ND	0
			Wisk	ND	0
			Water only	ND	0
	Polyester	Warm	All	ND	0
			Tide	0.70	1.1
			Wisk	1.1	1.6
			Water only	3.8	5.6
		Hot	All	3.1	4.6
			Tide	0.81	1.2
			Wisk	2.9	4.4
			Water only	1.9	2.8
Methomyl	Cotton	Warm	All	1.8	2.8
			Tide	2.6	4.2
			Wisk	1.9	3.0
			Water only	2.6	4.2
		Hot	All	1.4	2.4
			Tide	5.0	8.2
			Wisk	2.4	3.8
			Water only	6.9	11
	Polyester	Warm	All	42	62
			Tide	42	62
			Wisk	41	60
			Water only	34	50
		Hot	All	14	21
			Tide	14	21
			Wisk	16	24
			Water only	13	19

\* ND means no residue detected.

remaining after laundering and percent mortality of the fruit flies were analyzed according to the four factors as mentioned above by using Analysis of Variance and Duncan's Multiple Range Test.

## RESULTS AND DISCUSSION

The mean percentages of insecticide remaining on the cotton and polyester specimens, as presented in Table 1, range from 0% to  $62 \times 10^{-3}\%$ . Thus, all of the laundering procedures including the water only treatment were effective in reducing these carbamate insecticide contaminants on the cotton and polyester fabrics. Since there were slight differences among the percentages of insecticide remaining on the cotton and polyester specimens, depending on insecticide type, wash/rinse water temperature and detergent type, the data was analyzed by using the Analysis of Variance (ANOVA) and Duncan's Multiple Range Statistical Tests. According to the results to the ANOVA test, the variables and variable interactions that cause significant difference at the 0.05 level of confidence were fabric, insecticide, laundering temperature, fabric  $\times$  insecticide, fabric  $\times$  temperature, insecticide  $\times$  temperature, and fabric  $\times$  insecticide  $\times$  temperature. Hence, the significant effects of the main variables (fabric, insecticide, laundering temperature, and detergent) on the insecticide remaining were confounded by the second and third order interactions among these variables. Detergent type was not a significant variable.

In general, the polyester fabric had significantly higher percentages of insecticide remaining after laundering than did the cotton fabric. These differences may have been attributed to inherent fiber properties as well as yarn and fabric construction characteristics. Factors that may have facilitated carbamate contaminant removal from the cotton fabric during laundering include a nonuniform fiber cross-section compared to polyester which aided in lowering the interfacial tension at the fabric/water interface, the presence of hydroxyl groups in the cellulosic molecules which imparts hydrophilicity, and a looser warp yarn construction. These factors would assist in wicking and wetting of cotton fabric during

laundering to facilitate insecticide residue removal.

The methomyl-treated fabrics had significantly higher percentages of insecticide remaining after laundering than did the carbofuran-treated fabrics. This difference may have been attributed to the chemical properties of the insecticides as well as their formulations. The water suspension of granular carbofuran particles penetrated the fabric less readily and was more likely to distribute itself on the fabric surface, thus facilitating its removal during laundering. In contrast, the methomyl molecules were in solution form which increased fiber penetration and made its contaminant removal more difficult during laundering. Additionally, carbofuran is unstable in alkaline media. Since all of the detergent solutions used in this study were alkaline, this would further enhance the degradation of carbofuran in laundering.

The warm laundering procedure (49°C wash/40°C rinse) was slightly less effective in removing the carbamate insecticides compared to the hot laundering procedure (60°C wash/49°C rinse). The temperature effects could be related to increased polymer chain mobility and wetting, increased detergent efficiency, thermal degradation of the insecticide, or a combination thereof.

Statistical homogeneity was found for the three detergents (All, Tide and Wisk) and water-only laundering processes. Thus, the detergents were comparable in effectiveness. The carbamate insecticides evaluated in this study also were readily removed by hot or warm water wash without using detergents. Hence, the similarity among detergent types was attributed to the water solubility of the carbamate insecticide and their effective removal by water only.

In this study, none of the fruit flies died after 24 and 48 hours in the bioassay tests. Therefore, only the percentages of mortality after 72 hours, were used for data comparison and statistical analysis. The mean percentages of fruit fly mortality, as presented in Table 2 ranged from 0% to 40%. However, almost all specimens had 0% mortality of fruit flies, except the methomyl-treated polyester specimens laundered in warm water which had mean

Table 2. Mean Mortalities of Fruit Flies

Insecticide	Fabric	Laundering Temperature	Detergent	No. of Dead Flies	Mortality, %
Carbofuran	Cotton	Warm	All	0	0
			Tide	0	0
			Wisk	0	0
			Water only	0	0
		Hot	All	0	0
			Tide	0	0
			Wisk	0	0
			Water only	0	0
	Polyester	Warm	All	0	0
			Tide	0	0
			Wisk	0	0
			Water only	0	0
		Hot	All	0	0
			Tide	0	0
			Wisk	0	0
			Water only	0	0
Methomyl	Cotton	Warm	All	0	0
			Tide	0	0
			Wisk	0	0
			Water only	0	0
		Hot	All	0	0
			Tide	0	0
			Wisk	0	0
			Water only	0	0
	Polyester	Warm	All	6	30
			Tide	6	30
			Wisk	8	40
			Water only	7	35
		Hot	All	0	0
			Tide	0	0
			Wisk	0	0
			Water only	0	0

percentages of mortality ranging from 30% to 40%.

As mentioned previously, there was a significant three-way interaction among the variables: fabric, insecticide, and laundering temperature. The carbofuran insecticide was removed easily from both cotton and polyester fabrics by using either warm or hot laundering temperatures. The methomyl insecticide also could be removed effectively from cotton fabric by using warm or hot laundering procedures. Slightly higher percentages of methomyl residue remained on polyester specimens, especially after warm laundering with and without detergent. Additionally, this was the only treatment combination that caused the fruit flies to die at 72 hours in the bioassay test. Thus, the test data from both the HPLC and bioassay tests were in agreement with respect to the relative differences in the amount of insecticide on the fabrics after laundering.

### CONCLUSION

The percentages of insecticide remaining on the cotton and polyester fabrics ranged from 0% to  $62 \times 10^{-3}\%$ . The mean quantity of carbamate insecticide initially applied to cotton and polyester specimens was 60.9 mg and 67.0 mg, respectively. Therefore, the amounts of insecticide residues remaining on fabrics after laundering were no more than  $42 \times 10^{-3}$  mg which represents minute quantities. Thus, the significant differences among the concentrations of insecticide residue remaining on the fabrics after laundering may have little practical value. Additional research is needed to determine if water temperature has an appreciable effect on the efficiency of methomyl removal from polyester. The results of the bioassay tests, however, suggest that even small quantities of insecticide residue are biologically active.

The results of this study do show that carbamate insecticides are more readily removed in laundering compared to other classes of insecticides such as the organophosphates and organochlorines evaluated in previous studies. Furthermore, the warm and hot water laundering procedures used in this study were effective in removing

field strength concentration (4.0%) of carbofuran and methomyl from cotton and polyester medium weight fabrics. No previous research had evaluated the ease with which methomyl is removed from contaminated textiles during laundering. The results obtained are consistent with other laundering studies on carbamate insecticides.

In many instances, the use and handling of the more toxic, persistent and polluting pesticides cannot be avoided. However, if an agricultural worker, gardener, pesticide applicator, etc. is able to select an insecticide product for particular use, ease of removal during laundering should be considered in addition to other factors such as toxicity, applicability, availability, price, etc.

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# 清洗胺基碳酸酯殺蟲劑污染之 棉纖維和多元酯纖維織物

喬昭華 BARBARA REAGAN\*

## 摘 要

殺蟲劑是一種迅速有效控制蟲害的方法。它可以幫助增加農業產量和防止疾病的傳染。缺點是許多殺蟲劑本身有毒性，殘存量偏高，而且容易造成環境污染。在殺蟲劑的製造，運送及使用過程中人們所穿的衣服很容易受到污染。如果這些衣服未經過適當的清洗，則衣服上殘存的殺蟲劑很可能會被皮膚吸收，進入人身造成慢性痼疾，甚至可能致死。因此如何有效地清除污染衣服上的殺蟲劑是十分需要的。

以前的研究報告偏重於有機磷及有機氯殺蟲劑污染衣服的清洗方法。很少研究報告對清除污染衣服上的 carbamate 殺蟲劑作一有系統的分析。在坎州，carbofuran 及 methomyl 兩種具潛在性毒性的殺蟲劑使用非常廣泛。這篇論文的主題即在探討在不同的洗滌條件下（使用三種清潔劑 All, Tide, Wisk，及二種溫度 60°C 清洗 / 49°C 洗滌和 49°C 清洗 / 40°C 洗滌），如何清洗被 carbofuran 及 methomyl 污染的棉布及多元酯纖維布。殘留殺蟲劑的劑量用 HPLC 測定（使用螢光探測器）。果蠅用來作生物試驗，測定洗滌後留在纖維上殺蟲劑的相對毒性。

殘留在棉纖維及多元酯纖維上的 carbofuran 在所有實驗條件下都很容易移去。殘留在棉纖維上的 methomyl 也很容易移去。但多元酯纖維，methomyl 及洗滌溫度三者之間的交互作用使得殘留在多元酯纖維上的 methomyl 殺蟲劑劑量偏高。生物實驗中亦指出 72 小時後，殘留在多元酯纖維上的 methomyl 是唯一能使果蠅死亡的殺蟲劑。以上實驗結果均經反覆求證。而且 HPLC 及生物實驗的結果相符合。清潔劑種類的選擇在此研究報告中並未造成統計分析上有意義的差異。三種清潔劑顯示同樣的洗滌效果。

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**ABSTRACTS OF PAPERS BY FACULTY  
MEMBERS OF THE COLLEGE OF SCIENCE  
AND ENGINEERING THAT APPEARED  
IN OTHER JOURNALS DURING  
THE 1984 ACADEMIC YEAR**

**On the Simplification of Generalized Conjugate-Gradient  
Methods for Nonsymmetrizable Linear Systems**

KANG C. JEA and DAVID M. YOUNG\*

Linear Algebra And Its Applications 52/53: 399-417 (1983)

The conjugate-gradient (CG) method, developed by Hestenes and Stiefel in 1952, can be effectively used to solve the linear system  $Au = b$  when  $A$  is *symmetrizable* in the sense that  $ZA$  and  $Z$  are symmetric and positive definite (SPD) for some  $Z$ . A number of generalizations of the CG method have been proposed by the authors and by others for handling the nonsymmetrizable case. For many problems the amount of computer memory and computational effort required may be so large as to make the procedures not feasible. Truncated schemes are often used, but in some cases the truncated methods may not converge even though the nontruncated schemes converge. However, it is well known that if  $A$  is symmetric, the generalized CG schemes can be greatly simplified, even though  $A$  is not SPD, so that the truncated schemes are equivalent to the nontruncated schemes. In the present paper it is shown that such a simplification can occur if a nonsingular matrix  $H$  is available such that  $HA = A^T H$ . (Of course, if  $A = A^T$ , then  $H$  can be taken to be the identity matrix.) It is also shown that such an  $H$  always exists; however, it may not be practical to compute  $H$ . These results are used to derive three variations of the Lanczos method for solving nonsymmetrizable systems. Two of the forms are well known, but the third appears to be new. An argument is given for choosing the third form over the other two.

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## Phragmen-Lindelöf Theorem in a Cohomological Form

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Proceedings of the American Mathematical Society,  
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The main result of this paper is as follows. Given functions  $\phi_1(\varepsilon), \dots, \phi_v(\varepsilon)$  which are holomorphic in sectors  $S_1, \dots, S_v$ , respectively, where  $S_1 \cup \dots \cup S_v = \{\varepsilon: |\arg \varepsilon| < \pi/2\alpha, 0 < |\varepsilon| > \rho\}$  for  $\alpha > 1$ ,  $\rho > 0$ , set  $\phi_{jk} = \phi_j - \phi_k$  if  $S_j \cap S_k \neq \emptyset$ . Then  $\{\phi_{jk}\}$  satisfy cocycle conditions  $\phi_{jk} + \phi_{kl} = \phi_{jl}$  whenever  $S_j \cap S_k \cap S_l \neq \emptyset$ . In addition to the conditions  $|\phi_1| < M_0$  and  $|\phi_v| < M_0$  on the two rays of the boundary (i.e.  $\arg \varepsilon = \pi/2\alpha$ ), and  $|\phi_j(\varepsilon)| \leq A \exp(c/|\varepsilon|)$  in  $S_j$  for some positive numbers  $A$  and  $c$ ,  $j=1, 2, \dots, v$ , if the  $\{\phi_j\}$  satisfy the conditions  $|\phi_{jk}| < M_0$  on  $S_j \cap S_k (\neq \emptyset)$ , then we get  $|\phi_j| < M$  on  $S_j$ ,  $j=1, 2, \dots, v$ . (From the cohomological point of view, we can get global results for  $\phi_j$ , once the local data on cocycles is known.)

## Necessary Condition for Ackerberg-O'Malley Resonance

CHING-HER LIN

Chinese Journal of Mathematics,  
Volume 11, Number 3, September 1983, pp. 181-192

We consider boundary value problems for the differential equation  $\varepsilon y'' + f(x, \varepsilon) y' + g(x, \varepsilon) y = 0$ , where  $f(x, \varepsilon)$  has a single zero at  $x=0$  for all  $\varepsilon$ , with  $f > 0$  for  $x < 0$  and  $f < 0$  for  $x > 0$ . The main result of this paper is to determine necessary conditions for taking place of Ackerberg-O'Malley resonance.

## The Sufficiency of the Matkowsky Condition in the Problem of Resonance

CHING-HER LIN

Transactions of the American Mathematical Society,  
Volume 278, Number 2, August 1983, pp. 647-670

We consider the sufficiency of the Matkowsky condition concerning the differential equation  $\epsilon y'' + f(x, \epsilon) y' + g(x, \epsilon) y = 0$  ( $-a \leq x \leq b$ ) under the assumption that  $f(0, \epsilon) = 0$  identically in  $\epsilon$ ,  $f_x(0, \epsilon) \neq 0$  with  $f > 0$  for  $x < 0$  and  $f < 0$  for  $x > 0$ . Y. Sibuya proved that the Matkowsky condition implies resonance in the sense of N. Kopell if  $f$  and  $g$  are convergent power series for  $|\epsilon| < \rho$  ( $\rho > 0$ ),  $f(x, 0) = -2x$  and the interval  $[-a, b]$  is contained in a disc  $D$  with center at 0. The main problem in this work is to remove from Sibuya's result the assumption that  $D$  is a disc.

### Accelerating Nonsymmetrizable Iterative Methods

DAVID M. YOUNG\*, KANG C. JEA and DAVID R. KINCAID\*

Elliptic Problem Solvers II, G. Birkhoff & A. Schoenstadt, eds.  
Academic Press, 1984, pp. 323-342

In this paper we consider some iterative procedures for solving the linear system

$$Au = b \quad (1.1)$$

where  $A$  is a given real nonsingular  $N \times N$  matrix and  $b$  is a given real  $N \times 1$  vector. Occasionally, we will assume that  $A$  is symmetric and positive definite (SPD).

The algorithms which we will consider involve the use of a simple one-step, or "basic," iterative method usually combined with an acceleration procedure such as Chebyshev acceleration or conjugate gradient (CG) acceleration. For a certain class of basic iterative methods, referred to as "symmetrizable methods," these acceleration procedures are very effective. However, if the matrix  $A$  of the system (1.1) is not SPD, or is not at least *similar* to an SPD matrix, the basic iterative method may not be symmetrizable. Moreover, some iterative methods are not symmetrizable even if the matrix  $A$  is SPD. Acceleration procedures which are efficient and effective for the symmetrizable case may not be appropriate for the nonsymmetrizable case.

The object of this paper is to describe some recent work which has been done at The University of Texas at Austin and elsewhere on the development of procedures for accelerating nonsymmetrizable iterative methods. Because of space limitations our discussion cannot be in any sense complete, and a number of important contributions will not be discussed. Approaches which we do discuss include the use of the GCW method of Concus and Golub [1976] and of Widlund [1978], the use of the normal equations and related equations, Chebyshev acceleration, and some generalized CG acceleration procedures. Normally, the generalized CG acceleration procedures, in their idealized form, are too expensive in terms of computer time and storage for practical use. In the symmetrizable case the formulas simplify since many of the terms vanish. In some nonsymmetrizable cases, it is possible to achieve similar simplifications. We describe work on such simplifications done by Jea [1982] and Jea and Young [1983] as well as work of Faber and Manteuffel [1983]. We also show that the simplifications of Jea and Young [1983] can be used to derive three alternative forms of the Lanczos method (see Lanczos [1950, 1952]). A theoretical basis is given for choosing one of the forms in preference to the other two more frequently used forms.

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### **Energy Loss Scaling for Small Angle Rotationally Inelastic Scattering**

FRANK E. BUDENHOLZER, MING-HSIUNG CHANG  
and PING-PIAO LÜ

J. Phys. Chem. 89 (1985) 199-200

Using classical perturbation scattering theory, it has been previously shown that for small angle, rotationally inelastic scattering at moderately high energies the rotational energy transfer associated

with a specific reduced deflection angle,  $\tau = E\theta$ , scales as the center-of-mass energy  $E$ . This scaling relationship is discussed and a verification using full classical trajectories is presented.

## 防止坡面冲蝕之乳化瀝青之合成及應用

周 善 行

農發會「山坡地保育利用研究報告彙編」，73年6月

本計畫研究乳化瀝青之合成過程，及其對防止坡面冲蝕之效果。對於可能影響瀝青乳化過程之因素，諸如瀝青與陽離子界面活性劑之種類及其與水之混合比例，以及混合液之溫度與酸鹼度等，均曾加以詳細的分析研究。所製成之乳化瀝青並經過篩析試驗、殘渣試驗、儲存安定性試驗、以及靜置分離試驗等，獲得最理想之製造配方。氯化鈣與澱粉可加入製成之乳化瀝青中，以增加其儲存安定性。其中四種配方以不同的濃度與百喜草及百慕達草的種子混合，噴植於木柵萬芳社區一四〇高地之斜坡上，發現其植生效果良好，覆蓋率幾達百分之百，遠較未使用乳化瀝青者為佳。然而，草種植生效果受乳化瀝青之種類與濃度之影響不大。因此，我們建議採用市售之乳化瀝青以水稀釋後，普遍作為邊坡穩定綠化之用。

## Science and Religion: Seeking a Common Horizon

FRANK E. BUDENHOLZER

Zygon, Vol. 19, No. 3 (September 1984)

The thought of Bernard Lonergan provides an epistemological position that is both true to the exigencies of modern science and yet open to the possibility of God and revealed religion. In this paper I outline Lonergan's "transcendental method," which describes the basic pattern of operations involved in any act of human knowing, and discuss how Lonergan uses this cognitional theory as a basis for an epistemological position of critical realism. Then I explain how his approach handles some philosophical problems raised by classical and modern science and show how his thought provides an intelligible link between the scientific and religious horizons.

## Preparation of Enamines Catalyzed by Lewis Acids in the Presence of Solid Supports

SHANG-SHING P. CHOU and CHENG-WU CHU

*J. Chin. Chem. Soc.*, **31**, 351-356 (1984)

A simple and effective preparation of enamines from bulky ketones and secondary amines has been achieved with the aid of Lewis acid on various solid supports. The optimized yields were higher than those obtained without the solid support. Factors affecting the yield and regioselectivity of these reactions were also studied. Evidence showed that the reaction proceeded simultaneously in solution and on the solid support.

## Preparation, Structure and Reactivity of a (Pentamethycyclopentadienal) Titanium Dimer Bridged by Oxygen and Tetramethylenecyclopentadienyl

IVAN J. B. LIN, FRANK BOTTOMLEY\*,

GABRIEL O. EGHAREVBA\* and

PETER S. WHITE\*

*Organometallic*, **3**: 550, 1985

The reaction between " $\text{Cp}^*_2\text{Ti}$ " ( $\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$ ) and  $\text{N}_2\text{O}$  in toluene affords  $[(\text{Cp}^*\text{Ti})_2-\mu-(\eta^1:\eta^5\text{-C}_5(\text{CH}_3)_4\text{CH}_2)(\mu\text{-O})_2]$  (I). The structure of the product was determined by X-ray diffraction; it crystallizes in the orthorhombic space group *Pnma* with  $a=10.650$  (5) Å,  $b=15.283$  (3) Å,  $c=17.064$  (8) Å, and  $Z=4$ . The structure was refined to  $R=0.048$  and  $R_w=0.052$  for 256 parameters and 1226 observed reflections. The molecule consists of two  $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Ti}$  units bridged unsymmetrically by two oxygen atoms ( $\text{Ti}(1)\text{-O}=1.961$  (3) Å and  $\text{Ti}(2)\text{-O}=1.787$  (3) Å) and an  $\eta^1:\eta^5\text{-C}_5(\text{CH}_3)_4\text{CH}_2$  ligand ( $\eta^1$  to  $\text{Ti}(2)$  and  $\eta^5$  to  $\text{Ti}(1)$ ). The bond distances are in agreement with the description of the  $\text{C}_5(\text{CH}_3)_4\text{CH}_2$  bridge as a truly methylenic  $\eta^1:\eta^5$  ligand and not as an  $\eta^2:\eta^4$  olefinic ligand.

The Ti(2)-CH<sub>2</sub> distance is 2.178 (6) Å; all other C-C and Ti-C distances are normal for Cp\*Ti units. The methylenic description of C<sub>5</sub>(CH<sub>3</sub>)<sub>4</sub>CH<sub>2</sub> is supported by NMR ( $\delta$ (CH<sub>2</sub>) 50.4 in the <sup>13</sup>C spectrum) and IR ( $\nu$ (C-H) 2,960, 2,900, and 2,850 cm<sup>-1</sup>) spectroscopies and also explains the remarkable stability of I (no reaction with H<sub>2</sub>, CO, or C<sub>2</sub>H<sub>4</sub>) since both titanium atoms are Ti(IV). With HCl, I gives Cp\*<sub>2</sub>TiCl<sub>2</sub> and Cp\*TiCl<sub>3</sub>.

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### **Diseases and Mortalities of Cultured Marine Fish and Shellfish in Taiwan**

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and CHU-FANG LO

TML Conference Proceedings 1: 173-192 (1984)

With increasing demand and high prices for sea foods, the brackish water pond culture and marine aquaculture have been developed rapidly in Taiwan in the last decade. Due to current application of new methods to increase reproduction, fry or "seed" capture, and survival of larvae, juveniles and adults, the culture of marine animals is becoming popular and more efficient. The major cultured marine animals in Taiwan today include milkfish, *Chanos chanos*, shrimp, mainly grass shrimp, *Penaeus monodon*, and sand shrimp, *Metapenaeus ensis*, mangrove crab, *Scylla serrata*; oyster, mainly the pacific oyster *Crassostrea gigas* and native hard clams *Meretrix* spp.

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### **The Study of *Clinostomum Complanatum* (Rud., 1814)**

#### **III. *In Vivo* Cultivation and Development of *Clinostomum Complanatum* from the Metacercaria to the Adult**

CHU-FANG LO

COA Fisheries Series, No. 10, Fish Disease Research (VI), 12-23, 1984, 2

The ovary of *Clinostomum complanatum* was not capable of developing before the flukes had got the nourishment from its host's blood. On the contrary, the testes developed almost immediately after infection. The mature vitelline cells appeared 60 hours after infection. The uterus would not have eggs until the vitelline became fully developed. The time necessary for completing the total process of the maturation in *C. complanatum* was about 72 hours in heron's mouth. The amount of eggs in uterus seemed not to decrease as the flukes grew. This evidence indicates that the fluke was likely not to release its eggs from time to time. The flukes would release eggs only when they were irritated or pressed by the food of the heron.

The life span of worms was quite variable in heron's mouth cavity. Usually, the number of the worms decreased 15 days after infection. Most of the worms could not live more than thirty days. But a case indicated that the worms could stay in heron's mouth cavity up to 60 days. From these data, it is proper to stop culturing the 2nd intermediate host of *C. complanatum* for at least two months when there is the outbreak of this parasite disease.

**The Histological Changes in the Testis, Epididymis and Prostate Gland of the Red-bellied Tree Squirrel, *Callosciurus erythraeus*, During the Growth and Reproductive Cycle**

W. H. T'SUI and C. C. HUANG\*

Proceedings of the NSC- Part B, Vol. 9, No. 3, 220-229

The male reproductive glands of the red-bellied tree squirrel, *Callosciurus erythraeus*, in the infantile, and prepubertal males, as well as sexually functional, degenerating and redeveloping adults were studied histologically.

In the infant, testes are characterized with solid seminiferous tubules filled with primordial germ cells and Sertoli cells. Interstitial cells are sparse. The prostate is composed of condensed cell cords grouped into lobules dispersed with interlobular tissues rich

in fibroblasts. In the epididymis the highly convoluted tubule is lined with a simple cuboidal or columnar epithelium and thin smooth musculature without.

In the prepubertal male, germ cells are engaged actively in mitosis. Primary spermatocytes are readily recognized. Leydig cells appear in groups in the interstitial tissue. In the prostate, cell cords become highly branched and collecting tubules make their appearance. The tubules in the epididymis are enlarged in diameter but their peripheral musculature becomes thinner.

In functional males, meiosis is active and bundles of spermatozoa are scattered along the central lumen. Leydig cells have their cytoplasm highly enriched. The prostate is in secretory phase. The tubule in the epididymis is filled with sperm.

In the degenerating adult, meiosis is interrupted and necrotic germ cells are detached from germinal epithelium. In the prostate, secretory and collecting ducts are eventually reduced to condensed lobules separated by interlobular fibrous tissue. The tubule in the epididymis often fills with necrotic germ cells but no sperm.

In redeveloping adult, the histology of the testes, prostate and epididymis is similar to that of the prepubertal male. However, there is more fibrous tissue in the interlobular septa in the prostate gland and thick musculature at the periphery of the tubule in the epididymis.

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**Studies on the Fine Structure of the Ocellus in  
Relation to Pigment Migration in the Compound  
Eye of the Diamondback Moth,  
*Plutella Xylostella* (L.)**

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國立臺灣大學植物病蟲害第十一期 (民國73年)

Diamondback moth possesses two ocelli on dorsal region of the head, each ocellus is composed of a cornea, corneal crystalline cone,

one layer of corneogeneous cells and many layers of retinular cells. The retinular cells can be divided into three parts, the rhabdom in the apical region, the nucleus in the basal region and the middle region is occupied by a number of organelles which include mitochondria, rough endoplasmic reticulum, glycogen granules and many irregular-shaped electron dense granules.

The light- and dark-adaptation of the compound eye controlled by pigment migration can be achieved with or without ocelli. It is concluded that the pigment migration of the compound eye of this moth is a kind of "self-control mechanism" within the ommatidium.

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### **Postembryonic Development of the Compound Eye of Diamondback Moth, *Plutella Xylostella* (L.)**

CHUNG-HSIUNG WANG and YUN-HSIN DUANN

Chinese Journal of Entomology, 3: 3 (1984)

The postembryonic development of the compound eye of diamondback moth, *Plutella xylostella* (L.), has been examined from prepupa to imago by means of light microscopy.

From the progressive organization, 2 major stages, the cell differentiation stage and the organization stages, can be identified. The former consists of 3 substages. The cell dispersion stage, the early cell-cluster stage, and the last cell-cluster stage. The latter involves 4 substages: the forming cornea stage, the developing cone and rhabdom stage, the developing pigment cell stage and the mature ommatidium stage.

The subsequent structures of the developing ommatidium of each of the substages were described in this report.

小菜蛾複眼之後胚胎發育

王重雄 段筠心

中華昆蟲 4: 75-86 (1984)

小菜蛾複眼從前蛹期開始發育，至羽化前即完成，從外觀上的變化，可以分成六期，但從內部構造的形成，則可以分成兩個主要時期：一、細胞分化期和二、細胞器官化期。第一期發生於前蛹期，從視盤的變化又可以細分成3次期：(一)細胞散佈期；(二)細胞叢前期；(三)細胞叢後期。第二期於化蛹後即開始發生，亦可以細分成4次期：(一)角膜形成期；(二)晶錐體及小網膜細胞發育期；(三)主、副色素細胞發育期；(四)小眼成熟期。

本文以前蛹期及蛹體上複眼形成區之外觀上的變化，作為複眼發育程度之準則，討論其內的發育狀況。

### 小菜蛾單眼之超微構造及其與複眼色素顆粒移動的相關性研究

王重雄 徐世傑\*

國立臺灣大學植物病蟲害第十一期 (民國七十三年)

小菜蛾單眼具角膜、角膜晶錐、單層角膜晶體原細胞及多層小網膜細胞。小網膜細胞可分成3部份，上段具桿狀體，中段充滿粒腺體，粗糙內質網、肝醣顆粒及不規則形狀之電子緻密顆粒等，下段則為小網膜細胞核之位置。

小菜蛾單眼對複眼的色素顆粒移動不發生干擾，亦即複眼假瞳孔的變化不受單眼影響。

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### Studies on the Intention and Factors Affecting Breast Feeding

CHAO CHANG\* and NING-YUEAN LEE

Journal of the Chinese Nutrition Society,  
Vol. 10, 1, 2, July 1985

The chief purpose of this paper was to investigate the intention and factor analyses of infant feeding status of mothers from 9 large general hospitals in Taipei city. A questionnaire survey of 400 mothers was carried out in January, 1984. The data were collected by well-trained interviewers and analyzed with computer. The main results were summarized as follows:

1. In the mothers, 20.00% have fed or intended to feed infants

A mass spectrometric method was developed for quantifying stable iron isotope tracers present in blood and fecal samples. Volatile Iron acetylacetonate [ $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$ ] was prepared. A conventional mass spectrometer was used to measure ion abundance ratios of the diligand fragments [ $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2$ ]<sup>+</sup> which were formed during electron-impact ionization. Sample isotopic enrichment levels were obtained from standard curves that related ion abundance ratios to enrichment levels. Tracer concentration was calculated from the values for total iron content and enrichment level. The relative standard deviation for the ion abundance measurement was less than 2%. Recovery of tracers from spiked fecal samples ranged from 90% to 104%. The method was used to analyze samples collected from a human study. Iron availability from breakfast meals was determined in 6 young women by giving 7 mg of <sup>54</sup>Fe in apple juice on one day and 7 mg of <sup>57</sup>Fe in orange juice on the next. Absorption estimated with a fecal monitoring method ranged from -4.8% to 36.5% for <sup>54</sup>Fe and from 5.7% to 42.3% for <sup>57</sup>Fe. Enrichment of the hemoglobin iron pool by giving 7 mg/day of <sup>54</sup>Fe for 7 days was below calculated detection limits for accurate quantification.

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## **A Study on Physical and Chemical Changes in Frying Oils during Heating**

C. M. TSAI

Journal of the Chinese Nutrition Society,  
Vol. 9, No. 1, 2, May 1984

It has been known that deep fat frying oil can produce during frying some oxidized compounds and cyclic polymers which could

be hazardous to human health. The purpose of this study was trying to find out a simple and dependable test to determine the point at which the batch of frying oil has to be discarded.

The oil samples were heated at 160°, 175°, and 190°C individually, in some of which TBHQ, silicone antifoaming agent, moist cotton balls, or chicken were added and/or fried. Optical density, refractive index, viscosity by viscometer or falling ball, boiling point elevation and iodine value of each heated oil were determined.

The data showed that falling ball method was the most simple and dependable test to be an indicator of heated oil quality. The results also demonstrated that viscometry and refractive index were dependable, but the changes were not great. Optical density could be influenced by fried foods. Iodine value and boiling point elevation fluctuated.

### **A Study on the Relationship between Hypertension and Food Habits**

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Journal of the Chinese Nutrition Society,  
Vol. 10, No. 1, 2, July 1985

It has been known that the ratio of population with hypertension in Taiwan is higher than that in the most area of the world. This study attempted to understand whether food habit is one of key factors causing hypertension.

The results of this study demonstrated that the most of hypertension patients had a same habit preferring salty foods before knowing themselves had hypertension. Although many of them were warned to reduce salt in their foods, they still ingested high sodium foods, especially monosodium glutamate and cured foods, but not table salt, due to innocent. This study also found that hypertension seems not to be mainly due to genetic inheritance. It has been thought so, but it might be due to the learning of food habit from

the family. At least, genetic inheritance should not be a major factor causing hypertension.

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