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ON COVERING SETS OF GROUPS

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1. INTRODUCTION

Let G be an abelian group with a base of n elements of order q, i.e.

$$G = \{g_1^{\alpha_1} g_2^{\alpha_2} \ldots g_n^{\alpha_n} \mid 0 < \alpha_i \le q\}$$

where g_i's are independent elements of G, and the set

$$S = \{g_i^{\alpha_i} \mid i = 1, 2, \ldots, n; \ 0 < \alpha_i \le q\}.$$

Surely, the size of S is $V = 1 + n(q-1)$.

We say that a set H is a covering set or an (n, q) covering set of S in G iff $G = HS$, i.e. every element g of G can be expressed in the form $g = hs$ with h in H and s in S. In this paper, we will study the minimal value of the cardinality of H, which is denoted by $\lambda(n, q)$, because it just depends on n and q, (and then call H a minimal covering set). If we want H to be a subgroup of G, we denote the cardinality of the minimal covering set by $\lambda^*(n, q)$, clearly $\lambda(n, q) \le \lambda^*(n, q)$.

Consider the additive group Z_q of integer modulo q, then G is isomorphic to the additive group of $Z_q \times Z_q \times \ldots \times Z_q = Z_q^n$ with the isomorphism:

$$\psi: g_1^{\alpha_1} g_2^{\alpha_2} \ldots g_n^{\alpha_n} \longrightarrow (\alpha_1, \alpha_2, \ldots, \alpha_n).$$

We would treat elements of G as vectors in Z_q^n.

Definition 1. A vector $X = (x_1, x_2, \ldots, x_n)$ covers vector $Y = (y_1, y_2, \ldots, y_n)$ if $x_i = y_i$ for at least $n-1$ components of X and Y.

To find a covering of S in G is to find a set H of vectors covering all vectors of G.

Now, if $X \in H$, then X can cover $1 + n(q-1)$ vectors of G, hence we have

$$\lambda(n, q) \geq \frac{q^n}{1 + n(q-1)} = \frac{q^n}{v} \tag{1}$$

and if H is any covering of Z_q^{n-1}, then $H' = \{(x_1, x_2, \ldots, x_{n-1}, x_n) \mid (x_1, x_2, \ldots, x_{n-1}) \in H, x_n = 1, 2, \ldots, q\}$ is a covering set of Z_q^n, so we have

$$\lambda(n, q) \leq q\lambda(n-1, q) \tag{2}$$

Example 1.1. $\lambda(3, 2) = 2 = \lambda^*(3, 2)$, since $H_1 = \{(2, 2, 2), (1, 1, 1)\}$ is a minimal covering of the group $\{(2, 2, 2), (2, 2, 1), (2, 1, 2), (1, 2, 2), (1, 2, 1), (1, 1, 2), (2, 1, 1), (1, 1, 1)\}$.

Example 1.2. $\lambda(4, 2) = 4 = \lambda^*(4, 2)$, since $\lambda(4, 2) \geq 2^4/(1 + 4(2-1)) = 3.2$ and $\lambda(4, 2) \leq 2\lambda(3, 2) = 4$. In fact, $H_2 = \{(2,2,2,2), (2,2,2,1), (1, 1, 1, 2), (1, 1, 1, 1)\}$ is a minimal covering of the set $\{(a, b, c, d) \mid a, b, c, d = 1\}$.

2. SOME UPPER BOUNDS

To find an upper bound of $\lambda(n, q)$, we try to find a covering set. We let

$$G = \{(x_1, \ldots, x_n) \mid x_i = 1, 2, \ldots, q\}$$

and

$$S = \{(q, \ldots q, \alpha_i, q \ldots q) \mid i = 1, 2, \ldots, n; \ \alpha_i = 1, 2, \ldots q\}$$

Definition 2. By a "Block" we mean a set of q vectors in G where the first $n-1$ components are the same. By a "row" we mean a set of q block (q^2 vectors), where $n-2$ components of the first $n-1$ components are the same.

Thus, we have q^{n-1} blocks and $(n-1)q^{n-1}$ rows in the representation of G.

Example 2.1. In a representation of a $(3, 6)$ covering set Block $(1,2) = \{(1, 2, x) \mid x = 1, 2, \ldots 6\}$. We have $3^2 = 9$ blocks (x_1, x_2), $x_i = 1, 2, 3$ and Row $(x_1 = 1) =$ Block $(1, 2)$, Block $(1, 3)$, Block $(1, 1)$.

Example 2.2. The representation of a covering set when $n = 3$, $q = 6$. Since for every vector (x_1, x_2, x_3) in G, two of x_i's will be in $\{1, 2, 3\}$ or $\{4, 5, 6\}$ together,

$$H = \{(1, 1, 1), (1, 2, 2), (1, 3, 3), (2, 1, 2), (2, 2, 3),$$
$$(2, 3, 1), (3, 1, 3), (3, 2, 1), (3, 3, 2), (4, 4, 4),$$
$$(4, 5, 5), (4, 6, 6), (5, 4, 5), (5, 5, 6), (5, 6, 4),$$
$$(6, 4, 6), (6, 5, 4), (6, 6, 5)\}$$

is a $(3, 6)$ covering set of $2 \cdot 3^2 = 18$ elements. Now, we let the block (x_1, x_2) entry with x_3; if $(x_1, x_2, x_3) \in H$, we get the representation diagram:

In constructing a $(3, 2t)$ covering set, we begin with a $(3, 2)$ covering set, with representation

then, we enlarge every block into a $t \times t$ block, (t^2 blocks). The empty blocks are still empty; those from a block with entry 1 will contain a latin square of elements $1, 2, \ldots, t$; and those from a block with entry 2 will contain a latin square of elements $t + 1, t + 2, \ldots, 2t$; we thus get a representation of a $(3, 2t)$ covering set, and have $\lambda(3, 2t) \leq 2t^2$.

Example 2.3. $n = 3$, $q = 4$

$$x_1 \longrightarrow$$

1	2		
2	1		
		3	4
		4	3

$x_2 \downarrow$

H = {(1, 1, 1), (1, 2, 2), (2, 1, 2), (2, 2, 1),
      (3, 3, 3), (3, 4, 4), (4, 3, 4), (4, 4, 3)}.

For $n = 4$, every block is a 3-dimensional vector (x_1, x_2, x_3) and a row is a 2-dimensional vector (x_1, x_2). A plane is a 1-dimensional vector x_3. The entry in block (x_1, x_2, x_3) is x_4 when $(x_1, x_2, x_3, x_4) \in H$. A $(4, 3t)$ covering set is represented by enlarging the block of $(4, 3)$ covering set into a latin cube (dimension 3) with side t. The latin cube from block with entry 1, 2, 3 will contain the elements $1, 2, \ldots, t$; $t+1, t+2, \ldots, 2t$ and $2t+1, 2t+2, \ldots, 3t$ respectively.

Example 2.4.   Representation of a $(4, 3)$ covering set

$x_1 \longrightarrow$ $x_1 \longrightarrow$ $x_1 \longrightarrow$

$x_2 \downarrow$

1		
	2	
		3

$x_3 = 1$

	3	
		1
2		

$x_3 = 2$

		2
3		
	1	

$x_3 = 3$

H = {(1, 1, 1, 1), (2, 2, 1, 2), (3, 3, 1, 3), (1, 3, 2, 2),
      (2, 1, 2, 3), (3, 2, 2, 1), (1, 2, 3, 3), (2, 3, 3, 1),
      (3, 1, 3, 2)}.

Example 2.5.   Representation of a $(4, 6)$ covering set

$|H| = 72$.

The method mentioned above can be extended to a higher dimension by change the latin cubes into latin hypercubes for $n = q + 1$, (the existence of a $(q + 1, q)$ covering set when q is a prime of prime power will be proved in section 5); the cubes will of dimension $n - 1 = q$, a prime. We get a $(q + 1, tq)$ covering set with $tq \cdot t^{q-1} \cdot q^{q-1} = t^q q^{q-1}$ elements, so we have.

Theorem 2.A. $\lambda(q + 1, tq) \leq t^q q^{q-1}$ when q is a prime or prime power.

3. LOWER BOUNDS

Let H be a (n, q) covering set with m vectors in $m - r$ blocks $(r \geq 0)$. Suppose the ith row of G contains h_i vectors of H in b_i different blocks, (we may assume that H contains no repeated vector). Then

$$0 \leq b_i \leq h_i \leq q b_i \quad (1 \leq i \leq (n-1) q^{n-2}) \tag{3}$$

adding over rows of G, (since each vector of H is counted $n - 1$ times, once for each row containing it) we have

$$\sum_i h_i = (n - 1) m \tag{4}$$

similarly, by counting occupied blocks we get

$$\sum_i b_i = (n-1)(m-r) \tag{5}$$

Since $m-r$ blocks contain vectors of H, exactly $q(m-r)$ different vectors of G are covered directly, and thus at least $q^n - q(m-r)$ vectors of G must be covered indirectly. But if a row contains h_i vectors in b_i blocks, there are at most $h_i(q-b_i)$ different indirectly covered along that row (at most h_i in each of the $q-b_i$ unoccupied blocks). Adding over all rows and counting each indirect covered once, we get

$$\sum_i h_i(q-b_i) \geq q^n - q(m-r) \tag{6}$$

From (4), (5), (6) we get the Lemma

Lemma 3A. For any real number a,

$$\sum_{i=1}^{(n-1)\,q^{n-2}} \left(h_i - \frac{q}{n-1}\right)(b_i - a)$$
$$\leq -(q-a)\,[q^{n-1} - m(n-1)]$$

[pf]

$$\sum_i \left(h_i - \frac{q}{n-1}\right)(b_i - a)$$
$$= \sum h_i b_i - \sum h_i a + \sum \frac{aq}{n-1} - \sum \frac{qb_i}{n-1}$$
$$= \sum h_i(b_i - q + q - a)$$
$$\quad + \frac{aq}{n-1} \cdot (n-1)\, q^{n-2} - \frac{q}{n-1}\sum b_i$$
$$= \sum h_i(b_i - q) + \sum h_i(q - a)$$
$$\quad + aq^{n-1} - \frac{q}{n-1}\,(n-1)(m-r)$$
$$\leq -q^n + q(m-r) + (q-a)(n-1)(m-r)$$
$$\quad - q(m-r) + aq^{n-1}$$
$$= -(q-a)\,[q^{n-1} - m(n-1)].$$

Theorem 3A. If $n-1 < q \leq 2(n-1)$ then $\lambda(n, q) \geq q^{n-1}/(n-1)$

[pf] Let $a = 1$ in Lemma 3A

$$\Sigma \left(h_i - \frac{q}{n-1} \right)(b_i - 1) \le -(q-1)\left[q^{n-1} - m(n-1)\right]$$
$$= -q^{n-1} + q^{n-2} + m(q-1)(n-1)$$
$$\le q^{n-2}(1-q) + m(q-1)(m-1)$$

now $1 < q/(n-1) \le 2$, m_j^* is the number of vectors in a (n, q) covering set. If

$$h_i = 0 \text{ then } b_i = 0$$
$$h_i = 1 \text{ then } b_i = 1$$
$$h_i \ge 2 \text{ then } b_i \ge 1$$

So, each term in the sum on the left is nonnegative, thus

$$q^{n-1} - m(n-1) \le 0$$
$$m \ge \frac{q^{n-1}}{n-1}$$

Corollary 3A. $\lambda(q+1, 2q) \ge 2^q q^q$.

From Theorem 3A and Corollary 3A, we get

Theorem 3B. $\lambda(k+1, 2k) = 2^k k^{k-1}$ for k is a prime or prime power.

Theorem 3C. If $2(n-1) < q \le 3(n-1)$ then $\lambda(n, q) \ge q^{n-1}/(n-1) - c$, where q is a prime or a prime power and c be the greatest number for which $q^{n-1}/(n-1) - c$ is an integer and

$$c\left[\frac{(q-2)(n-1)}{q(n-2)} + \frac{(q-1)(n-1)}{q-2(n-1)} \right] \le q^{n-2}$$

[pf] Suppose there exist a (n, q) covering set with $m = q^{n-1}/(n-1) - c$ elements. Letting $a = 1$ in Lemma 3A we obtain

$$\Sigma \left(h_i - \frac{q}{n-1} \right)(b_i - 1)$$
$$\le -(q-1)\left[q^{n-1} - \left(\frac{q^{n-1}}{n-1} - c \right)(n-1) \right]$$
$$= -(q-1)(n-1)c$$

Since $2 < q/(n-1) \leq 3$, the terms on the left are negative only if $h_i = b_i = 2$, with value $2 - q/(n-1)$. Thus $h_i = b_i = 2$ for at least $((q-1)(n-1)^2 c)/(q-2(n-1))$ values of i. Also, for $a=2$ in Lemma 3A

$$\Sigma \left(h_i - \frac{q}{n-1} \right)(b_i - 2) \leq -(q-2)(n-1)\,c$$

A term on the left is negative if $b_i = 1$ and $h_i \geq 3$, and then by (3), $h_i \leq q$, the value is at least $-(q - q/(n-1))$ $= (-q(n-2))/(n-1)$, and $b_i = 1, h_i = 3$ for at least $((q-2)(n-1)^2 c)/(q(n-2))$ values of i. But $1 \leq i \leq (n-1)\, q^{n-2}$, so

$$\frac{(q-2)(n-1)^2 c}{q(n-2)} + \frac{(q-1)(n-1)^2 c}{q-2(n-1)} \leq (n-1)\, q^{n-2}$$

$$c\left(\frac{(q-2)(n-1)}{q(n-2)} + \frac{(q-1)(n-1)}{q-2(n-1)} \right) \leq q^{n-2}$$

Corollary 3C. $\lambda(k+1, 3k) \geq (9k-1)(3k)^{k-2}$ for k a prime or prime power.

[pf] When $q = 3k$, $n = k+1$

$$c \leq (3k)^{k-1} \left[\frac{(3k-2)\,k}{3k(k-1)} + \frac{(3k-1)\,k}{3k-2k} \right]^{-1}$$

$$= (3k)^{k-1} \frac{3k-3}{9k^2 - 9k + 1} < (3k)^{k-2}.$$

Theorem 3A and 3C are substantial improvements of (1), i.e.

$$\lambda(n, q) \geq \frac{q^n}{v} = \frac{q^n}{1 + n(q-1)}$$

when $q > n - 1$

4. Value of $\lambda(3, q)$

It is clear that $\lambda(1, q) = 1$, $\lambda(2, q) = q$, so the first interesting case, for fixed n, is $\lambda(3, q)$.

Consider the q^3 vectors (a, b, c) where $1 \leq a, b, c \leq q$. Pick

any number $r < q,$ and let $K_r = \{(a, b, c) \mid 1 \leq a, b \leq r$ and $c \equiv a + b \pmod{r}\}.$

Lemma 4A. For each order pair $(s . t)$ with $1 \leq s, t \leq r,$ there exists exactly one u and $v,$ $u \equiv s + t,$ $v + s \equiv t \pmod{r}$ such that $(s, t, u),$ $(s, v, t),$ (v, s, t) belongs to $K_r.$ Thus, K_r covers all vectors (a, b, c) with the property that $\{a, b, c\} \cap \{1, 2, \ldots, r\}$ has at least two elements.

Similary, let $K_{q-r} = \{(a, b, c) \mid r + 1 \leq a, b \leq q, c \equiv a + b \pmod{q-r}\}.$ Then K_{q-r} covers all vectors (a, b, c) with the property that $\{a, b, c\} \cap \{r + 1, r + 2, \ldots, q\}$ has at least two elements.

Combining K_r and $K_{q-r},$ we get a covering set of $r^2 + (q - r)^2$ elements, i.e. $\lambda(3, q) \leq r^2 + (q - r)^2,$ for all $1 \leq r \leq q,$ hence we have.

Theorem 4A. $\lambda(3, q) \leq [(q^2 + 1)/2]$ the greatest integer not larger than $(q^2 + 1)/2.$

[pf] When $q = 2t,$ let $r = t$ then $\lambda(3, 2t) \leq t^2 + (2t - t)^4 = 2t^2 = [(q^2 + 1)/2].$ When $q = 2t + 1,$ let $r = t, \lambda(3, 2t) \leq t^2 + (t + 1)^2 = 2t^2 + 2t + 1 = [(q^2 + 1)/2].$

In finding a lower bound of $\lambda(3, q),$ we let H be a covering set of m elements; $(a_i, b_i, c_i),$ $i = 1, 2, \ldots, m,$ and a partition of H, as follows:

(1) Consider all subsets of H consist of all elements identical in at least one component, and let H_1 be the one with the least number of elements, say the elements are identical in the first component. $H_1 = \{(a, b_i, c_i) \mid i = 1, 2, \ldots, \alpha\}$ with α elements, then $\alpha \leq [m/q],$ since $q\alpha \leq m.$

(2) Let β be the number of distinct b_i in $H_1;$ clearly $\beta \leq \alpha.$ Let $H_2 = \{(x, b_i, y) \; x \neq a, (a, b_i, c_i) \in H_1$ for some $c_i\}.$ Since α is minimal, each b_i appears in H_2 at least α times; hence, the number of elements in H_2 is at least $\beta\alpha - \alpha.$

(3) Let $H_3 = \{(s, t, u) \mid s \neq a, t \neq b_i, u = c_1, c_2, \ldots, c_\alpha\}$ with γ elements.

(4) Let $H_4 = \{(d, e, f) \mid d \neq a,\ e \neq b_i,\ f \neq c_i (i = 1, 2, \ldots \alpha)\}$ then the number of elements in H_4 is at most $m - \gamma - \beta\alpha$ and, $H = H_1 \cup H_2 \cup H_3 \cup H_4$ is a partition of H.

Now, look at vectors (a, b, c) where a is as in H_1, $b \neq b_i$, $c \neq c_i (i = 1, \ldots, \alpha)$. These vectors differ from those in H_1, H_2, H_3 in two components, and so can only be covered by vectors from H_4. Also, they can only be covered one at a time. Since the number of such vectors is at least $(q - \beta)(q - \alpha)$, and they can only be covered one at a time by vectors from H_4, we have

$$(q - \beta)(q - \alpha) \leq m - \beta\alpha - \gamma.$$

Case 1. $q = 2t,\ m \leq 2t^2$

If $m = 2t^2 - \delta (\delta \geq 0)$, then

$$(2t - \beta)(2t - \alpha) \leq 2t^2 - \delta - \beta\alpha - \gamma$$
$$2(t - \beta)(t - \alpha) \leq -\delta - \gamma$$

But

$$\alpha \leq \left[\frac{2t^2 - \delta}{2t}\right] \leq t \text{ and } \beta \leq \alpha \leq t$$

the only solution is $\delta = \gamma = 0$, $\alpha = \beta = t$ and we have $m = 2t^2$.

Case 2. $q = 2t + 1,\ m \leq 2t^2 + 2t + 1$

If $m = 2t^2 + 2t + 2t + 1 - \delta$, then

$$(2t + 1 - \beta)(2t + 1 - \alpha) \leq 2t^2 + 2t + 1 - \delta - \gamma - \beta\alpha$$
$$2t^2 + 2t - (\alpha + \beta)(2t + 1) - 2\alpha\beta \leq -\delta - \gamma$$
$$(2t + 1 - 2\alpha)(2t + 1 - 2\beta) \leq -\delta - \gamma + 1 \leq 1$$

But

$$\alpha \leq \left[\frac{m}{q}\right] = \left[\frac{2t^2 + 2t + 1 - \delta}{2t + 1}\right] = \left[t + \frac{t + 1 - \delta}{2t + 1}\right]$$
$$= t,\ \beta \leq \alpha \leq t$$

the only solution is $\alpha = \beta = t$, $\delta = \gamma = 0$, and we have $m = 2t^2 + 2t + 1$

We can express Case 1 and Case 2 in the theorem

Theorem 4B. $\lambda(3, q) = [(q^2 + 1) / 2]$.

5. FOR $q = p^k$, A PRIME POWER, AND
$V = 1 + n(q-1)$ DEVIDES q^n

Lemma 5A. Let K be an abelian group with kn base elements $g_{ij} (i = 1, 2, \ldots, n, j = 1, 2, \ldots, k)$ each of order p, and T be the set of $V = 1 + n(p^k - 1)$ elements of the form $\prod_{j=1}^{k} g_{ij}^{\alpha_{ij}}$ $(\alpha_{ij} = 0, 1, \ldots, p-1; j = 1, 2, \ldots, k; i = 1, 2, \ldots, n)$.

If V is a divisor of q, then there exists a subgroup X of K such that $K = XT$ with the order of $X = q^n / V$.

[pf] Let $V = 1 + n(q-1) = q^r$, and A be an abstract abelian group with kr base elements of order p. We can [1] tratify A into subgroups $A_1, A_2, \ldots$, of order p^k such that (i) $A_i \cap A_j = e$, $i \neq j$ (e the identity element of A) (ii) The number of A_i is $(p^{kr} - 1) / (p^k - 1) = (q^r - 1) / (q-1) = n$. Let $a_{i1}, a_{i2}, \ldots, a_{ik}$ be a base for A_i, and define a mapping θ from K onto A by $g \in K$, $g\theta = \prod_{i,j} g_{ij}^{\alpha_{ij}} \theta = \prod_{i,j} a_{ij}^{\alpha_{ij}} \in A$ then θ is a homomorphism. Now, let $X = \ker (\theta)$, then $K = XT$ and X is a subgroup of K with $p^{kn} / V = q^n / q^r = q^{n-r}$ elements.

Theorem 5A. If G is an abelian group with n base elements $g_1, g_2, \ldots, g_n$, each of order $q = p^k$ (p is a prime) and S is the set of $V = 1 + n(q-1)$ elements $g_i^{\alpha_i} (i = 1, 2, \ldots, n; \alpha_i = 1, 2, \ldots, q)$ and V is a power of q, then there exists a covering subset H of G containing q^n / V elements and $G = HS$.

[pf] Let $V = q^r = p^{kr}$, since for every $\alpha_i, 0 \leq \alpha_i < p^k - 1, \alpha_i$ can be represented uniquely as a combination of powers of p, say $\alpha_i = \alpha_{i1} p^0 + \alpha_{i2} p^1 + \ldots + \alpha_{ik} p^{k-1}$, with $0 \leq \alpha_{ij} \leq p - 1$, $j = 1, 2, \ldots, k$. Let X and K be as set mentioned in Lemma 5A, and define the mapping

$\psi: G \rightarrow K$

$g_1^{\alpha_1} g_2^{\alpha_2} \ldots g_n^{\alpha_n} \rightarrow \prod_{ij} g_{ij}^{\alpha_{ij}}$

Then ψ is one to one and onto, and hence an isomorphism. Let $H = \psi^{-1}(X)$, then H is a subgroup of G with p^{kn} / V elements, and $G = HS$ since $K = XT$

By the theorem above, we know $\lambda(n, q) \leq q^n / V$, when $V = q^r$ and q is a power of a prime number. But we know $\lambda(n, q) \geq q^n / V$ in (1). Thus

Theorem 5B. When $q = p^k$ is a prime power and $V = 1 + n(q-1) = q^r$ for some natural number r, then $\lambda(n, q) = q^{n-r} = \lambda^*(n, q)$.

Corollary 5B. $\lambda(n, p) = p^{n-r} = \lambda^*(n, p)$, where $1 + n(p-1) = p^r$, r natural number and p is a prime.

6. WAYS TO FIND $\lambda(n, q)$

It is not quite easy to find $\lambda(n, q)$, when n and q are not of the special type we have mentioned. In this section, we try some methods to find them, or to improve the bounds.

6.1 Lift a lower bound of $\lambda(n, q)$

Let H be a covering set of m elements and use A, B, C, ... to denote the first, second, third, etc., component and define the following number

$(X)_i$ is the number of how often i appears as X component.

$(XY)_{ij}$ is the number of how often i appears as X component and j as Y component.

$(XYZ)_{ijk}$ is the number of how often i, j, k appear as X, Y, Z component respectively.

X, Y, Z... selected from A, B, C, etc.

Clearly $\sum_i (X)_i = m$, $\sum_i (XY)_{ij} = (Y)_j$ etc.

Now the number of elements in G with i in X component is q^{n-1}, and simply $1 + (n-1)(q-1)$ of them are covered by a vector of H with i in X component, the remaining vectors of G with i in X component must be covered by vectors of H whose X component is not i, thus

$$(X)_i \{(n-1)(q-1) + 1\} + \sum_{j \neq i} (X)_j \geq q^{n-1}$$

$$(X)_i \{(n-1)(q-1)\} + \sum_j (X)_j \geq q^{n-1}$$

but $\sum_j (X)_j = m$, we have

Theorem 6A. $(X)_i \{(n-1)(q-1)\} \geq q^{n-1} - m$

Similarly, the number of vectors in G with i in X component and j in Y component is q^{n-2}; of these, only $(n-2)(q-1)+1$ vectors can be covered by a vector of H with i in X component and j in Y component, thus

$$(XY)_{ij} \{(n-2)(q-1)+1\} + \sum_{k \neq i} (XY)_{kj} + \sum_{t \neq j} (XY)_{it} \geq q^{n-2}$$

hence

$$(XY)_{ij} \{(n-2)(q-1)-1\} + \sum_{k} (XY)_{kj} + \sum_{t} (XY)_{it} \geq q^{n-2}$$

and

$$(XY)_{ij} \{(n-2)(q-1)-1\} \geq q^{n-2} - (X)_i - (Y)_j.$$

Similar inequalities are extensible

$$(XYZ)_{ijk} \{(n-3)(q-1)-2\}$$
$$\geq q^{n-3} - (XY)_{ij} - (YZ)_{jk} - (XZ)_{ik}$$
$$(XYZW)_{ijkt} \{(n-4)(q-1)-3\}$$
$$\geq q^{n-4} - (XYZ)_{ijk} - (XYW)_{ijt} - (XZW)_{ikt} - (YZW)_{jkt}$$

etc.

Example 6.1. $\lambda(5, 3) = 27$, $n = 5$, $q = 3$

since

$$\frac{3^5}{11} < \lambda(5, 3) \leq 3\lambda(4, 3) = 3 \cdot 3^{3-1} = 27$$

$$\therefore \lambda(5, 3) = 23, 24, 25, 26, \text{ or } 27$$

Consider a covering set H of m elements

(i) If $m = 23$ then $8(X)_i \geq 3^4 - 23 = 58$, $(X_i) \geq 8$ and $m = \sum_{i=1}^{3} (X)_i \geq 24$ which is a contradiction

(ii) If $m = 24$, $8(X)_i \geq 57$, $(X)_i \geq 8$ and $m = \sum_{i=1}^{3} (X)_i \geq 24$. Thus $(X)_1 = (X)_2 = (X)_3 = 8$, but $5(XY)_{ij} \geq 3^3 - (X)_i - (Y)_j = 11$ hence $(XY)_{ij} \geq 3$ and $(X)_i = \sum_{j=1}^{3} (XY)_{ij} \geq 9$ which is a contradiction

(iii) If $m = 25$, $8(X)_i > 3^4 - 25$, $(X)_i \geq 7$ we suppose some

$(X)_i = 7$, say $(X)_1 = 7$, then $5(XY)_{1j} \geq 27 - (X)_1 - (Y)_j = 20 - (Y)_j$ add over j, $35 = 5(X)_1 \geq 60 - m = 35$. Hence the inequality is an equality and $5(XY)_{1j} = 20 - (Y)_j \leq 20 - 7 = 13$. We have $(Y)_j = 10$, 15, or 20 which is impossible since $(Y)_1 + (Y)_2 + (Y)_3 = 24$. It follows that for $X = A, B, C, D, E$ we must have $(X)_1 = (X)_2 = 8$ and $(X)_3 = 9$, Now

$$5(XY)_{ij} \geq 3^3 - (X)_i - (Y)_j = \begin{cases} 11 & i, j = 3 \\ 10 & \text{exactly one of } i, j \text{ is } 3 \end{cases}$$

$(XY)_{ij} \geq 3$ when $i, j \neq 3$

$(XY)_{ij} \geq 2$ exactly one of i, j is 3

and

$$8 = (X)_1 = \sum_{j=1}^{3} (XY)_{1j} \geq 3 + 3 + 2$$

We must have

$$(XY)_{11} = (XY)_{12} = (XY)_{21} = (XY)_{22} = 3$$
$$(XY)_{13} = (XY)_{23} = (XY)_{31} = (XY)_{32} = 2$$
$$(XY)_{33} = (X)_3 - (XY)_{13} - (XY)_{23} = 5$$

Now

$$2(XYZ)_{ijk} \geq 9 - (XY)_{ij} - (XZ)_{ik} - (YZ)_{jk}$$

we have

$$(XYZ)_{ijk} = \begin{cases} 1 & \text{if one of } i, j, k \text{ is } 3 \\ 0 & \text{if two of } i, j, k \text{ are } 3 \end{cases}$$

and

$$(XYZ)_{333} = (XY)_{33} - (XYZ)_{331} - (XYZ)_{331} = 5.$$

Now $(XYZW)_{3331} = (XYZW)_{3332} = 0$ since $(XYW)_{331} = (XYW)_{331} = 0$ and the $(XYZWT)_{33331} = (XYZWT)_{33332} = 0$, so

$$(ABCDE)_{33333} = (ABCD)_{3333} - (ABCD)_{33331} - (ABCD)_{33332}$$
$$= (ABCD)_{3333}$$
$$= (ABC)_{333} - (ABCD)_{3331} - (ABCD)_{3332}$$
$$= (ABC)_{333}$$
$$= 5$$

Thus H contains five repeated vectors (3, 3, 3, 3, 3) and then $|H| = 25 - 4 = 21$, which is impossible.

(iv) If $m = 26$, $8(X)_i \geq 55$, $(X)_i \geq 7$ the value of $(X)_1$, $(X)_2$, and $(X)_3$ may be 7, 7, 12; 7, 8, 11; 7, 9, 10; or 8, 8, 9 If some $(X)_i = 7$, say $(X)_1 = 7$ then

$$5(XY_{ij} \geq 27 - (X)_1 - (Y)_j = 20 - (Y)_j$$

and for all possibilities of $(Y)_j$, we have

$$(XY)_{ij} \geq 3 \quad \text{for} \quad (Y)_j = 7, 8, 9$$
$$(XY)_{ij} \geq 2 \quad \text{for} \quad (Y)_j = 10, 11, 12$$
$$\sum_{j=1}^{3} (XY)_{1j} = (X)_1 \geq 8,$$

a contradiction. So, the only solution for all $(X)_i = 8, 8, 9$, $i = 1, 2, 3$

$$(XY)_{1j} = 3, 3, 2 \quad j = 1, 2, 3$$
$$(XY)_{2j} = 3, 3, 2$$
$$(XY)_{3j} = 2, 2, 5$$

Now, $2(XYZ)_{ijk} \geq 3^2 - (XY)_{ij} - (XZ)_{ik} - (YZ)_{jk}$, we have

$$(XYZ)_{ijk} = \begin{cases} 1 & \text{when one subscript is 3} \\ 0 & \text{when two subscripts are 3} \end{cases}$$
$$(XYZ)_{333} = (XY)_{33} - (XYZ)_{331} - (XYZ)_{332} = 5$$

the same case as in (iii), a contradiction. So, finally, we have $\lambda(5, 3) = 27$

Example 6.2. $\lambda(4, 4) \geq 24$, $n = q = 4$

By theorem 3A $\lambda(4, 4) \geq 4^3 / 3$, $\lambda(4, 4) \geq 22$

(i) If $m = 22$

$$9(X)_i \geq 4^3 - 22 \quad \therefore \quad (X)_i \geq 5$$
$$(X)_i = 5, 5, 5, 7 \quad \text{or} \quad 5, 5, 6, 6 \quad i = 1, 2, 3, 4$$

but $5(XY)_{1j} \geq 4^2 - (X)_1 - (Y)_j = 11 - (Y)_j$

$$(XY)_{ij} \geq 2 \qquad j = 1, 2$$
$$(XY)_{ij} \geq 1 \qquad j = 3, 4$$
$$(X)_1 = \sum_{j=1}^{4} (XY)_{1j} \geq 6,$$

a contradiction.

(ii) If $m = 23$

$$9(X)_i \geq 4^3 - 23, \quad (X)_i \geq 5$$
$$(X)_i = 5, 5, 5, 8; \; 5, 5, 6, 7 \text{ or } 5, 6, 6, 6 \qquad i = 1, 2, 3, 4$$
$$5(XY)_{ij} \geq 4^2 - (X)_1 - (Y)_j = 11 - (Y)_j.$$

The only possible solution is $(Y)_j = 5, 6, 6, 6, \; j = 1, 2, 3, 4$. Since $(X)_1 = 5$, $Y = A, B, C, D$ and then $(XY)_{1j} = 2, 1, 1, 1; \; j = 1, 2, 3, 4$ But $(XY)_{hj} \geq 1$, $h = 2, 3, 4$ the only possible solutions for $(XY)_{hj}$ are

(1)	X \ Y	1	2	3	4
	1	2	1	1	1
	2	1	2	2	1
	3	1	2	1	2
	4	1	1	2	2

(2)	X \ Y	1	2	3	4
	1	2	1	1	1
	2	1	1	3	1
	3	1	3	1	1
	4	1	1	1	3

Now, $(XYZ)_{ijk} \geq 4 - (XY)_{ij} - (YZ)_{jk} - (XY)_{ij}$. In (1), (2) we have $(XY)_{33} = 1$ but $(XYZ)_{333} \geq 4-1-1-1 = 1$ and $(XYZ)_{331} \geq 4-1-1-1$ which is a contradiction.

Example 6.3. For some value of $\lambda(n, 2)$

(1) $\lambda(5, 2) = 7$

We have $2^5 / 6 \leq \lambda(5, 2) \leq 2\lambda(4, 2) = 8$.

If $m = 6$ then $4(X)_i \geq 2^4 - 6 = 10$, $(X)_i = 3$

$$(X)_1 = (X)_2 = 3$$
$$2(XY)_{ij} \geq 2^3 - (X)_i - (Y)_j = 2 \qquad \therefore (XY)_{ij} \geq 1$$
$$\therefore (XY)_{ij} = 1, 2, \; j = 1, 2$$

Say $(AB)_{11} = 1$, then $(AB)_{12} = 2$, $(AB)_{21} = 2$, $(AB)_{22} = 1$

$$0 \cdot (ABX)_{111} \geq 2^2 - (AB)_{11} - (BX)_{11} - (AX)_{11}$$
$$= 3 - (BX)_{11} - (AX)_{11}$$
$$\therefore \ (BX)_{11} + (AX)_{11} \geq 3 \ \text{ for all } \ X = C, D, E$$
$$(BX)_{ii} = (AX)_{ij} \ \text{ or } \ (BX)_{ij} \equiv (AX)_{ij} + 1 \pmod 2$$

But for any case we can find a vector which is not covered by H, a contradiction.

In fact, we can find a (5, 2) covering set with 7 elements

$$H = \{(1, 1, 1, 1, 1), \ (2, 1, 1, 1, 1), \ (1, 2, 1, 1, 1),$$
$$(1, 1, 2, 2, 2), \ (2, 2, 2, 2, 1), \ (2, 2, 2, 1, 2),$$
$$(2, 2, 1, 2, 2)\}$$

(2) $\lambda(6, 2) = 12$

$$\frac{2^6}{7} \leq \lambda(6, 2) \leq 2\lambda(5, 2), \quad 10 \leq \lambda(6, 2) \leq 14$$

(i)   If $m = 10$

$$5(X)_i \geq 2^5 - 10 \quad \therefore \ (X)_i \geq 5$$
$$\therefore \ (X)_1 = (X)_2 = 5$$
$$3(XY)_{ij} \geq 16 - (X)_1 - (Y)_j = 6 \quad \therefore \ (XY)_{ij} \geq 2$$

$(XY)_{ij} = 2, 3$ for any pair of column X, Y.

With components suitably named, we have

$$(XY)_{ij} = \begin{cases} 2 & i = j \\ 3 & i \neq j \end{cases}$$

then

$$(XYZ)_{111} \geq 8 - 2 - 2 - 2 = 2$$
$$\therefore \ (XYZ)_{ijk} = \begin{cases} 2 \\ 1 \end{cases}$$

$(ABCDEF)_{111111} = 2$, a contradiction.

(ii)   If $m = 11$

$$5(X)_i \geq 2^5 - 11 = 21, \ (X)_i \geq 5$$

$(X)_i = 5, 6$ and $(XY)_{ij} \geq 2$ say

$$(XY)_{ij} = \begin{cases} 2 & i = j = 1 \\ 3 & \text{otherwise} \end{cases}$$

$(XYZ)_{111} \geq 8 - 2 - 2 - 2 - 2 = 2$ for all X, Y, Z

Thus $(ABCDEF)_{111111} \geq 2$, a contradiction.

(iii) and when $m = 12$

We find a $(6, 2)$ covering set

$$\begin{aligned} H = \{&(2, 2, 2, 2, 2, 2),\ (2, 1, 2, 1, 2, 2),\ (1, 2, 1, 2, 1, 1), \\ &(1, 2, 1, 1, 2, 1),\ (1, 1, 1, 1, 1, 1),\ (1, 1, 1, 2, 2, 2), \\ &(1, 1, 2, 2, 2, 1),\ (2, 2, 2, 1, 1, 1),\ (2, 1, 2, 2, 1, 2), \\ &(1, 2, 2, 1, 1, 2),\ (2, 1, 1, 2, 2, 1),\ (1, 2, 2, 1, 1, 2)\} \end{aligned}$$

(3) $\lambda(8, 2) = 32$

Since $1 + 7(2 - 1) = 2^3$, $\lambda(7, 2) = 2^{7-3} = 16$

$$\frac{28}{1 + 8} \leq \lambda(8, 2) \leq 2\lambda(7, 2),\ \ 29 \leq \lambda(8, 2) \leq 32$$

(i) If $m = 29$

$7(X)_i \geq 2^7 - 29 = 99,\ \ (X)_i \geq 15$

$m = (X)_1 + (X)_2 \geq 30$ a contradiction.

(ii) If $m = 30$

$7(X)_i \geq 2^7 - 30 = 98,\ \ (X)_i \geq 14$

$(X)_i = 14, 16$ or $(X)_i = 15, 15$

$5(XY)_{ij} \geq 2^6 - (X)_i - (Y)_j \geq 33\ \ \ (XY)_{ij} \geq 7$

If there are two columns with $(X)_1 = 14$, $(X)_2 = 16$ then $5(XY)_{11} \geq 2^6 - (X)_1 - (Y)_1 = 36$, $(XY)_{11} \geq 8$, $(X)_1 = (XY)_{11} + (XY)_{12} \geq 15$ contradiction. So there is at most one column with $(X)_i = 14, 16$, and at least seven columns, say the first seven columns, with $(X_1) = (X)_2 = 15$

Say $(XY)_{ij} = \begin{cases} 7 & i = j \\ 8 & i \neq j \end{cases}$

$$3(XYZ)_{ijk} \geq 32 - (XY)_{ij} - (XZ)_{ik} - (YZ)_{jk}$$
$$\therefore (XYZ)_{ijk} \geq 3$$

and

$$(XYZ)_{111} \geq 4$$
$$\therefore (XYZ)_{111} = 4$$
$$(XYZ)_{121} = (XYZ)_{211} = (XYZ)_{112} = 3$$
$$(XYZ)_{221} = (XYZ)_{212} = (XYZ)_{122} = 5$$

$(XYZ)_{222} = 2$ a contradiction.

(iii)　If $m = 31$

$$7(X)_i \geq 2^7 - 31 = 97, \quad (X)_i \geq 14$$
$$(X)_i = 14, 17 \text{ or } 15, 16$$

If there are two columns with $(X)_i = 14, 17$, say $X = A, B$, then

$$5(AB)_{11} \geq 64 - 14 - 14 = 36 \qquad (AB)_{11} \geq 8$$
$$5(AB)_{12} \geq 64 - 14 - 17 = 33 \qquad (AB)_{12} \geq 7$$

$(A)_1 = (AB)_{11} + (AB)_{12} \geq 15$, a contradiction. Hence there must be at least seven columns with $(X)_i = 15, 16$, let them be the first seven columns. For any two columns X, Y, at least one of $(XY)_{ij}$ is 7. Assume

$$(XY)_{ij} = \begin{cases} 7 & i = j = 1 \\ 8 & \text{otherwise} \end{cases}$$
$$(XYZ)_{ijk} \geq 32 - (XY)_{ij} - (YZ)_{jk} - (XZ)_{ik}$$
$$(XYZ)_{ijk} \geq 3 \text{ and } (XYZ)_{111} \geq 4.$$

We have for $X = C, D, E, F, G$ with the components suitably named.

$$(XYZ)_{111} = 4$$

and

$$(XYZ)_{121} = (XYZ)_{211} = (XYZ)_{112} = 3$$
$$(XYZ)_{221} = (XYZ)_{212} = (XYZ)_{122} = 5$$
$$(XYZ)_{222} = 3$$

For X, Y, Z, W be four of the first seven columns

$$(XYZW)_{2222} \geq 2^4 - (XYZ)_{222} - (XYW)_{222} - (XZW)_{222} - (YZW)_{222}$$
$$\geq 4$$

We only have the case

$$(ABCDEFG)_{2222222} \geq 4$$

and the last component is 1 or 2, i.e. H must have two repeated vectors, a contradiction.

Hence: $\lambda(8, 2) = 32$

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A SIMPLE PHYSICAL MODEL OF THE MECHANISM RESPONSIBLE FOR THE PRODUCTION OF THE EQUATORIAL EVENING MINIMUM AND ITS ACCOMPANYING EQUATORIAL SCINTILLATION

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INTRODUCTION

The first published report concerning severe equatorial scintillations in radio star observations at Legon, Ghana appeared in 1954. Since that time, they have been the subject of numerous studies. Excellent reviews by Basu and Kelly (1979) and Basu and Basu (1980) give the present state of our knowledge of this rather intricate problem. Scintillations obviously involve an ionospheric plasma instability. Their occurrence has a pronounced diurnal variation, a seasonal variation, a solar cycle variation, a longitudinal variation and a variation with magnetic activity. Efforts to construct a simple physical model thatwill agree with experiment in all the above aspects have proved difficult, and have not as yet been completely successful.

The aim of this paper is to present a simple physical model of a mechanism responsible for the production of these seemingly complex phenomena, and to demonstrate that the model agrees with all currently known experimental results.

BASIC ASSUMPTIONS OF THE MODEL

A basic ingredient of this model is the phenomenon variously mentioned in the literature as the "equatorial evening minimum" (Koster 1971, 1972, 1973, 1978), radar plumes (Woodman and LaHoz, 1976) and plasma bubbles (McClure, Hansen and Hoffman, 1977). The equatorial evening minimum and the plasma bubbles manifest themselves as a "bite out" in the total electron content plots of the equatorial ionosphere immediately prior to, and coincident with

severe scintillations. The radar plumes appear in the digital power maps of the Jicamarca radar in accompaniment with severe scintillations. These plumes are manifestations of the bubble phenomenon, and it has been suggested by McClure (1977) that the equatorial evening minimum is another manifestation of the same phenomenon. The question of whether the equatorial evening minimum is the causative mechanism in irregularity production, or whether it is merely a triggering mechanism for the onset of one of the well known plasma instabilities (e. g., the Rayleigh Taylor instability) is not addressed here.

A second basic assumption in our model is that the driving force in the irregularity production/triggering is provided by the thermospheric neutral winds. These winds in the F-region are dominated by ion drag in the E-region and blow across isobars outward from the so-called "diurnal thermal bulge".

DESCRIPTION OF THE MODEL

The phenomenon under study involves the transport of charge in a plasma. It is conceptually simplest to approach this from the viewpoint of hydromagnetics. The F-region ions and electrons are "frozen" to the magnetic field lines. During the daytime these field lines terminate in a relatively highly conducting E-region, and any convective motion of the field lines is opposed by the frictional collision forces acting on the ions in the E-region. Around E-region sunset, however, the E-region ionization largely disappears, and a much freer 3-dimensional field line convection becomes physically possible. The probability that field line interchange, and hence that charge movement will take place after sunset is directly proportional to the availability of forces capable of effecting these interchange motions.

In our model we define a dimensionless quantity called the "probability of disturbance" (PROB) in the plasma as the ratio of the thermospheric wind pressure (WP) on the magnetic field to the

magnetic field energy density or pressure (MP) at the height in question.

Our variable WP depends on the following:

(a) We shall assume that the dynamic neutral wind energy density is given by: $\frac{1}{2}\rho_n v_n^2$, where ρ_n is the neutral particle density and v_n is the velocity of the neutral wind.

(b) This wind exerts pressure on the field via collisions with ions in the plasma, and this is assumed to be proportional to ρ_i/ρ_n, where ρ_i is the ion density in the plasma.

(c) The velocity in question is the component of the neutral wind velocity normal to the field lines. Hence we replace v_n with $v_n \cos \alpha$, where α is the angle between the neutral wind direction and the normal to the field lines.

Hence we have the expression:

$$\text{WP} \propto \rho_i\, v_n^2 \cos^2 \alpha \tag{1}$$

All the above variables in our model are functions of thermospheric temperature. Hence thermospheric temperature and its gradient play a crucial role in our model. We shall adopt the simplified model of Jacchia (1964). It states:

$$T(\chi) = (T(0)/1.28)\,(1 + 0.28\cos^{2.5}(\chi/2))$$

where χ is the angle between any point in the thermosphere and the thermospheric bulge. The latter is a point at the same latitude as the subsolar point, but displaced 30° (2 hours) eastward from it.

It should be noted that the horizontal temperature gradient can easily be obtained from the above expression by differentiation. $T(0)$ in the equation is the temperature at the thermospheric bulge. In an initial test of our model, published values of $T(0)$ were used (see Jacchia, 1967).

Jacchia's simplified model will also be used to provide another important parameter—the direction of the neutral wind at any time. This will be taken as the direction away from the thermospheric bulge.

Having chosen our thermospheric temperature model, we use it to derive the following:

(d) $v_n^2 \propto$ Grad T

(e)   From the model, Grad T at any time is given by:

$$\text{Grad } T \propto T(0) \cos^{1.5} (\chi/2) \sin (\chi/2).$$

(f)   The daily maximum value of ρ_i, $\rho_{i\,(max)}$ is taken as being proportional to $T(0)$.

ρ_i, χ and α are also functions of time. Simple analytical expressions for χ and α as functions of time are easily derivable, and are not given here. In a rather crude test of our model, we shall assume that $\rho_i = \rho_{i\,(max)} \exp(-(t-t_0)/\tau)$, where t_0 is taken as 17 hours local time, and the time constant τ is of the order of 3 hours. This fits actual TEC plots reasonably well in the evening hours, where it will be used. Our final expression for WP then becomes:

$$\text{WP} \propto T(0)^2 \cos^2 \alpha \cos^{1.5} (\chi/2)$$
$$\cdot \sin(\chi/2) \exp(-(t-t_0)/\tau) \tag{2}$$

Finally, our magnetic field pressure term is given by:

$$\text{MP} = B^2/\mu_0$$

Hence, the expression for PROB in our model is of the form:

$$\text{PROB} \propto T(0)_2 \cos^2 \alpha \cos^{1.5} (\chi/2)$$
$$\cdot \sin(\chi/2) \exp(-(t-t_0)/\tau)/B^2 \tag{3}$$

In testing our model, we shall limit our discussion to times around sunset or later, for the following reason. The E-region critical frequency is observed to follow an approximate law given by the expression:

$f_0 E(\chi) = f_0 E(0) \cos^n(\chi)$, where $n=0.25$ to 0.30 and χ is the solar zenith angle. Since the E-region conductivity is proportional to the E-region electron density N, and the latter is proportional to $(f_0 E)^2$, our conductivity follows a $\cos^{0.5}(\chi)$ law. Field line interchange becomes possible, therefore, when χ has a value of about 85° at the earliest.

In our model we determine the location of the north and south ends of the field lines passing over the dip equator at some appropriate longitude and height (350 km was used in the results shown) and determine the time of ground sunset under each. The later of the two times determines the earliest time at which rapid field line interchange can begin. Since the F-region ion density is also decreasing quite rapidly at this time, our neutral wind pressure is likely to become a decreasing function of time soon thereafter. These two opposing conditions normally cause the probability of field line interchange to have a rather sharp maximum around sunset.

It is also worth noting that the rates and times at which these two processes occur could easily spell the difference between a slow and relatively smooth onset of field line interchange and an abrupt and almost explosive onset when the rates are rapid. Ion density depends on local time at the point over the dip equator; field line E-region sunset depends on local time at a point a considerable distance away. Field geometry and solar declination can therefore play a crucial role. These differ at each observing station.

COMPARISON OF MODEL PREDICTIONS WITH EXPERIMENTAL RESULTS

To test the model, we investigate values of PROB, as defined above, at four equatorial stations with differing longitude and field geometries. Reliable seasonal variations of scintillation at these stations have recently appeared in the literature (Aarons *et al.* 1980). The stations, with their appropriate subionospheric longitudes are:

Huancayo, Peru (65.8° W)   Natal, Brazil (33.7° W)
Legon, Ghana   (1.1° W)   Guam   (147.0° E)

The value of PROB is determined for each station when the solar zenith angle is 85° at the north or south (whichever is later) end of the field line crossing the dip equator at a neight of 350 km. Values are computed for the 15th of each month for a year. Values of PROB against month for each of the four stations are plotted in
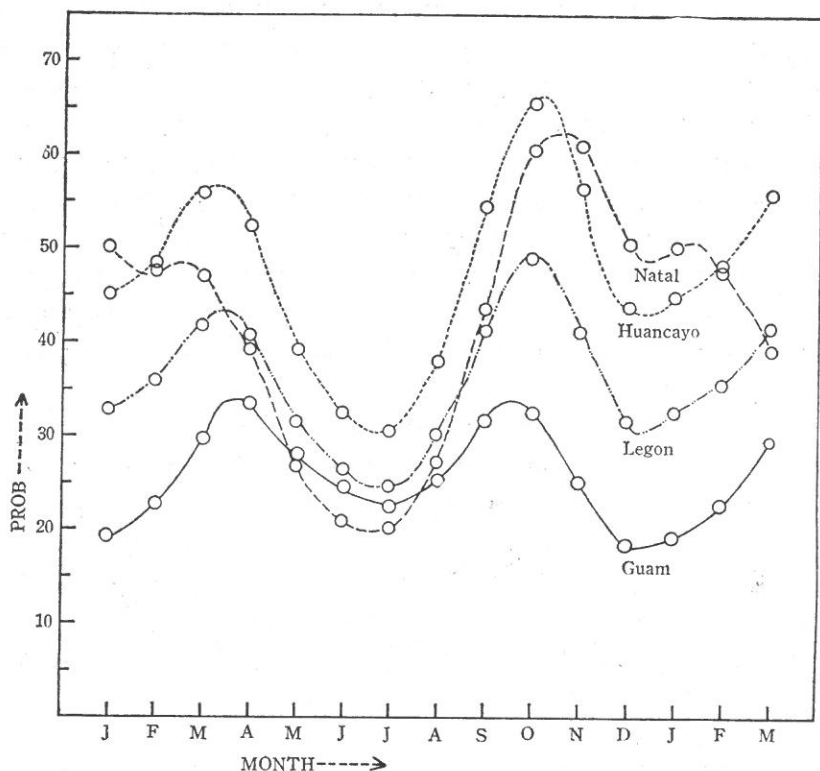
Fig. 1. Monthly values of PROB predicted by the model for Natal, Huancayo, Legon and Guam.

Fig. 1. It should be noted that values of PROB are in arbitrary units, but these are identical for the four stations. We note the following points:

(a) The longitudinal variation of PROB agrees well with the experimental variations of scintillation given by Basu and Basu (1980).

(b) The seasonal variation of PROB at each of the four stations is in qualitative agreement with the observed seasonal behaviour of scintillation at all of the stations. Note especially that Guam has its deepest minimum in December, while the other stations have minimum values in July.

(c) The model predicts the observed diurnal variation of scintillation. Field line interchange can only begin around ground sunset. If the mechanism is going to give rise to scintillations, these should develop within an hour or two of the onset of rapid interchange.

(d) The model predicts a sunspot cycle variation in accord with observations, since the neutral wind velocity is a function of thermospheric temperature, which has a marked 11 year cycle, with maximum temperatures around sunspot maximum.

(e) The model predicts a dependence of scintillations on magnetic disturbances, since the thermospheric temperature and its gradient are likely to be seriously disturbed at these times. The large 20–22 hour local time maximum in scintillation might well be significantly reduced. However, increases in scintillation might well be expected at other hours of the night during storm time, especially around sunrise. Irregularities could easily be formed in the newly created F-region around dawn. Both of these effects are observed to happen at equatorial stations.

Further comparisons of model predictions with experimental scintillation results are currently under way. To date, no serious discrepancies between model predictions and experimental results have been found.

CONCLUSION

A physical model for the production of equatorial field line interchange and for the triggering and/or production of its accompanying scintillations, bubble formation and radar plume production has been given. Agreement with experiment is excellent. Some of the assumptions made in designing and testing the model are relatively crude and can, no doubt, be significantly improved. But the relative simplicity of the model, together with its agreement with experimental results suggests that it is basically valid.

A much more extensive description of the model, and a wider comparison of its predictions with observation is in advanced state

of preparation, and will be published soon. It is hoped that enough detail has been given here so that others can test the model as well.

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AN INTELLIGENT CHINESE TERMINAL
WITH CHARACTER GENERATOR

Yeong-Wen Hwang

ABSTRACT

The character generator way of implementing a Chinese computer system is proposed. This method of approach makes the resultant system outstanding in many aspects.

Memory is saved and vocabulary increased. Characters are composed instantly within the terminal by the generator program in microprocessor, therefore the displaying speed is fast and costs no computer time. Slow access time of disk storage and mechanical wearing-out of disk is avoided.

The terminal accepts multiple input code systems including the quick-learning Component System code. Code systems may even be mixed in input. Abbreviated and varient characters together with regular forms are acceptable in input without ambiguity.

System commands are tabled. Internal code and sampled TV output characters are shown.

I. INTRODUCTION

Most Chinese processing systems use pre-stored character patterns. Due to their complicated forms and a large number of characters needed (especially in names and addresses), pre-storing character patterns calls for a tremendous memory space, thus requiring large secondary storages, such as disk. Using disks in such a system has two basic drawbacks. One is the slow response in generating Chinese characters, far slower than alphanumeric characters. The other is the rapid wear of the disk mechanism due to the extremely heavy use of the disk required for retrieving character patterns for display.

Some systems have part of the patterns in main memory. The memory space required by these patterns is still quite large and available space seems always inadequate for efficient usage in most cases.

The Chinese character generator proposed in this paper resolved these problems by generating patterns locally in the terminal, just

similar to the alphanumerical case.

II. PHYSICAL IMPLEMENTATION

The terminal is implemented with Intel 8080 microprocessor. Monitor, editor, as well as the character generator are installed in firmware form in read only memory.

The incoming message in internal code form is buffered in a RAM memory. The editor displays it on the CRT. To display, each code is first searched in a conversion table. If the internal character code is found in the table, the address of the corresponding component code is sent to the character generator which generates a composed character pattern from the code and displays in on CRT (or prints it on a local printer). A whole screen can be displayed in just about a second, much faster then existing systems.

Characters are decomposed into 471 components in the Geometrical Component System.[1-3]   In order to reconstruct characters from the components, a few operators are devised to furnish geometrical positioning information about components for the character generator.

Therefore the component code consists of two parts: the components and the operators. In most cases (93%) only one operator is needed and there is no need of a delimiter between characters since the operator serves this function too. Several examples are given below:

Character	Component code	
	Components	Operator
計	言十	H
算	竹目廾	V
機	木㡬人	H
會	會	H
議	言羊我	L

where H, V, L represent horizontal, vertical and left operator respectively. In the third example, a containing operation, (component 㡬 contains component 人) is included, but this is no user's concern as the containing operation is done automatically by the generator program.

Each component code uniquely defines a character without any ambiguity and it contains just sufficient information for reconstructing the character pattern.

The editor of the terminal accepts character input from the keyboard which is interfaced to the μp. The keyboard has 256 keys with a shift key to accommodate the 471 components and control functions.

Since very few characters have identical component sequences (of the fifty thousand characters, there are only around ten), operators in the component code are omitted during input (with the insertion of a delimiter). This further simplifies the input procedure.

The component sequence from keyboard input is searched in a table to find its equivalent internal code.

The character generator together with component patterns and alphanumerical patterns take 12K byte PROM memory. The monitor and text editor take 3K bytes. The rest of memory space may be devoted to the conversion table. The author uses actually 14KB for this table accommodating 1663 characters. If all 64KB capacity of 8080 is used, about 48KB may be used for the table, therefore over 5,700 characters may be implemented. This is a remarkable saving in memory as compared with the direct method using pre-stored character patterns which requires at least 4 to 5 times more memory.

Besides, there are two advantages over the direct method. First, it provides two ways to input—through component code or through traditional telegraph code (if telegraph code is used as the internal code). The two codes may even be mixed in any manner during keying-in. In the direct method, only one (telegraph) code may be used. Secondly, the displayable characters are not limited by the conversion table. Basically, all 50,000 characters can be displayed using the Geometrical Component System if one keys in the components together with the operator or if such information is supplied by the computer.

A CRT oriented editor was written and worked well. Its functions are very similar to those used in Univac terminals, except dealing mainly with Chinese instead of English.

Table 1. Functioning codes

(i) Line control codes:

013 Cursor position (followed by two bytes)

012, x, y: y=line number; x=character number (040, 041,...)

012 Line feed

015 Carriage return

025 Home up cursor

026 Erase to end of line

027 Erase to end of screen

007 Beep

030 Cursor on

031 Cursor off

032 Local printer on

024 Local printer off

010 Back space

003 End of transmismission

016 Protect begins

017 Protect ends

! Code not in disk's list

Returned codes follow

Format: #$b_1b_2b_3$, component code & operator, 003

(ii) Editor commands:

(key) ⇐	Move cursor left one place
⇒	Move cursor right one place
⇑	Move cursor up one place
⇓	Move cursor down one place
始端	Home up (first unprotected position)
終了	Go to end (last unprotected position)
去字	Delete a character
去行	Delete a field
去盡	Delete from cursor to end
ⓩ	Component code mode
ⓝ	Telegraph code mode
ⓣ	Other code system mode
字終了	End of a character
ⓟ	End of editing, transmit
英數	Alphanumerical mode
印	Local print
Component key Insert automatically	

Two versions of CRT are developed. Both have 13 line screens, but one has 13 characters per line, the other 25 characters per line. Two alphanumeric characters share one character space. The editor has commands to protect or de-protect fields with underlined user keying areas, position cursor, insert or delete text in a field, etc. as listed in Table 1.

The μp in the terminal takes care of keying-in or screen editing job which cost no CPU time to the computer. It also stores a whole transaction or message from computer into the buffer. With only internal code blocks appearing on the communication line, the Chinese terminal behaves quite similar to an ASCII terminal. It can work simultaneously with ASCII terminals or many terminals may be connected.

The internal code used has 3 bytes for each character based on traditional telegraph code. Although 2 bytes/character is the theoretical minimum (and it may be used in the system with slight modification), the 3-byte internal code makes it completely compatible with the ASCII oriented software and hardware systems of present-day commercial computers.

The format of internal code is shown in Fig. 1. The code of each byte is within octal 040 to 177, coincides with the ASCII symbol range, leaving control codes and the 8th bit intact. Therefore all
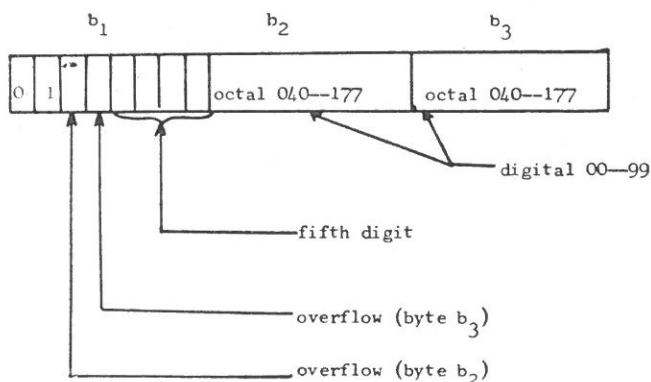

Fig. 1. Internal code structure

the software utilities in the original computer may be fully used to handle the Chinese files just like alphabets. If we were to modify system programs for handling Chinese, then constant and frequent modifications would be necessary to keep up with the change made by the computer manufacturers.

The four digits of telegraph code are divided into two-digit groups to be added with octal 040. 00–95 are thus converted to 040–177. For numbers 96–99, 0–3 are used with overflow bits set in the first byte b_1. In this way, very simple arithmetic operations are needed to convert between telegraph and internal codes (no multiplication/division, digital/binary transforms or tables needed). The first code byte also has 4 bits for the expanding of telegraph digits. The range of the telegraph code is expanded over the traditional 9999 to 99999 or even 16×9999 for the appending of additional characters.

Abbreviated characters and characters of variant forms are allowed in this system. 163 of them have been implemented. Their component codes are different from regular forms, but the same unique internal code will always be obtained and the regular form displayed. Such functions are accomplished through design in the conversion table.

In order to expand vocabulary having standard internal code, one needs only to establish the remainder of the conversion table in disk storage in the main computer. (Here we again have a saving in memory space because the table is smaller than pattern size.)

Table 2. Message from terminal to computer

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1. Message format
   $...data...015...data...015...014
       015—field identifier
       014—end
       Only unprotected areas are sent
2. Component code asking
   &...component code...014
3. Telegraph code asking
   * b_1 b_2 b_3 014

Occassionally the μp can consult the computer for unfound characters in the table to get both operators and internal codes. Symbol "&" is used for consulting with component code and "*" with telegraph code. Answering from computer is in one format for both codes. This is illustrated in Table 2.

III. RESULTS/CONCLUSION

The generated characters are sometimes slightly inferior in appearance to patterns if matrixed to the best as whole characters. Great efforts were made to improve their appearance with success,[2] this problem is now a very minor one especially when used at terminals. For dainty applications, one can additionally store whole patterns in the computer like usual Chinese systems do. The generated characters are shown in Fig. 2 as example.
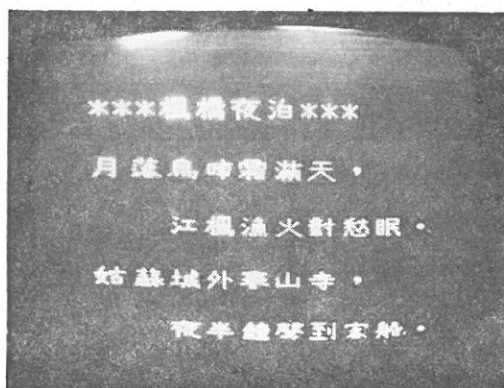

Fig. 2. Output character samples on TV

The terminal setup consists of an Intel SBC 80/10 board as processor, PROM memory board for character genertor and table, a CRT interface board and a component keyboard as shown in Fig. 3. The system is implemented using a Datapoint 2200 or 5500 computer. The computer's interface with μp is RS232. With adjustment, the terminal may be used with any computer.
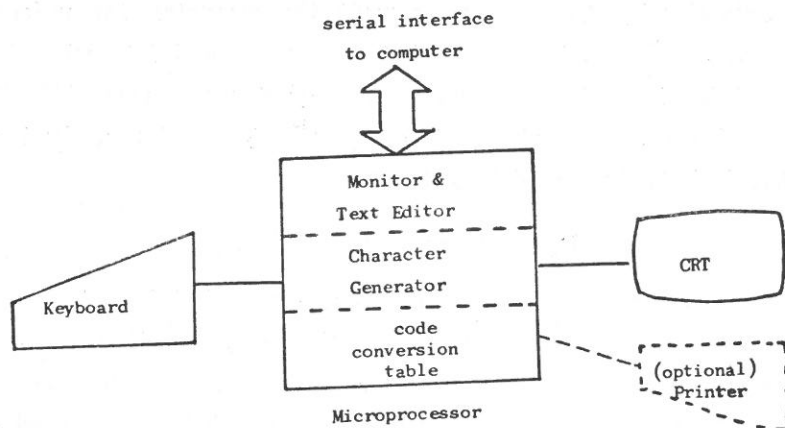
Fig. 3. Terminal block diagram

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A FACILE METHOD FOR THE PREPARATION OF 2-CHLORO-N-(*n*-ALKOXYMETHYL)-N-(2, 6-DIETHYLPHENYL)-ACETAMIDES AND THEIR MASS SPECTRA

Yung-Nan Chen

INTRODUCTION

A series of six 2–chloro–N–(*n*-alkoxymethyl)–N–(2, 6–diethyl-phenyl)-acetamides were prepared by a facile method in high yields and their mass spectra were studied.

2–Chloro–N–(*n*-alkoxymethyl)–N–(2, 6-diethylphenyl) – acetamides (III) are well known weed killers. Alachor (R=Me) and butachlor (R=*n*-Bu) for example are widely used here in Taiwan as weed killers. These amides were prepared from 2, 6–diethylaniline by the following steps. First, 2, 6–diethylaniline is reacted with formalde-hyde to give the corresponding imine (I). Then (I) is allowed to react with 2–chloroacetyl chloride to give 2–chloro–N–(chloromethyl) –N–(2, 6-diethylphenyl)-acetamide (II). Finally (II) is mixed with sodium *n*-alkoxides[1] or with *n*-alkyl alcohols in the presence of tertiary amines such as triethylamine or pyridine[2] to give (III).
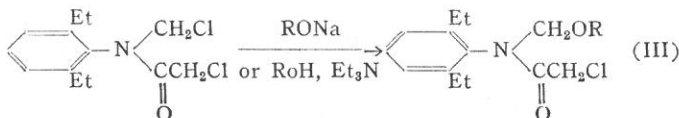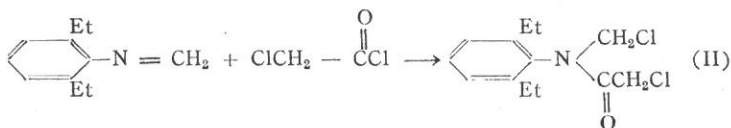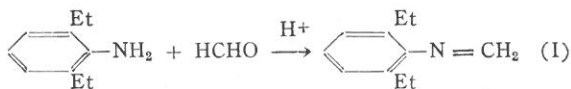
Compounds (III) can be prepared by many possible synthetic

paths; one of the best is the N–*n*–alkoxymethylation of 2–chloro–N–(2, 6–diethylphenyl)–acetamide (IV). In general amides are neutral in nature (PKa$\approx$15). However the inductive effect of chlorine makes 2–chloro–N–(2, 6–diethylphenyl)–acetamide more acidic and its conjugated base (IVa) is present to some extent in the presence of a strong base.

$$\underset{(IV)}{\underset{Et}{\overset{Et}{\bigcirc}}-NH-\overset{\overset{O}{\|}}{C}CH_2Cl} \underset{\rightleftarrows}{\overset{OH^-}{}} \underset{Et}{\overset{Et}{\bigcirc}}-\overset{-}{N}-CH_2Cl \quad (IVa)$$

In the presence of strong alkoxymethylation agents, (IVa) may produce (III). We found that chloromethyl alkyl ethers are strong SN1 like reagents[3] for alkoxymethylation. Therefore we chose six ROCH$_2$Cl (R=Me, Et, *n*-Pr, *n*-Bu, *n*-Pen, *n*-Hex) as the alkoxymethylation agents. We found this to be an easier method to prepare 2–chloro–N–(*n*-alkoxymethyl)–N–(2, 6- diethylphenyl)–acetamides. The products were obtained in high yields in only two steps from 2, 6-diethylaniline. First 2, 6–diethylaniline was reacted with 2–chloroacetic acid in the presence of phosphorus trichloride to give 2–chloro–N–(2, 6–diethylphenyl)–acetamide (IV). Then (IV) reacted with chloromethyl *n*-alkyl ethers in the presence of a strong base (NaOH) to give the title compounds.

$$\underset{Et}{\overset{Et}{\bigcirc}}-NH_2 + ClCH_2CO_2H \overset{PCl_3}{\longrightarrow} \underset{Et}{\overset{Et}{\bigcirc}}-NH-\overset{\overset{O}{\|}}{C}CH_2Cl$$

$$\underset{Et}{\overset{Et}{\bigcirc}}-NH-\overset{\overset{O}{\|}}{C}CH_2Cl + R-O-CH_2Cl \overset{OH^-}{\longrightarrow} \underset{Et}{\overset{Et}{\bigcirc}}-N\overset{CH_2OR}{\underset{\underset{O}{\overset{\|}{C}CH_2Cl}}{}} \quad (III)$$

(IIIa): R=Me
(IIIb): R=Et
(IIIc): R=*n*-Pr
(IIId): R=*n*-Bu
(IIIe): R=*n*-Pen
(IIIf): R=*n*-Hex

EXPERIMENT

(I) Preparation of 2-chloro-N-(2, 6-diethylphenyl)-acetamide

To a mixture of 15g of 2, 6-diethylaniline, 10g of 2-chloroacetic acid and 250 ml of toluene in a 500 ml flask 6 g of phosphorus trichloride was carefully added. The mixture was then refluxed until the evolution of hydrogen chloride ceased and the mixture in the flask became a clear solution. It was then cooled to room temperature, washed with three portions (100 ml) of water, and the organic layer dried over anhydrous calcium chloride. After evaporating the toluene, a white solid was obtained. Recrystallization from n-hexane gave 2-chloro-N-(2, 6-diethylphenyl)-acetamide, (22g, 95%) mp. 133-134°C, $C_{12}H_{16}ClNO$, (M$^+$ m/e 225, M$^+$/M$^+$ + 2 = 3/1). IR. 3280, 3040, 2950, 1660, 1595, 1540, 1470, 810, 790, 720 cm^{-1}. N. M. R. δ 7.07 (3H, m,

Ar–H), 4.18 (2H, s, $-\overset{\overset{O}{\|}}{C}-CH_2Cl$), 2.58 (4H, q, J=8Hz, Ar–$C\underline{H}_2$–CH$_3$ ×2), 1.60 (1H, br, N–H), 1.20 (6H, t, J=8Hz, Ar–CH$_2$–$C\underline{H}_3$ ×2). Mass spectrum m/e 227, 225, 176, 148, 147, 132, 120, 117, 106, 104, 91, 77, 65, 51 (base peak m/e 176).

(II) Preparation of chloromethyl n-alkyl ethers

Chloromethyl n-alkyl ethers were prepared according to the Hill Keach method[4] for the preparation of chloromethyl n-butyl ether. $ClCH_2$-O-CH_3 bp. 52°C, $ClCH_2$-O-C_2H_5 bp. 80°C, $ClCH_2$-O-$CH_2C_2H_5$ bp. 112°C, $ClCH_2$-O-n-Bu bp. 134°C, $ClCH_2$-O-n-Pen bp$_{500}$ 140°C, $ClCH_2$-O-n-Hex bp$_{500}$ 164°C.

(III) Preparation of 2/chloro-N-(2, 6-diethylphenyl)-N-(methoxymethyl)-acetamide

To a mixture of 22.5 g of 2-chloro-N-(2, 6-diethylphenyl)-acetamide in 100 ml of acetone and 20 g of 40% NaOH solution was added 10g of chloromethyl methyl ether. During mixing, the solution was vigorously stirred and the temperature maintained between 25°C and 30°C. After the addition, stirring was continued and the temperature was maintained constant for half an hour. Then the organic layer was concentrated to give a white solid. Recrystallization from

n-hexane gave 2-chloro-N-(2, 6-diethylphenyl)-N-(methoxymethyl)-acetamide ($C_{14}H_{20}ClNO_2$, M$^+$ m/e 269, M$^+$/M$^+$+2=3/1), mp. 38–39°C (4.2g, 90%). IR. 3040, 2950, 2850, 1680, 1595, 1460, 1320, 1240, 1090, 810, 790 cm^{-1}. N. M. R. δ 7.15 (2H, s, Ar–H), 4.90 (2H, s, –N–CH$_2$–O–),

3.58 (2H, s, $-\overset{\overset{\text{O}}{\|}}{\text{C}}$–CH$_2$Cl), 3.42 (3H, s, -O–CH$_3$), 2.62 (4H, q, J=8Hz, Ar–C$\underline{\text{H}}_2$–CH$_3$×2), 1.20 (6H, t, J=8Hz, Ar–CH$_2$–C$\underline{\text{H}}_3$×2). Mass spectrum m/e 269 (M$^+$), 238, 237, 234, 224, 220, 202, 188, 160, 77, 45 (base peak m/e 45).

(IV) Preparation of 2-chloro-N-(ethoxymethyl)-N-(2, 6-diethyl-phenyl)-acetamide

To a mixture of 2-chloro-N-(2, 6-diethylphenyl)-acetamide (22.5g) in 100 ml of acetone and 20g of NaOH (40%) solution was added 12g of chloromethyl ethyl ether with vigorous stirring. The temperature was maintained between 25°C and 30°C. After the addition, stirring was continued and the temperature held constant for half an hour. Then the organic layer was concentrated. This was followed by vacuum distillation to give 2-chloro-N-(ethoxymethyl)-N-(2,6-diethylphenyl)-acetamide ($C_{15}H_{22}ClNO_2$, M$^+$ m/e 283, M$^+$/M$^+$ + 2 = 3/1), bp$_{0.5}$ 136–139°C (24.9 g, 88%). IR. 3040, 2950, 2850, 1680, 1595, 1460, 1320, 1240, 1090, 810, 790 cm^{-1}. N. M. R. δ 7.15 (3H, m, Ar–H),

4.94 (2H, s, –N–CH$_2$–O–), 3.60 (2H, s, $-\overset{\overset{\text{O}}{\|}}{\text{C}}$–CH$_2$Cl), 3.54 (2H, q, J=8Hz, –O–C$\underline{\text{H}}_2$–CH$_3$), 2.60 (4H, q, J=8Hz, Ar–C$\underline{\text{H}}_2$–CH$_3$×2), 1.26 (6H, t, J=8Hz, Ar–CH$_2$–C$\underline{\text{H}}_3$ × 2), 1.22 (3H, t, J=8Hz, –O–CH$_2$–C$\underline{\text{H}}_3$). Mass spectrum m/e 283 (M$^+$), 248, 238, 237, 234, 224, 202, 188, 160, 77, 59 (base peak m/e 59).

(V) Preparation of 2-chloro-N-(2, 6-diethylphenyl)-N-(n-propoxy-methyl)-acetamide

To a mixture of 2-chloro-N-(2, 6-diethylphenyl)-acetamide (22.5g) in 100 ml of acetone and 20g of 40% NaOH solution, was added 13 g of chloromethyl n-propyl ether with vigorous stirring. The temperature was maintained between 25°C and 30°C. After the addition,

stirring was continued and the temperature control was maintained for half an hour. Then the organic layer was concentrated and vacuum distilled to give 2–chloro–N–(2, 6–diethylphenyl)–N–(n-propoxymethyl)-acetamide ($C_{16}H_{24}ClNO_2$, M^+ m/e 297, $M^+/M^+ + 2 = 3/1$), bp$_{0.5}$ 145–148°C (25.8g, 87%). IR. 3040, 2950, 2850, 1680, 1595, 1460, 1320, 1240, 1100, 810, 790 cm^{-1}. N. M. R. δ 7.15 (3H, m, Ar–H), 4.90

(2H, s, –N–CH$_2$–O–), 3.60 (2H, s, $\overset{\overset{\text{O}}{\|}}{-\text{C}}$–CH$_2$Cl), 3.57 (2H, t, J=8HZ, –O–CH$_2$–CH$_2$–CH$_3$), 2.59 (4H, q, J=8Hz, Ar–CH$_2$–CH$_3$×2), 1.58 (2H, h, J=8Hz, –O–CH$_2$–CH$_2$–CH$_3$), 1.26 (6H, t, J=8Hz, Ar–CH$_2$–CH$_3$ × 2), 0.87 (3H, t, J=8Hz, –O–CH$_2$–CH$_2$–CH$_3$). Mass spectrum m/e 297 (M^+), 262, 248, 238, 237, 224, 202, 188, 160, 77, 73, 45, 43 (base peak m/e 43).

(VI) Preparation of 2–chloro–N–(n-butoxymethyl)–N–(2, 6-diethylphenyl)-acetamide

To a mixture of 2–chloro–N–(2, 6–diethylphenyl)–acetamide (22.5g) in 100 ml of acetone and 20 g of 40% NaOH solution was added 15 g of chloromethyl n-butyl ether with vigorous stirring. Again the temperature was kept between 25°C and 30°C. After the addition, the temperature control and stirring were continued for half an hour. The organic layer was concentrated and then vacuum distilled to give 2–chloro–N–(n-butoxymethyl)–N–(2, 6–diethylphenyl)–acetamide ($C_{17}H_{26}ClNO_2$, M^+ m/e 311, $M^+M^+ + 2 = 3/1$), bp$_{0.5}$ 154–156°C (26.4 g, 85%). IR. 3040, 2950, 2850, 1680, 1595, 1460, 1320, 1240, 1100, 810, 790 cm^{-1}. N. M. R. δ 7.15 (3H, m, Ar–H), 4.90 (2H, s, –N–CH$_2$–O–), 3.64 (2H, t, J=8Hz, –O–CH$_2$–CH$_2$C$_2$H$_5$), 3.60 (2H, s, $\overset{\overset{\text{O}}{\|}}{-\text{C}}$–CH$_2$Cl), 2.64 (4H, q, J=8Hz, Ar–CH$_2$–CH$_3$×2), 1.22 (6H, t, J=8Hz, Ar–CH$_2$–CH$_3$×2). Mass spectrum m/e 311 (M^+), 276, 262, 238, 237, 224, 202, 188, 160, 87, 77, 57, 45, 43 (base peak m/e 57).

(VII) Preparation of 2–chloro–N–(2, 6-diethylphenyl)–N–(n-pentoxymethyl)-acetamide

To a mixture of 2–chloro–N–(2, 6–diethylphenyl)–acetamide (22.5g) in 100 ml of acetone and 20 g of 40% NaOH solution was added 16 g

of chloromethyl n-pentyl ether with vigorous stirring. The temperature was kept between 25°C and 30°C. After the addition, the temperature control and stirring were continued for half an hour. The organic layer was concentrated, then vacuum was distilled to give 2–chloro–N–(2,6–diethylphenyl)–N–(n-pentoxymethyl)-acetamide ($C_{18}H_{28}ClNO_2$, M^+ m/e 325, $M^+/M^+ + 2 = 3/1$), $bp_{0.5}$ 160–162°C (27.6g, 85%). IR. 3040, 2950, 2850, 1680, 1595, 1460, 1320, 1240, 1100, 810, 790 cm^{-1}. N.M.R. δ 7.15 (3H, m, Ar–H), 4.90 (2H, s, –N–CH$_2$–O–), 3.60

(2H, s, $-\overset{\overset{\textstyle O}{\|}}{C}-CH_2Cl$), 3.58 (2H, t, J=8Hz, –O–CH$_2$CH$_2$–C$_3$H$_7$), 2.62 (4H, q, J=8Hz, Ar–CH$_2$–CH$_3$×2), 1.24 (6H, t, J=8Hz, Ar–CH$_2$CH$_3$×2). Mass spectrum m/e 325 (M$^+$), 290, 276, 238, 237, 224, 202, 188, 160, 101, 77, 71, 45, 43 (base peak m/e 43).

(VIII) Preparation of 2–chloro–N–(2,6-diethylphenyl)–N–(n-hexoxymethyl)-acetamide

To a mixture of 2–chloro–N–(2,6–diethylphenyl)–acetamide)22.5g) in 100 ml of acetone and 20 g of 40% NaOH solution was added 17 g of chloromethyl n-hexyl ether with vigorous stirring. The temperature was kept between 25°C and 30°C. After the addition the temperature control and stirring were continued for half an hour. Then the organic layer was concentrated and then vacuum distilled to give 2–chloro–N–(2,6-diethylphenyl)–N–(n-hexoxymethyl)-acetamide ($C_{19}H_{30}ClNO_2$, M^+ m/e 339, $M^+/M^+ + 2 = 3/1$), $bp_{0.5}$ 168–170°C 28.1g, 83%). IR. 3040, 2950, 2850, 1680, 1595, 1460, 1320, 1240, 1100, 810, 790, cm^{-1}. N.M.R. δ 7.15 (3H, s, Ar–H), 4.90 (2H, s, –N–CH$_2$–O–), 3.60

(2H, t, J=8Hz, –O–CH$_2$CH$_2$C$_4$H$_9$), 3.60 (2H, s, $-\overset{\overset{\textstyle O}{\|}}{C}-CH_2Cl$), 2.62 (4H, q, J=8Hz, Ar–CH$_2$–CH$_3$×2), 1.22 (6H, t, Ar–CH$_2$–CH$_3$ × 2). Mass spectrum m/e 339 (M$^+$), 304, 290, 238, 237, 224, 202, 188, 160, 115, 85, 77, 57, 45, 43 (base peak m/e 43).

DISCUSSION

Both IR and N.M.R. spectra indicate that 2–chloro–N–(n-alkoxymethyl)–N–(2,6-diethylphenyl)–acetamides are similar in structure.

All of their IR spectra show absorptions at 3040, 2950, 2850, 1680, 1595, 1460, 1320, 1240, 1090, 810, 790 cm^{-1} and only slight differences appear in the fingerprint region. Similarly, their N. M. R. spectra show peaks at $\delta \approx 7.15$ (3H, m, Ar–H), 4.90 (2H, s, –N–CH_2–O–), 3.60

(2H, s, $-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-Cl$), 2.60 (4H, q, J=8Hz, Ar–CH_2–$CH_3 \times 2$), 1.20 (6H, t, J=8Hz, Ar–CH_2–$CH_3 \times 2$). The differences are only due to the different alkyl groups present. R=Me, $\delta = 3.42$ (3H, s, –O–CH_3). R=Et, $\delta = 3.66$ (2H, q, J=8Hz, –O–CH_2–CH_3), 1.22 (3H, t, J=8Hz, –O–CH_2–CH_3). R=n-Pr $\delta = 3.57$ (2H, t, J=8Hz, –O–CH_2–CH_2–CH_3), 1.50 (2H, h, J=8Hz, –O–CH_2–CH_2–CH_3), 0.8 (3H, t, J=8Hz, –O–CH_2–CH_2–CH_3), and R=n-Bu, n-Pen, n-Hex, $\delta \approx 3.60$ (2H, t, J=8Hz, –O–CH_2–CH_2–R′, R′=Et, n-Pr and n-Bu) and complex signals from δ 1.80 to 0.7.

Mass spectra (Charts 1–6) not only show that these compounds have similar structures, but also show the differences among them. By comparing the mass spectra we can explain the fragmentation processes of 2–chloro–N–(n-alkoxymethyl)–N–(2, 6–diethylphenyl)–acetamides (Fig. 1). All the parent patterns show that these molecule contain one nitrogen (M^+ with m./e odd mass number) and one chlorine ($M^+/M^+ + 2 = 3/1$). Each spectrum has some peaks with identical mass number and peak patterns. This indicates that some fragments independent of R are identical for all compounds. Other peaks have different mass numbers but similar peak patterns. The mass number differences of the relative peaks are $(CH_2)n$ (n=1, 2, 3, 4, 5), indicating these peaks result from the fragments containing R or a part of R. In Table 1 we list some of these peaks and suggest the fragments to which they correspond.

Peaks with mass number m/e 238 and 240 result from simple fission of the molecular ion ($M^{+\cdot}$–RO·). This fragment contains one nitrogen and one chlorine atom. Therefore the peak ratio of 238/240 is 3/1. Peaks with mass number m/e 237 and 239 are the result of complex fission of the molecular ion with the loss of ROH ($M^{+\cdot}$–ROH). Again the peak ratio of 237/239 is 3/1. Peaks of mass number m/e 202, 188, 160 are the result of further fragmentation of the more active radical cation ($M^{+\cdot}$–ROH, m/e 237, 239). Complex peak
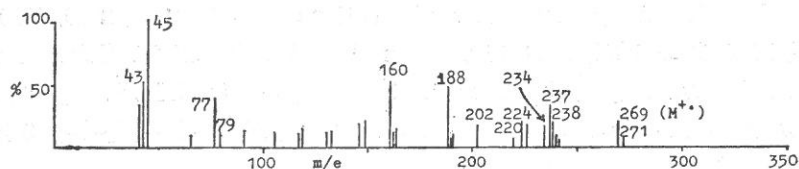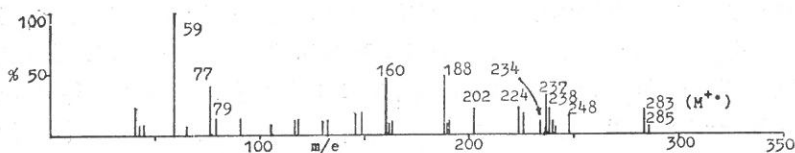
Chart 1. Mass spectrum of (IIIa).
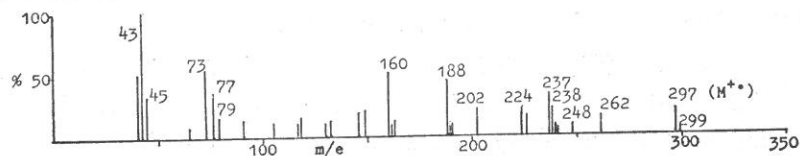

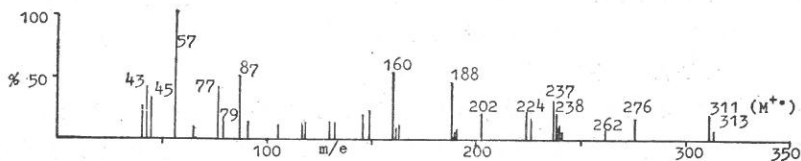Chart 2. Mass spectrum of (IIIb).

Chart 3. Mass spectrum of (IIIc).
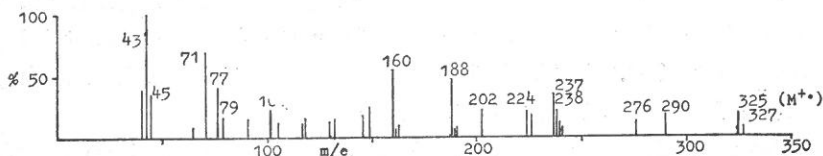

Chart 4. Mass spectrum of (IIId).
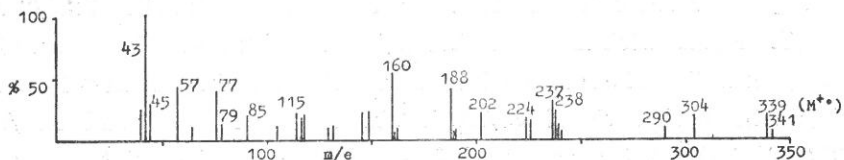

Chart 5. Mass spectrum of (IIIe).
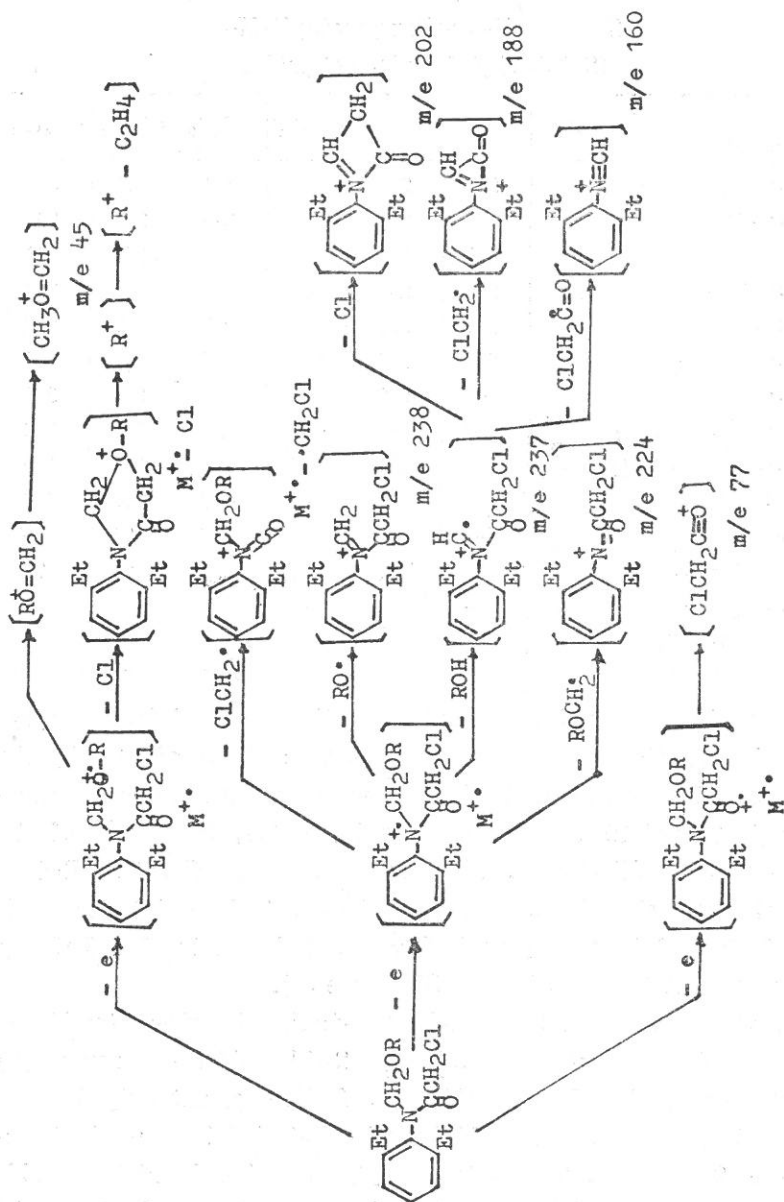

Chart 6. Mass spectrum of (IIIf).

Fig. 1. The fragmentation process of 2-chloro-N-(*n*-alkoxymethyl)-N-(2,6-diethylphenyl)-acetamides (R=Me, Et, *n*-Pr, *n*-Bu, *n*-Pen and *n*-Hex).

Table 1. Mass number (m/e) and suggested fragments of
2–chloro–N–(n-alkoxymethyl)–N–
(2, 6-diethylphenyl)-acetamides

Fragments R	CH$_3$	C$_2$H$_5$	n-C$_3$H$_7$	n-C$_4$H$_9$	n-C$_5$H$_{11}$	n-C$_6$H$_{13}$
M$^{+\cdot}$	269	283	297	311	325	339
M$^{+\cdot}$—Cl	234	248	262	276	290	304
M$^{+\cdot}$—CH$_2$Cl	220	234	248	262	276	290
M$^{+\cdot}$—RO$\cdot$	238	238	238	238	238	238
M$^{+\cdot}$—ROH	237	237	237	237	237	237
M$^{+\cdot}$—ROCH$_2^{\cdot}$	224	224	224	224	224	224
M$^{+\cdot}$—ROH—Cl	202	202	202	202	202	202
M$^{+\cdot}$—ROH—ClCH$_2^{\cdot}$	188	188	188	188	188	188
M$^{+\cdot}$—ROH—ClCH$_2\dot{C}$=O	160	160	160	160	160	160
RO$^+$=CH$_2$	45	59	73	87	101	115
R$^+$	—	—	43	57	71	85
ClCH$_2$C≡O$^+$	77	77	77	77	77	77
R$^+$—C$_2$H$_4$	—	—	—	—	43	57
CH$_3$—O$^+$=CH$_2$	45	—	45	45	45	45

patterns of mass number below 150 are the result of further frag-
mentation of the fragments shown above and are affected by the
substituted benzene ring. Each spectrum shows peaks of mass num-
ber m/e 77 and 79 with peak ratio 77/79=3/1, the result of the
fragment of ClCH$_2$–C≡O$^+$. Most spectra, except Chart 2 (R=Et),
have strong peaks of mass number m/e=45. This peak is the result
of α-fission of M$^{+\cdot}$ to give R–O$^+$=CH$_2$ followed by Mc Lafferty
rearrangement to give CH$_3$–O$^+$=CH$_2$ (m/e 45).

The method using 2–chloro–N–(2, 6–diethylphenyl)–acetamide as
an intermediate in the preparation of 2–chloro–N–(n-alkoxymethyl)
–N–(2, 6–diethylphenyl)–acetamides is a facile one, not only because
it is a simple process with high yield, but also because the inter-
mediate 2–chloro–N–(2, 6–diethylphenyl)-acetamide is highly stable
and easy to handle. Our study, therefore suggests a useful industrial
method in the preparation of the herbicides Alachor and Butach-
lor.

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"Beside reason we must also set the results of necessity. For this world came into being from a mixture and combination of necessity and intelligence."

PLATO, *Timaeus*

"Life advances by mass effects, by dint of multitudes flung into action without apparent plan."

PIERRE TEILHARD DE CHARDIN,
The Phenomenon of Man

THERMAL EFFECTS ON THE TOXICITY OF DEEP-FAT FRYING OILS

Ching-Min E. Tsai

INTRODUCTION

The edible oils have been used to fry foods for thousands of years. Foods may become more palatable and colorific after proper frying. Frying operations fall into two distinct types; namely, pan or griddle frying, and deep-fat frying. The latter can be further divided into continuous operations, as in manufactories, and intermittent frying, as in many restaurants or at home.

In pan frying, there is a high food/oil ratio, and a very high surface/volume ratio, consequently, there is a large exposure of the oil to air. Temperature is variable, depending partly on the skill and attention of the cook. Oils used for pan-frying may undergo extensive deterioration in a short time. However, they have received very little attention in the literature. In contrast, a great deal of concern has been expressed over deep-fat frying.

Deep-fat frying is one of the most commonly used procedures for the preparation and manufacture of foods in the world. Many Chinese foods, e. g. bread sticks, meat balls, fried fish, steak, chicken and bean curd, are usually deep-fat fryed thoroughly. In the United States, the consumptions of fried chicken, potato chips, and french fries have increased very rapidly in recent years. Evidently, a major portion of the ten billion pounds of edible oils consumed each year in the United States is used in fried foods[1].

During deep-fat frying, the oil is continuously or repeatedly used at elevated temperatures, where air and moisture are mixed into the hot oil. Both thermal and oxidative reactions in the oil may take place under such conditions. Therefore, a number of known and unknown chemicals, which vary with the nature of oils and heating conditions, are formed in the heated oil. Substantial quantities of the heated oil, with these new chemical products can

be absorbed into the fried foods and they become part of our diet. For instance, about 6% for French fries, 40% for potato chips, and 19–27% for doughnuts have been reported by U. S. Department of Agriculture[2].

THERMAL OXIDATION IN HEATED OILS

Oxidation of a fat at high temperature differs from autoxidation of the same fat at low temperature. Not only is the reaction speeded up at higher temperatures but also quite different reactions take place. This is because the initial oxidative products which form at low temperatures are too unstable to exist more than transiently at high temperatures[3].

When a fat is heated in air, it first shows a gain in weight as oxygen is absorbed, and its peroxide value may also increase. But as heating continues, the peroxides decompose and part of these scission products start to volatilize, leading to a net loss in weight. Eventually the fat turns brown in color, and the darkness increases with the increase in heating[1,4]. The color has been attributed to the degradative fragments, α, β and α, α'-unsaturated carbonyl compounds[3].

It has been reported[5-7] that the fatty acids in positions 1 and 3 of a triglyceride molecule are more susceptible to oxidative attack than they are in position 2. The iodine value of an oil decreased during frying[8-10] and was considered to be a measure for judging the extent of heating. However, the determination of iodine value, which is used to indicate the saturation of an oil, is greatly interfered, with the presence of peroxides in the oil. Therefore, using the iodine value as an indicator of the extent to which a oil has been fried is still questionable. In Chang's recent study[1], no changes in iodine value were found during frying.

Substantial levels of peroxides can build up during autoxidation of unsaturated oils at low temperature, plus the ones formed during frying. These are rapidly destroyed by heating. Thus, this unavoidable deterioration of the oil causes formation of both volatile and

nonvolatile decomposition products, some of which, in excessive amounts, are hazardous to human health.

The volatile substances which may cause undesirable flavor, produced when an oil is heated in air, appear to be generally like those formed in air at low temperature[3]. Products found include free fatty acids, the lower alkanes, saturated and unsaturated aldehydes, ketones, alcohols, half esters of dibasic acids, methylcyclopentane, cyclohexane, benzene, acrolein, crotonaldehyde, carbon monoxide, carbon dioxide and water[3]. A more extensive study has been done recently at Rutgers University[1], and a total of 211 volatile decomposition compounds were identified in heated oils.

Water forms in the heated oils, and not only distills off, carrying other volatiles with it, but also brings about hydrolysis of the oils, with the liberation of free fatty acids. From slight changes[11] to 1%[12] or 1.37%[1] free fatty acids in heated oils were reported. Any hydrolysis of fat to free fatty acids, must be accompanied by liberation of a corresponding amount of mono- and di-glycerides or glycerol.

It is generally supposed that the changes brought about in a fat during thermal oxidation result from the formation and rapid decomposition of hydroperoxides. From many studies[1,3,13], it is clear that alternate heating and cooling is more destructive than continuous heating for the same total number of hours at high temperature. An increase in ultraviolet absorption in the neighborhood of 231 nm during frying has been reported[3]. In my laboratory[14], however, a much better correlation between the absorption at 420 nm and heating of the oil was observed by using a scanning method. A slight increase in refractive index also has been observed during frying[8,15] and autoxidation[16].

POLYMER FORMATION IN HEATED OILS

Polymerization reactions are intermolecular combinations which are functionally capable of proceeding indefinitely and thus may theoretically lead to molecules of unlimited size. The reactions involved in thermal polymerization of drying oils have, for the

most part, been clarified. Nonconjugated unsaturated fatty acids are isomerized at the high bodying temperatures to conjugated derivatives. These conjugated derivatives react with nonconjugated derivatives, so called Diels-Alder addition reaction, to give dimeric products (see Fig. 1).
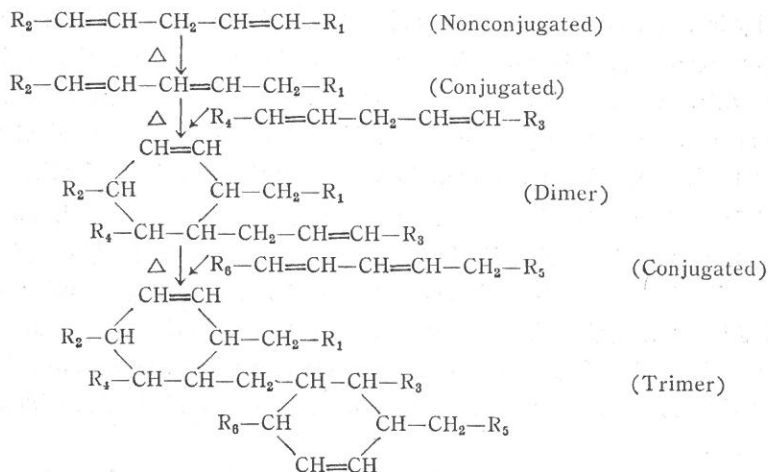
$$R_2-CH=CH-CH_2-CH=CH-R_1 \quad \text{(Nonconjugated)}$$

$$\triangle \downarrow$$

$$R_2-CH=CH-CH=CH-CH_2-R_1 \quad \text{(Conjugated)}$$

$$\triangle \downarrow \swarrow R_4-CH=CH-CH_2-CH=CH-R_3$$

$$CH=CH$$

$$R_2-CH \qquad CH-CH_2-R_1 \quad \text{(Dimer)}$$

$$R_4-CH-CH-CH_2-CH=CH-R_3$$

$$\triangle \downarrow \swarrow R_6-CH=CH-CH=CH-CH_2-R_5 \quad \text{(Conjugated)}$$

$$CH=CH$$

$$R_2-CH \qquad CH-CH_2-R_1$$

$$R_4-CH-CH-CH_2-CH-CH-R_3 \quad \text{(Trimer)}$$

$$R_6-CH \qquad CH-CH_2-R_5$$

$$CH=CH$$

Fig. 1.   Reaction of conjugate derivatives with nonconjugate derivatives.

In studies with methyl linoleate, Wheeler[17] stated that conjugation rises rapidly during thermal polymerization but only to a fairly low concentration, 5-7%. Chances of collision of a conjugated with a nonconjugated linoleate are consequently much greater than chances of collision between to molecules of conjugated linoleate. Rate studies, however, on mixtures of conjugated with nonconjugated linoleate show that the two do react with one another.

Whatever the mechanism of polymerization of the polyene acid groups, it is well known that dimerization is the principal reaction, with some trimerization, but probably no higher degree of polymerization[18]. Triglycerides, however, usually contain two or more polyene acid groups per molecule. Therefore this carbon-to-carbon dimerization (and trimerization) in heated oils may occur between polyene acid groups in the same molecule (intramolecular) and/or

in different molecules (intermolecular). Theoretically, these poly-
mers can grow to very high molecular weights, up to infinity (gela-
tion).

Many studies[3,8,16,18-24] have showed that both the average mole-
cular weight and viscosity of oils were increased with the increasing
heating time and temperature. The increase in viscosity is due to
molecular growth with the logarithm of the viscosity being propor-
tional to the square root of the average molecular weight. A more
recent study[73] reported that heating caused considerable damage
of test oils through the formation of oxirane-oxygen, conjugated
double bonds, oxidized and non-urea adduct forming fatty acids.
Associated with these, there were continuous deteriorative physical
and chemical changes as reflected in increase in Lovibond colour
units, viscosity, foaming property, free fatty acids, refractive index
and decrease in the smoke point and iodine value. In the presence
of added dimethyl polysiloxane (silicone), the above changes were
substantially retarded.

Barker et al.[25] postulated that the earliest stages of dimerization
is largely intramolecular. The sudden rise in viscosity in the later
stages of the reaction, with very little apparent change in linoleate
and linolenate content, suggested that there was rearrangement
from intra- to inter-dimerization by ester interchange. They demon-
strated that ester interchange did occur slowly at bodying tempera-
tures with non-polymeric triglycerides. They also converted some
of the bodied oils to methyl esters and determined the molecular
weight of the methyl esters. The theoretical molecular weight of
the glycerides was calculated from that of the derived methyl esters.
The most viscous oil which they studied was a 5.4 poise linseed oil
with an observed molecular weight of 1,276 compared to the calculated
value of 1,481. This difference of 14% may indicate some intra-
dimerization, but not very extensive.

Paschke and Wheeler[18] separated polymeric glycerides from
monomeric glycerides, and analyzed the derived methyl esters of
each fraction for monomers, dimers, and trimers. They found that
the monomeric glycerides had very little interdimerization, ranging

from 3 to 4% of the total polymeric acid groups in the whole oil, and the polymeric glycerides had appreciable intradimerization, from 10 to 20% of their total polymeric acid groups. They concluded that there was no evidence that a shift from intra- to inter-dimerization was the major cause of the sudden increase in viscosity in the later stages of thermal polymerization. They explained that the methods of measuring the extent of the reaction of poly-unsaturated fatty acids such as by iodine number, polybromide number, and spectral analysis became less accurate as the extent of the reaction increase. Lower values, were obtained due to the interference by trans double bonded isomers and by cyclic monomers. The relationship of average molecular weight to viscosity will vary with factors which affect the molecular weight distribution; such as temperature, composition of fatty acids, polymerization or ester interchange catalysts, and any other factors which would affect the dimer to trimer ratio in the polymeric acid groups.

Autoxidative polymerization may occur at low temperatures during an intermittent period of non-heating. Instead of carbon-carbon linkages between polyene acid groups in the same or differ-ent molecules, C-O-O-C or C-O-C bindings were formed, and the mechanism was postulated[26-32] as in Fig. 2.
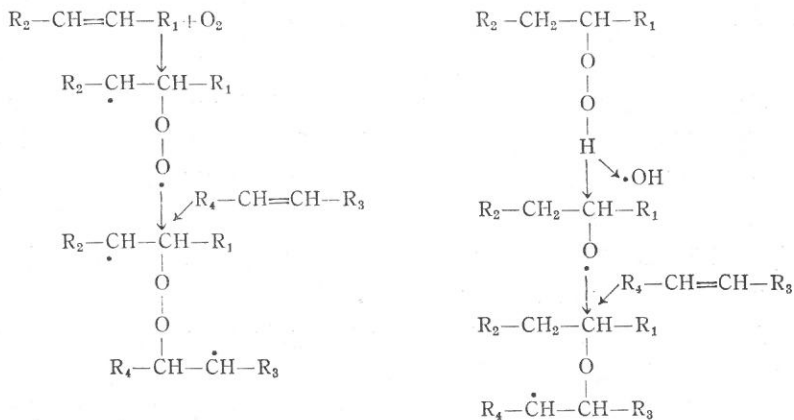

Fig. 2. Mechanism of C-O-O—C or C-O-C bindings.

Thus, autoxidative polymerization is a secondary reaction of per-oxide, but instead of taking a hydrogen from the other molecule to form hydroperoxide or alcohol, it binds with another polyene acid group. In Privett's study[33], he observed that this autoxidative polymerization was an autocatalytic reaction.

BIOLOGICAL EFFECTS OF HEATED OILS

Effects of heated oils on animal experiments can be divided into two categories, nutritional and pathological. It is, however, very difficult to distinguish clearly between these two categories. Many studies[34-36,40,42,47,52,54] were concerned with toxicity, but used "nutritional values" in their titles of the studies.

Of the visible and invisible contributions of fats or oils to the human diet, the only one which is specific is the contribution of the essential fatty acid (EFA), linoleic acid. Linoleic acid is a straight chain fatty acid containing 18 carbons with 2 double bonds. Because of this unsaturation linoleate is very sensitive to oxidation, poly-merization and any other type of chemical change. Indeed, any chemical change in the EFA impairs its specific biological value.

The best sources of linoleic acid are the so-called semi-drying oils; namely, corn, cottonseed, safflower and soybean oils which readily oxidize in air, even at ordinary temperatures. Prolonged heat treatment of oils promotes thermal polymerization, and exposure of the hot oil to the atmosphere favors autoxidation. Both pheno-mena would significantly reduce the availability of the EFA in oils.

Recent understanding shows us that the EFA, or the total unsaturated fatty acid content, may have some effect in lowering the blood cholesterol level, allegedly a factor in the development of atherosclerosis. Raju et al.[37] fed heated oils to rats and found the blood cholesterol and glucose were elevated.

Oils became unpalatable at low peroxide levels and probably toxic at high levels with the decomposition products of hydroper-oxides. In my laboratory[38] and also in many others' studies[3,39,55], it has been observed that heated oils reduced the appetite of ani-mals. The polymers formed during frying may not be hydrolyzed

easily by lipase and are not readily absorbed, thus may cause diarrhea[40-44].

Weanling rats fed heated oils at low vitamin levels gained significantly less weight than those fed fresh oils[3,45,46]. When the diets, however, were enriched with large quantities of vitamins, there was no significant difference in subsequent weight gains between any paired groups of animals receiving similar diets. It is possible that these vitamins are destroyed by contact with the heated oils in the mixed diet or in the gut, as in the case of vitamin A, or that the consumption of heated oils represents a stress condition which increases the animals' need for vitamins, as has been shown to be the case with some of the B vitamins[3,42]. The protein levels of diets also influenced the nutritional value of the oils and, at lower levels, appeared to be related to pyridoxine intakes as growth was depressed[45,46] This growth depression could be overcome, in part, by increasing the protein level of the ration[39,45]. Riboflavin enrichments apparently aided the animals in coping with autoxidized oils, but did not contribute any protective action against thermal polymers[45].

A vitamin E deficiency was also noticed[47,48] after feeding heated oil diets, and this deficiency could be corrected by vitamin E supplementation. An interference with reproductive performance and lactation of the female rats was reported by Farmer et al.[49] using only 10% by weight of thermally polymerized oils in the diets. This interference was alleviated by supplementation with α-tocopherol[47].

It has been known for years that the growth of animals is depressed by feeding heated oils [34-39,43-48,50]. It may be due to the reduction of nutritive value, lower feed intake, irritation of the digestive mucosa with consequent loss of ability to absorb nutrient [1,3,39], interference with absorption of nutrients by the presence of less absorbable polymers in the intestinal contents[3], and/or toxic effects. The differences in absorption between fresh and oxidized fats were greater for highly unsaturated oils, such as corn and olive oils, than for butter fat and coconut oil[3].

It is also clear that feeding heated oils may cause enlargement

of the liver, kidney and thymus[36,51-54]; fatty necrosis of the liver [3,37,55], and a low triglyceride content which is attributed to the extra accumulation of protein[50]. Besides the increase of relative liver weights, Andia and Street[53] also found increases in the hepatic microsomal proteins, endogenous malondialdehyde, activities of a complex of microsomal enzymes and smooth endoplasmic reticulum proliferation.

The reduction of red blood cell counts, hemoglobin, hematocrit, serum proteins, and the increase of cellular protein in the liver of rats fed the heated oil diets, were noticed by Miller and Landes[56]. They postulated that an abnormal portion of the dietary protein was being retained in the liver to cope with the metabolic effects of the damaged fat. Possibly, the protein is used to synthesize hepatic enzymes which metabolize the nonphysiological portion of the dietary lipid to a form, or forms, which can be expelled either through the lungs or the kidneys.

Studies conducted in Perkins' laboratory[55] have shown that very low levels of cyclic fatty acids incorporated into nutritionally adequate diets generally produced lower weight gains and feed consumption in rats fed low levels of protein compared to control animals. Animals fed as low as 0.15% of this cyclic material in diets with low level of protein (8–10%) also developed fatty livers. In their more advanced studies[57], they found that cyclic fatty acids are absorbed by the rat, 13–15% of them oxidized to CO_2 and approximately 40% excreted in the urine in 48 hours after ingestion. Decreased rates of lipogenesis were noticed in livers of animals fed 8% and 10% protein and higher levels of cyclic fatty acids. An increased rate of lipogenesis was observed in adipose tissue of animals fed 10% protein and higher levels of cyclic fatty acids.

Nonspecific focal myocarditis and focal fibrosis has been examinated in rats fed thermal oxidized oils[58]. A more recent study in Canada[59] showed that incorporation of the isolated cyclic monomer and dimer derivatives from heated oil samples into rat diets produced distended flatulent stomachs and intestines, gastric ulcers, and multiple focal hemorrhages. Histological evaluation of heart,

liver and kidney tissue sections indicated extensive cellular damage, especially in the liver and kidney. Cellular damage included pyknosis, vacuolization of the cytoplasm, and mitotic aberrations. Uptake of ^{14}C-labeled fatty acid by the triglyceride fraction of the cells was increased with heated oils in diets.

Off and on for many years there has been speculation that heated oils may be carcinogenic. The classical reports on this subject were issued by Roffo[60-63] during 1939–44. He found tumors in rats to which he fed olive oil, sunflower oil and lard oxidized by heating to 250–350°C. Sugai et al.[64] ran several experiments in which they fed a known carcinogen, 2-acetylamino-fluorene, along with fresh oil, artificially heated oil, used frying oil, the non-urea-adductable fraction of oxidized oil, or the non-lipase-digestible fraction of oxidized corn oil. The results showed that the heated corn oils acted synergistically with 2-acetylaminofluorene and enhanced its carcinogenic activity. Artman[3], however, reviewed about twenty articles on carcinogenesis of this subject. He concluded that used frying oils do not represent a source of dietary carcinogens. Whether the abused frying oils are carcinogenic, is still a question. Further advanced studies are needed to find the true answer.

Kaunitz et al.[65] aerated lard and cottonseed oil at 95°C for 200 hours and then molecularly distilled them. 20% of the nonvolatiles (275–300°C) autoxidatively produced polymeric residue in the diets was fed to rats. This led to diarrhea and rapid death. When this residue was reduced to 4 or 7%, their growth was depressed. Much of the toxicity of severely heated oils, is associated with the non-urea-adducting fatty acid (urea filtrate) fraction. Shue et al.[66] fed this fraction on two consecutive days to weanling rats, causing inanition, fatty liver, a decline in body temperature and death within 2 to 7 days. They also found the LD_{50} of this fraction to be approximately 0.6 ml/100 g/day for 2 days for rats weighing 40 to 50 g and 0.9 ml/100 g/day for 2 days for 60 to 100 g rats.

Poling et al.[67] pointed out that the severity of heating conditions, plays an important role in the degree of deterioration of oils. The nature of oils, however, containing a large proportion of

polyunsaturated fatty acids yielded more toxic substances than the ones containing a majority of saturated fatty acids, at the same heating condition[40,43,65,68,69]. Many investigators[10,70-72] also claimed that concentrates from thermally oxidized fats, containing mostly monomeric and dimeric materials, were absorbed more readily and were therefore more toxic than longer chain polymers.

There is no doubt that overused or highly abused frying oils contain oxidized and polymerized materials which are hazardous to human health. Since deep-fat fried food products are a major item of human diets today, not only in Taiwan but all over the world, it is necessary to ascertain the extent to which a frying oil can be used without producing oxidized and polymerized hazards which cause an adverse effect on human metabolism. A simple and dependable test must be developed to allow those who conduct deep-fat frying, in the manufactory, restaurant, or home, to determine the point at which the batch of frying oil has to be discarded.

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"It is not as important to make the right decision as to make the decision right."

T. V. LEARSON, PRESIDENT, IBM

"I do not think that computers should wear the pants or make the decisions. They are deficient in humor."

E. B. WHITE, in *The New Yorker*

STUDIES ON THE PROTEIN REQUIREMENTS OF YOUNG ADULTS FED WITH CHIANON-8 AND IR 480-5-9 RICE DIETS

NING-YUEAN LEE and PO-CHAO HUANG

ABSTRACT

Protein requirements of Chinese young men were studied by a newly recommended method with two varieties of rice and egg as the protein sources, which were supplied separately in different N balance periods. Medium protein Chianon-8 rice or high protein Philippines' IR 480-5-9 rice contributed about 90% of total N of the test rice diets. In the case of test egg diets, egg N contributed more than 95% of the total N. Each protein source was incorporated in test diets at 3 levels nearly or below the presumed maintenance protein requirements. Energy intake was on "non-excess" basis, between 40 to 46 kcal/kg. From the N balance data obtained with each protein source at different protein levels, a regression equation was derived and protein requirements calculated. The mean protein requirements (PRm) for Chianon-8 rice, IR 480-5-9 rice and egg were 0.70, 0.63 and 0.53 g/kg/day respectively. The safe protein intake levels which would cover the protein needs of 97.5% of the population (PR.975) were estimated to be 0.87, 0.78 and 0.66 g/kg respectively for proteins mentioned above. The apparent digestibilities of Chianon-8 rice, IR 480-5-9 and egg were 77, 74 and 83%, while the true digestibilities were 88.2, 84.5 and 100% respectively. By comparing the essential amino acid pattern with the 1973 FAO/WHO reference pattern, lysine and threonine were regarded as the first and second limiting amino acids and the chemical scores were about 60 for both of the two varities of rice.

INTRODUCTION

Rice (*Oryza Sativa L.*) is the main dietary staple in Asian countries. Although protein content of most varieties of rice is rather low, 6 to 7%, nevertheless it supplies about one third or more of the total daily protein intake in Taiwan[1] as well as in many other Asian countries. Therefore, the protein nutritive value

of rice is important to the people in this area of the world, and some high to moderately high protein varieties of rice have been bred both in the Philippines and Taiwan. However, few studies on rice protein requirements in adults have been published[2-4].

The main purpose of this study is to determine the rice protein requirements in young Chinese adults using N balance technique at 3 submaintenance levels of N intake, principally according to the method of Rand et al[5]. In two series of experiments a medium protein variety of Taiwan rice (Chianon-8) and a high protein variety of Filipino rice (IR 480-5-9) wer e used. Whole egg protein used as a reference protein was studied similiarly.

MATERIALS AND METHODS

Food sources

IR–480–5–9 milled rice, a high protein variety with 11.03% protein ($N \times 5.95$), was generously donated by Dr. B. O. Juliano of the International Rice Research Institute (IRRI), Philippines. Chianon-8 milled rice, a medium protein variety with 9.23% protein, was donated by Chia-Yi Agricultural Experimental Station located in southern Taiwan. Throughout the experimental period the same batch of rice was used. The other food items were all purchased from the market.

Subjects

Nine subjects who participated in this study were all medical college students of 21 to 26 year of age. Physical examination was conducted before the subjects were accepted for the experiment. All their characteristics are listed in Table 1. For each N balance study 5 subjects have participated. The subjects were admitted to the metabolic ward in the college campus allowed to continue their daily school activities but physical exercises were limited to light to moderate activities, and were supervised carefully by the authors.

Test diets and experimental design

Rice contributed about 90% of protein in the rice diets and whole egg contributed 94.8 to 97.4% of protein in the egg diets which were used as the control, A limited amount of nitrogen was supplied

Table 1. Characteristics of the subjects

Subject	Age (yr)	Height (cm)	Body wt[c] Initial (kg)	Final (kg)
CYY[a]	21	166.5	51.6	50.0
FCF[a]	24	165	55.6	54.7
LCL[a]	22	168.5	60.9	60.8
HDC[a]	23	170	55.5	54.8
FFP[b]	23	172	67.8	67.6
ZWZ[b]	21	165.5	58.3	57.0
LWM[d]	25	167	63.1	62.1
LBN[d]	23	168.5	57.1	56.5
SMD[d]	23	173.5	64.8	63.5
SSK[d]	26	167.5	64.0	63.2
SYT[d]	22	171	66.6	65.6
Mean	23	168.6	60.5	59.6

[a] These subjects participated in all N balance studies except the 9th.

[b] FFP participated in the first two N balance studies, and replaced by ZWZ from the 3rd to 8th N balance studies.

[c] Average of the initial and final 3 days.

[d] These 5 subjects participated in the 9th balance study with egg diet only.

by vegetables and fruits. The order of offering different test diets was randomly arranged (Table 2). Only a limited amout of nitrogen was supplied by vegetables and fruits. The energy intake was varied from 40 to 46 kcal/kg body weight depending on the individual difference in energy consumption to keep the subjects' body unchanged or slightly decreased. Corn oil was added to adjust the daily caloric intake. Vitamin and mineral supplements were given daily at least to meet the recommended daily nutrients allowance of China[6]. The daily diet was divided into four meals taken at 7:30 AM, 12:00 PM, 5:00 PM and 9:30 PM. Lunch and supper were composed of cooked rice, cooked vegetables and soup. Breakfast and the last meal were served with a liquid diet of which the composition of rice series and egg series was shown in Table 3. Each nitrogen balance study was counducted for 11 days. A protein free diet was

Studies on Protein Requirements

Table 2. Dietary plan

Bal. period	Test diet	Calorie intake (kcal/kg/day)	Protein level[a] (g/kg/day)	Rice or egg N / Total N (%)	Rice or egg cal. / Total N (%)
I	Chianon-8	46	0.689	88.0	56.5
II	IR 480-5-9	46	0.775	88.8	46.4
III	IR 480-5-9	43	0.472	92.5	35.1
IV	Chianon-8	43	0.457	92.2	46.3
V	Egg	43	0.535	96.1	15.3
VI	IR 480-5-9	43	0.701	95.2	46.6
VII	Chianon-8	43	0.822	89.8	79.7
VIII	Egg	43	0.310	94.8	12.5
IX	Egg	40	0.447	97.4	14.0

[a] N×5.95 for rice; N×6.25 for egg

Table 3. Composition of the liquid diets

Ingredient	Rice series (g/100 g)	Egg series (g/100g)
Egg	—	Variable[a]
Cooked rice	none or variable[b]	—
Starch	4	4
Sugar	1	1
Salad oil	1	1
Butter	1	1
Methyl cellulose	0.6	0.6
Potassium phosphate, dibasic	0.3	0.3
Calcium phosphate, dibasic	0.3	0.3
Sodium chloride	0.1	0.1
Water	made up to 100 g	made up to 100 g

[a] Major portion of egg was supplied by the liquid diet.

[b] Rice was mostly served separately as boiled rice. When the amount of rice used was large, a small portion of it was incorporated in the liquid diet.

given on the first day in order to deplete the so called labile body protein. Between each balance period there was three to five days rest period during which self-chosen foods were eaten. Complete 24-hr urine specimens were collected daily, and fecal sample marked by carmine was collected for the last 8 days. The mean protein requirements (PRm) and the protein allowance covering 97.5% of population (PR.975) were obtained by the multiple level-constant variance method proposed by Rand et al[5].

Chemical analysis

Urinary creatinine was determined by the Jaffe's reaction[7] to check the completeness of daily urine collection. Skin nitrogen loss was measured three times during the whole study period by the method described previously[8]. Pooled samples of foods, urine specimens and fecal specimens of each subject were analyzed for total N by the semi-micro Kjeldahl method[9]. Both the Chianon-8 rice and IR 480-5-9 rice were hydrolyzed and subjected to amino acid analysis with the amino acid auto-analyzer, Beckman model

Tale 4. N balance data with Chinanon-8 rice diets, IR 480-5-9 rice diets and egg diets

Diet	Balance period	Protein intake[a] (g/kg/day)	N intake (mg/kg/day)	Urinary N	Fecal N	Skin N	Total N loss	Nitrogen balance (mg/kg/day)
Chianon-8	IV	0.457	76.8±0.5[b]	61.6±3.5	21.9±3.1	2.4±0.4	85.9±4.9	− 9.1±5.2
	I	0.689	115.8±2.3	87.1±5.6	17.2±1.4	9.3±2.4	113.6±6.5	+ 2.2±6.6
	VII	0.822	138.2±2.3	99.5±4.2	32.9±3.8	2.4±0.4	134.8±5.4	+ 3.4±5.7
IR 480-5-9	III	0.472	79.4±0.6	63.3±3.6	22.2±3.1	2.4±0.4	87.8±3.6	− 8.4±3.7
	VI	0.701	117.8±1.3	79.3±6.6	27.3±6.4	2.4±0.4	108.9±10.0	+ 8.9±9.8
	II	0.775	130.2±1.8	80.3±2.1	35.4±2.8	9.3±2.4	125.0±5.9	+ 5.3±6.2
Egg	VIII	0.310	49.6±2.2	66.8±7.0	12.0±2.9	2.4±0.4	81.2±7.9	−31.6±8.6
	IX	0.447	71.6±0.7	72.6±8.0	10.7±1.8	7.3±1.8	90.6±8.4	−19.0±8.9
	V	0.535	85.6±1.1	66.6±7.5	10.3±1.7	2.4±0.4	79.3±8.6	+ 6.3±8.9

[a] N × 6.25.
[b] Mean±SD

120. The amino acid scores were calculated taking 340 mg lysine/g
N as 100%[7].

RESULTS

N balance studies

On Chianon-8 rice diets the N intakes were 76.8, 115.8, and
138.2 mg/kg. The mean nitrogen balances of five subjects at each
level were −9.1, +2.2 and +3.4 mg/kg/day. The N intakes of IR
480–5–9 rice were 79.4, 117.8, 130.2 mg N/kg and the mean nitrogen
balances were −8.4, +8.9 and +5.2 mg/kg/day respectively. With N
intakes of egg diets being 49.6, 71.6 and 85.6 mg/kg, the mean
nitrogen balances of the five subjects were −31.6, −19.0 and
+6.3 mg/kg respectively (Table 4). N intake and N balance data of
all subjects of a group were then processed with the WANG–2200
electronic calculator, and a linear regression equation was obtained.
The results are as follows: with Chianon-8 rice diet, $Y = -24.56 + 0.21$
X, d. f. = 13, $r = +0.7102$, $P < 0.01$; where X denotes N intakes and Y
denotes the N balance. For IR 470–5–9 rice diet, $Y = -31.93 + 0.31 X$,
d. f. = 13, $r = +0.6910$, $P < 0.01$. For the egg diet, $Y = -85.50 + 1.03 X$,
d. f. = 13, $r = +0.8672$, $P < 0.01$. These three linear regression equations
all revealed that the X and Y had a significant positive correlation-
ship, and they are plotted in Fig. 1, Fig. 2 and Fig. 3. The mean
nitrogen requirements were estimated from the points where the
extrapolated linear regression lines intersect with the zero nitrogen
balance line. Thus, the nitrogen requirements for Chianon-8 rice,
IR 480–5–9 rice and the egg diets were 115.3, 103.2 and 83 mg/kg/day,
respectively. If we consider the miscellaneous N losses which include
N losses from nail, hair, semen, and saliva etc., the real mean
nitrogen requirements will be 2 mg/kg higher than the figures
mentioned above, according to the opinion of 1973 FAO/WHO expert
committee[10]. Therefore, the mean protein requirements for the
two varieties of rice protein of Chianon-8 and IR 480–5–9 are 0.70
and 0.63 g/kg (N×5.95) respectively, and that of the egg diet is
0.53 g/kg (N×6.25) per day. (Table 5).
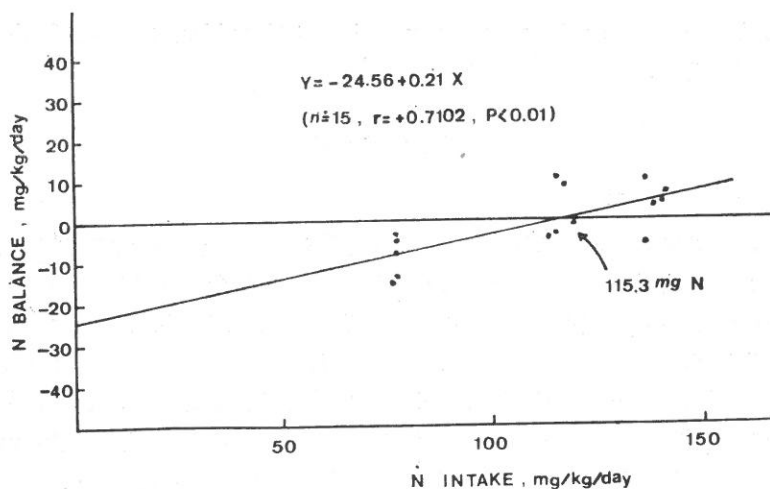
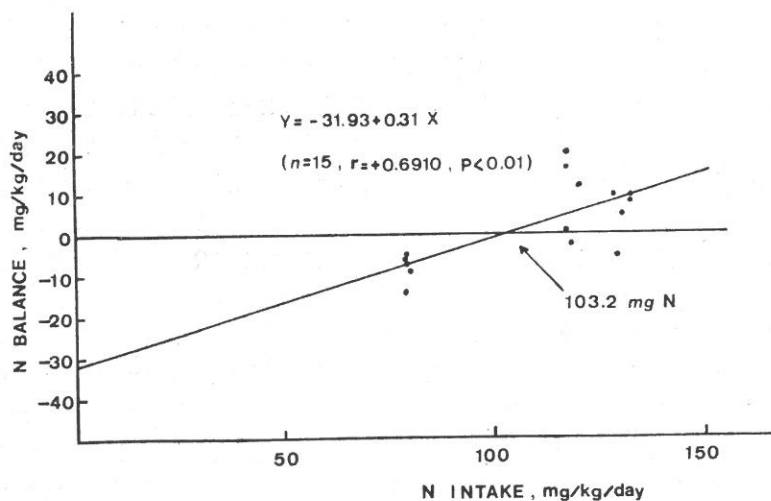Fig. 1. Regression of N balance with Chianon-8 rice diets on N intake.

Fig. 2. Regression of N balance with IR 480-5-9 rice diets on N intake.

tibility of egg protein was assumed to be 100%, the true digestibilities of Chianon-8 and IR 480-5-9 rice were 88.2 and 84.5% respectively. (Table 7)

The amino acid patterns of IR 480-5-9 and Chinanon-8 rices were shown in Table 7 and the chemical scores estimated were 60 and 62 respectively as compared with the 1973 FAO/WHO reference.[10]

DISCUSSION

In the present study, the mean protein requirement of young men for IR rice was found to be lower than that for Chianon rice by 10% (0.63 v. 0.70 g/kg). This means that IR higher protein rice is slightly better in quality than the Chianon rice. The result was similar to that of Roxas *et al.* who reported that the quality of high protein rice (IR 480-5-9, 11%)-mung bean diet was better than the low protein rice (IR-8, 7.7%)-mung bean diet in Filipino children.[12] Although the chemical score of the first limiting amino acid—lysine was almost the same (60 v. 62). We may explain this partially by the fact that the IR rice has higher level of the second limiting amino acid-threonine than Chianon rice (Score: 90 v. 84), or IR rice probably has a high availablity of lysine. As to the apparent digestiblity we may assume that these two kinds of rice are slightly different (77 v. 74), considering the unadvoidable technical errors in human balance study. Apparent digestibility of our study is also comparable with that of a IRRI study feeding the IR 480-5-9 to Filipino children, 75%[12] and the study feeding BPI-76-I to human adults by Clark *et al.*[3], 77-79%, respectively. We have also purified the Fecal Protein Particle (FPP) by repeated washing, centrifugation and finally freeze drying. The FPP was later confirmed by Juliano by electronic microscopy[13]. So how to elevate the utilization of rice protein by human being is also one of the goals of rice improvement in the near future.

ACKNOWLEDGMENTS

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