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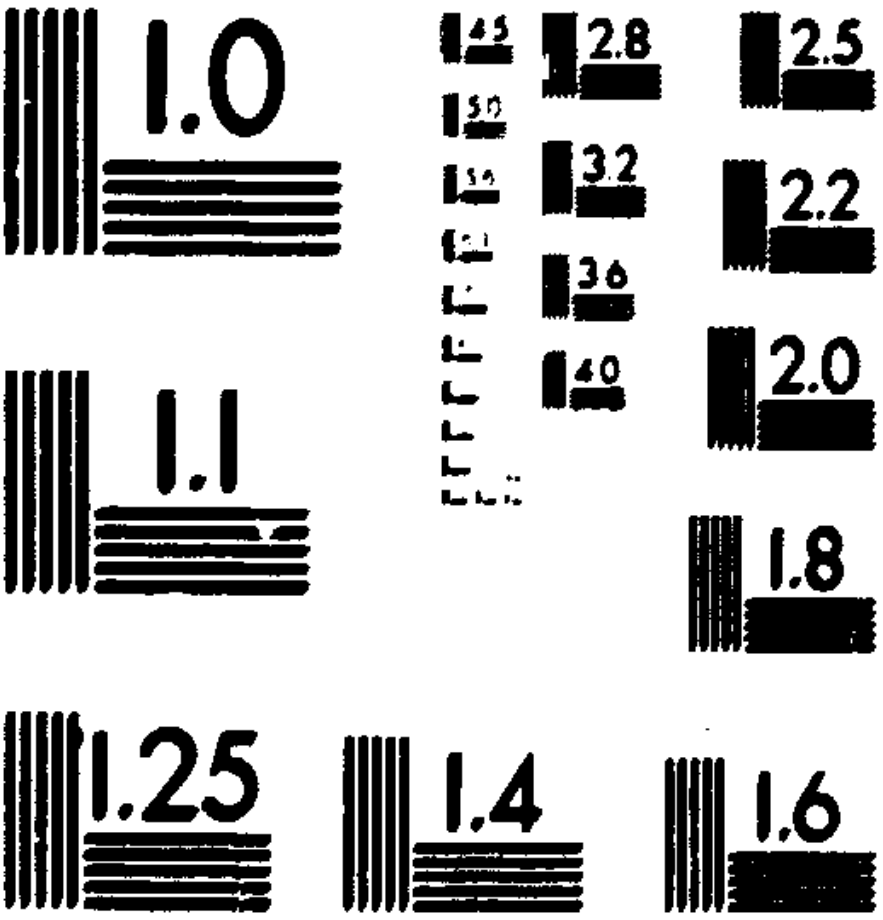

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DP/ID/SER.A/594
24 April 1985
English

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REGIONAL NETWORK FOR PRODUCTION MARKETING AND CONTROL OF PESTICIDES IN ASIA AND THE FAR EAST

DP/RAS/82/006

Technical report: Training Course in Pesticide Residue Analysis*.

Prepared for the Governments of:
Afghanistan, Bangladesh, India, Indonesia, Republic of Korea,
Pakistan, Philippines, Sri Lanka and Thailand
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of P.A. Greve,
consultant on pesticide

United Nations Industrial Development Organization
Vienna

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V.85-26912

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I. BACKGROUND AND TERMS OF REFERENCE OF THE CONSULTANCY

In the framework of the Regional Pesticide Network in Asia (project DP/RAS/82/006), a training course on pesticide residue analysis was organised by the Department of Agriculture (DOA) of the Thai Ministry of Agriculture and Cooperatives, in cooperation with FAO and UNIDO. The course was held at the laboratory of the Agricultural Toxic Substances Division, Bangkhen, Bangkok, from January 21 to February 5, 1985.

Undersigned had been asked by UNIDO to fulfill a consultancy during this course for giving technical assistance, lectures and laboratory exercises, together with Dr.E.Bolygó (Hungary). On behalf of GIFAP (Groupement international des associations nationales de fabricants de produits agrochimiques), Dr.K.Ohta (Japan) and Mr.S.Kennedy (UK) conducted laboratory exercises, and Dr.F.Kopisch-Obuch (FAO) gave lectures on the work of FAO, WHO and the Codex Alimentarius Committee on Pesticide Residues.

The objectives of the training course, as specified in the programme booklet, were:

- enable trainees to conduct residue analysis of the most commonly used pesticides in the region;
- harmonise analytical procedures;
- enable countries in the region to supply data for the work of the JMPR (FAO/WHO Joint Meeting on Pesticide Residues).

The terms of reference for the consultant are given in Job Description DP/RAS/82/006/11-67/32.1.G, dated 15-10-1984 (copy attached as Appendix I). Stay of the consultant in Bangkok lasted from January 17 to February 5, 1985. The first days of his stay were devoted to setting-up the practical exercises in the laboratory.

II. SUMMARY REPORT

A. SUBJECT MATTER

During the course, the consultant:

1. assisted the DOA-staff in setting-up the exercises (see 3);
2. gave lectures on the following topics:
   - set-up of the laboratory; good analytical practice
   - clean-up procedures; standardisation of adsorbents
   - derivatisation procedures for HPLC and GLC
   - HPLC-techniques
   - spectrophotometric methods
   - screening procedures; "simplified" methods
   - confirmatory tests
   - metabolites relevant to the MRL
   - reporting of data; analytical errors; when is an MRL exceeded?
   - collaborative tests; international standardisation
   - automation; data processing
   - future trends
   - organochlorine pesticides; interferences by PCBs
   - carbamates and dithiocarbamates
   - polar fungicides
   - fumigants; inorganic bromide
   - phenyl- and phenoxy-acetic acid herbicides
   - urea herbicides and other derivatives of aromatic amines
   - triazine and other herbicides
   - growth regulators

   As background information, Interim Document 14, issued by WHO-Copenhague and supplied by FAO, and 32 overhead transparencies were used. Copies of the transparencies were handed out to the participants; the originals were left with Ms.Supranee Impithuksa (DOA). The topics mentioned above were discussed by the consultant in 16 lectures; the duration of each lecture was approx. 40 min, followed by approx. 20 min discussion. On the average, 6 lectures per day were given by the consultant and by Dr.Bolygó, with 15 min coffee breaks in the morning and afternoon, and 1 hour break for lunch. The topics covered by Dr.Bolygó are given in his report.
3. supervised laboratory exercises on:
   - determination of residues of α- and β-endosulfan and vinclozolin

in onion and cabbage by GLC/ECD after clean-up over alumina coated with silver nitrate;

- determination of residues of carbendazim in grape by HPLC.

Procedures were supplied to the participants and discussed with them prior to their carrying out the exercises in the laboratory. During the practical exercises, DOA staff members actively assisted in keeping the stock of glassware and reagents complete and in keeping the instruments in a running condition, incl. setting-up calibration curves. The support of GIFAP by sending standards and equipment is gratefully acknowledged here.

B. ORGANISATIONAL ASPECTS

1. The course was organised as follows:

- 3 days of lectures on general topics/techniques (see A. 2)
- 2 days of lectures on special topics/compounds (see A. 2)
- 6 days of laboratory exercises. To this end, the participants were divided in 3 groups of 6-7 participants; each group performed 6 exercises, dealing with the determination of endosulfan/vinclozolin, carbendazim, diazinon/malathion/monocrotophos, dithiocarbamates, paraquat and butachlor respectively.

  Each day, the results of the previous day were discussed with the group which had performed the exercise and when necessary, adaptations were introduced in the procedures. The practical exercises were organised in such a way, that each participant could handle at least one sample from the beginning to the end.

  The exercises on endosulfan/vinclozolin and on carbendazim were supervised by the consultant. The exercises on diazinon/malathion/monocrotophos and on dithiocarbamates were supervised by Dr.Bolygó. The exercise on paraquat was supervised by Mr.Kennedy and the exercise on butachlor by Dr.Ohta.
- 1 day of evaluation. To this end, problems were handed out to the participants (4 problems per participant). All problems were different in order to make individual assessment of each participant possible. The participants were asked to hand in their answers by writing within 3 days and comments by the lecturers on the answers were handed back to the participants under cover at the last day of the course, together with one page

of personal advice to each participant individually. The comments and advices were handed out as confidential; no copies were held by the lecturers.

Evaluation of the problems in general terms was given during an extra session on Monday February 4, after the laboratory exercises.

Examples of questions (in total, approx. 80 problems were given out) are given in Appendix II.

- 2 field excursions (on Saturday, January 26, and on Sunday, February 3) were organised by DOA and GIFAP respectively in order to enable the participants and lecturers to see the application of pesticides under practical conditions.
- during the first week, country papers submitted by the member countries of the Network were discussed. These sessions were chaired by Dr.Kopisch-Obuch and the information was brought by him back to FAO.
- for future evaluation, a questionnaire, drafted by Ms.Cecilia Gaston, was handed out to the participants in which the participants could give their views and comments on the organisation and content of the course. The answers could be sent in anonymously, if so desired, and were collected by Ms.Annie Ylagan (Philippines) for remittal to Ms.Gaston.

2. The course was attended by 7 participants from abroad (viz. Bangladesh, Republic of Korea, India, Indonesia, Pakistan, Philippines and Sri Lanka) and 12 participants from Thailand. During the first week, 25 observers from Thailand were also permitted to attend the lectures.
3. The course was opened by the Director-General of DOA, Dr.Yookti Surikapukti, and closed by Dr.Tanongchit Wongsiri, Deputy Director-General of DOA. At the closing ceremony, certificates of attendance were handed out to the participants.

III. OBSERVATIONS AND RECOMMENDATIONS

1. It is to be hoped, for all parties concerned, that follow-up and continuity can be given to the course. Although attention and motivation have been high among the participants during the whole course, its beneficial effect will get lost if no perspectives for continuity can be given. It is the consultant's firm belief, that this continuity can best be achieved by setting-up a fixed training center for pesticide residue analysis in the region. Such a center does not need to be of large dimensions, but should be equipped with up-to-date instruments and adequate staff. On the long term, such a training center will show off to be cheaper than other ways of training, such as sending staff members abroad or organising courses on an ad-hoc basis.
2. A problem often brought forward by the participants is the poor service and follow-up given by the suppliers of the instruments. This results in practice in the unfavourable situation, that servicing must be carried out by the laboratory technicians, who have had no or very scarce training on those particular instruments. Consultants from abroad can not solve this problem wholly satisfactorily, as they often have no experience on the instruments concerned and, if they have, their help will be lacking after their departure.

   The only durable solution to this problem is convincing the suppliers of the instruments of their task to keep up a good service system, preferably based on contract basis. Spare parts must be made available against local currency and lack of service should be reported to top-management in the home-country of the supplier. It must be made clear to the supplier that lack of service is a serious negative point when considering the purchase of a new instrument.

   Performance of an instrument must be checked before the bill is paid. The criteria for the performance must be laid down in the purchase order. The performance should further be checked frequently and kept on record. In case of failure, the supplier must see to it that the original performance is attained again. Agreement between supplier and purchaser must be reached as to what reparations the purchaser can do himself and what reparations

should be left to the supplier. It can be of help, if several purchasers of the same instrument work together to put pressure on the supplier for good service.

3. Another frequently mentioned problem is the lack of continuity in supplying funds. It is relatively easy to install an instrument, but in order to keep it in optimum condition, funds are necessary for servicing and up-dating. Depreciation (depending on the instrument: 5-10 years) must be accounted for. Prior to purchasing an instrument, it must be sure that the infrastructure of the purchasing country (or town) is sufficiently developed to allow the instrument to function properly.
4. It has been noted, that some participants are not yet fully conversant with basic organic and analytical chemistry (notably in the quantitative aspects of the analysis). As this knowledge is independent on the kind of analysis, it is recommendable that people working in the laboratory can attend general courses on organic chemistry, instrumental analysis (GLC, HPLC) and in some cases also English. Such courses do not have to pertain to pesticides (on the contrary, general courses will broaden the vision of the worker), and can probably be provided for by Universities in the vicinity. It is also recommendable that workers in the laboratory are given the opportunity to upgrade and update their knowledge by self-study. Suggestions for textbooks are given in Appendix III. Apart from this, relevant journals must be available.
5. At the end of this report, the consultant wants to mention the great support and enthousiasm from the side of the Thai hosts during the whole course. All possible help was given, even when this entailed improvisation and inconvenience to the ongoing work. It was a great pleasure for the consultant to work with them, as well as with the consultant's fellow-lecturers.

   Also the generous support by GIFAP and their local representatives must be acknowledged again here. Without their help, the course would have missed many essential features.

Dr.P.A.Greve
Expert in Pesticide Residue Analysis

cc: Mr.Adul, DOA, Bangkok
Dr.Kopisch-Obuch, FAO, Rome
Ms.Cecilia Gaston, Philiprines
Dr.Bolygó, Hungary
Dr.Willis, GIFAP, UK

UNITED NATIONS

APPENDIX I

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

UNIDO

15 October 1984

JOB DESCRIPTION

DP/RAS/82/006/11-67/32.1.G.

Post title Consultant on Residue Analysis of pesticides

Duration Three weeks (including travel days)

Date required 16 January - 5 February 1985

Duty station Bangkok, Thailand

Purpose of project To establish a Regional Co-operation Programme for the Production, Marketing and Control of Pesticides in Asia and the Pacific, based on a Network of existing National Institutions, which are expected to co-ordinate their development policies and to standardize relevant pesticide control measures.

Duties The consultant should provide technical assistance to the Regional Network on Pesticides in a training workshop on Residue Analysis. In this capacity, he will specifically be expected to:

- Evaluate training requirements for residue analysis among member countries of the Network, based on replies to a questionnaire;
- Assist the host authority of Thailand to prepare the laboratory for the Workshop;
- Give lectures in the workshop;
- Assist in the preparation of Workshop Syllabus.
- Assist in preparation of Workshop report.

..../..

Qualifications Chemist with extensive experience in residue analysis and familiar with the work of the Codex Committee on Pesticide Residues (CCPR).

Language English

Background information The Regional Pesticide Network was established in 1982, through a project executed by UNIDO (DP/RAS/82/006) based on UNDP funded inputs amojnting to US $550,000. The initial phase of the project which is the first of its kind implemented in the region, attempts to develop a lasting co-oeprative system in Asia involving Government institutions and bodies dealing with pesticides at all levels of the national economy. On behalf of member Governments the project is managed by the Regional Project Co-ordinator who has been assigned by the Government of the Philippines at the Fertilizer and Pesticide Authority in Manila. Members of the Network are Afghanistan, Bangladesh, India, Indonesia, the Republic of Korea, Pakistan, Sri Lanka, the Philippines and Thailand.

The activities of the project comprise expert consultations, workshops, study tours, fellowships, and technical advisory services rendered by experts from within and outside the region. A supplementary function of the Network is the creation of active sub- :tworks covering specific subjects of common interest to member countries, such as data collection and exchange of information. In particular, the exchange of expertise is being promoted through the implementation of various project activities relating to registration requirements, quality control, pesticide residues, toxicology, pesticide trade and tariff regulations etc.

Residue Analysis is one of the important activities of the Regional Network, workshop aimed at training residue analysts is being organized to be held in Bangkok, Thailand in January 1985.

APPENDIX II

Examples of problems to be solved by the participants

1. In one of the lectures, the following table has been given for the reproducibility R as a function of the level of the residue:

residue (mg/kg)	R (%)
0.01	100
0.1	50
1.0	25

Now using the values given above for R as "latitudes", decide whether a found residue level of 2.4 mg/kg exceeds an MRL of 2 mg/kg or not. Make the same calculation according to the "round-off" principle.
(the same question was asked to several participants, using different figures for the residue level found and the MRL).

2. Suppose the following figures (in mg/kg) have been found for the level of a pesticide X in commodity Y:
0.21 0.19 0.30 0.24 0.28 0.25 0.20 0.31 0.24

(a) What is the median value?
(b) What is the arithmetic mean?
(c) Is there reason to suppose that the distribution is "skew" or does
it appear to be fairly "normal"?
(the same question was asked to several participants, using different figures)

3. In one of the lectures, the determination of derivatives of aromatic amines after alkaline hydrolysis and bromination was given.

What aromatic amine and what brominated derivative do you expect from:

(a) isoproturon

(b) phenmedipham

(c) chlordimeform

(d) benodanil

4. How would you separate:

(a) propoxur from its metabolite 2-isopropoxyphenol

(b) binapacryl from its metabolite dinoseb

(c) diuron from its metabolite 3,4-dichloroaniline

(d) lindane from fat

(e) chlormequat from sugars

(f) aniline from proteins

5. Using the Codex Guidelines for the sample preparation as a reference indicate:

(a) how you would prepare an Analytical Sample from a lot of 100 kg carrots (average weight of one carrot: 100 g)

(b) whether you have to remove the adhering soil from a sample of carrots prior to blending or not

(c) whether you have to remove the stone from an avocado prior to blending or not

(d) whether the stone is to be taken into account when calculating the residue level in a mango or not

6. Which one of the following pairs of two compounds will be the best amenable to HPLC with UV detection:

(a) HCB or β-HCH

(b) azinphos-methyl or methamidophos

(c) biphenyl or maneb

7. Explain why DNOC (dinoseb, dinoterb) can be determined more sensitively by HPLC in the ion-pair mode than in the ion-suppression mode.

8. Normally, ethylene oxide is determined by head-space GLC with flame-ionisation detection. Suppose we want to use ECD instead of

FID, what derivative would you suggest to make?

9. Electron capture detection is based on the use of (check):
   - ☐ α-particles
   - ☐ β-particles
   - ☐ γ-particles
   - ☐ thermal electron irradiation

10. What are the advantages and disadvantages of:
   (a) 63Ni-ECD compared to 3H-ECD
   (b) H_2 as a carrier gas in GLC compared to N_2
   (c) FPD(P) compared to AFID(P)

11. What reagent(s) would you suggest for the the detection on TLC-plates of:
   (a) monuron
   (b) simazin
   (c) dichlorvos
   (d) dieldrin
   (e) carbendazim

12. Give the reaction equation for the reaction of:
   (a) 2,4-D with pentafluorobenzyl bromide
   (b) 2,4,5-T with boron trifluoride and methanol
   (c) pentachlorophenol with diazomethane
   (d) 2,3,6-TBA with diazomethane
   (e) linuron with heptafluorobutyric anhydride

13. What are the reaction products upon oxidation with (1) bromine-water, (2) potassium permanganate and (3) m-chloroperbenzoic acid of:
   (a) fenthion
   (b) disulfoton
   (c) aldicarb
   (d) fensulfothion
   (e) phorate

APPENDIX III

Suggestions for textbooks for self-study

(1) ANALYTICAL CHEMISTRY

C.F.Poole and S.A.Schuetle, Contemporary practice of chromatography, ISBN 0-444-42410-5, Elsevier Science Publishers B.V., Molenwerf 1, P.O.Box 211, 1000 AE Amsterdam, The Netherlands (1984), 708 p.

This book gives an excellent, up-to-date survey of all relevant modern chromatographic techniques in use in pesticide residue analysis. It is above all a practical guidebook for those who use chromatography in their daily work. It should be used together with the manuals on the specific instruments issued by the suppliers of the instruments.

(2) ORGANIC CHEMISTRY

J.M.Cram and D.J.Cram, The essence of organic chemistry, ISBN 0-201-01031-3 (1978), 544 p.

This book gives the essential background for analysts working with biological samples. The backgrounds of the reactions are discussed in up-to-date terms and can be understood by any student of B.Sc. level or higher.