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Technical report: Workshop on impurities in technical grade pesticide material, Suweon, Republic of Korea, 11-18 October 1992*

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Table of Contents

Introduction	1
Objectives of the Workshop	1
Opening of the Workshop	2
Designation of Officers	4
Adoption of Agenda	5
Technical Session	5
Keynote Session	5
Country Paper Presentation	6
Presentation of Technical Papers	12
Laboratory Work for Identification of Impurities	14
Report on Field Visits	16
Recommendation	17
Appendix I	18
Appendix II	22
Appendix III	25
UNIDO Comments	33

I. INTRODUCTION

1. The regional workshop on impurities in Technical Grade Pesticide Material organized under the auspices of the UNIDO/RENPAP in cooperation with the Agricultural Chemicals Research Institute, Rural Development Administration, Ministry of Agricultural Forest and Fisheries, Government of Republic of Korea was held from 12th -17th of October 1992 at Suweon, Republic of Korea.

2. The workshop was attended by 14 delegates from 12 member countries of the network viz Bangladesh, P.R.China, India, Rep.of Korea, Indonesia, Malaysia, Myanmar, Philippines, Pakistan, Sri Lanka, Thailand and Vietnam. Six out the 14 delegates were women who represented their countries in this meeting.The list of participants is attached as Appendix-I.

II. OBJECTIVES OF THE WORKSHOP

The workshop intended to cover:

i) Pesticides:Recent Development in Chemistry of Pesticides

ii) Impurities in the technical grade pesticides and its impact on the environment;

iii) Impurities in technical grade materials and its effect on phytotoxicity and mammalian toxicity of its formulated products;

iv) Influence of the impurities on the degradation and shelf-life of pesticide formulations;

v) Identification and quantification of impurities present in the technical grade pesticides;

vi) Recent advances in the instrumentation analysis of impurities present in the technical grade materials;

vii) Need for limiting of the impurities in the technical grade materials at the manufacturing stage;

viii) Standardization of the analytical procedure for the estimation of active ingredients as well as the impurities through the Regional Analytical Council for Asia and the Pacific(RENPAC)

ix) Need for harmonization of pesticides product specifications including a)required parameters for the setting up of pesticide specifications, and b) confirmation of the specifications in particular impurities in technical and formulated products;

x) Increasing the efficiency and productivity of pesticides testing laboratories particularly in the determination of the impurities.

III. OPENING OF THE WORKSHOP

The workshop was inaugurated by Dr.Young-Sun Park, Director General, Agricultural Chemicals Research Institute, Rural Development Administration, Ministry of Agriculture, Forest & Fisheries, Govt. of Republic of Korea.

While welcoming the delegates, UNIDO staff member stated that the Regional Network came into existence exactly a decade ago and with the excellent support from UNDP and the member countries, dedicated and conscientious work by the Regional Coordinator and the National Coordinators the network grew from strength to strength. Today there are 14 member countries covering about 5th of the world's surface and with more than half its population. He mentioned that UNIDO puts great emphasis on networking which is the most efficient way of disseminating knowledge and exchange of experience in an area such as pesticides which is getting very complicated due to introduction of highly active compounds with complex structure, expensive and time consuming procedure for registration of pesticides. The great changes in formulation and application technologies and above all the pressure put on by environmentalists will all make this subject of pesticides a fascinating and challenging field in the future years and definitely in the 21st century.

He said that UNIDO is well committed to ecologically sustainable industrial development(ESID) in developing countries and in this respect collaborates with other international agencies and non-governmental organizations in support of Agenda 21 ratified in the recent Earth Summit held in Brazil. He mentioned that to day the most alarming thing facing our planet is pollution from toxic and hazardous chemicals coming from industries especially from chemical industries. It is well recognized that chemical industries play vital role in the economy of both developed and developing countries because of their direct use in many outlets and in other industries such as leather, plastics, food industries, paint, engineering electronics etc.

Pesticides also, called crop protection chemicals,he said, occupy an unique position in that industries and the governments have to face extreme views both in the production and use of these chemicals. At the same time they have to make policies and adopt legislative measures in order to follow a rational approach to reap the benefits from these agrochemicals and removing side effects from water, soil and air contamination.While the developed countries are

trying to control the problems by moving towards low volume-high value pesticides, the majority of developing countries do not have the resources in terms of technology, expertise or finance to introduce newer and safer technologies. In this, the UNIDO technical co-operation projects in developing countries address to these issues and more and more emphasis is placed on safety, health and environment in pesticide production.

Recently UNIDO developed after a series of expert group meetings and workshops, an Integrated International Safety guidelines in Pesticide Formulation in Developing countries in a meeting held at Brussels. He said that UNIDO is now looking for a suitable mechanism to implement the Brussels Guidelines in cooperation with various international and national agencies. Apart from funding, it was emphasized that dedicated support from all parties concerned is required and to take every effort to follow these guidelines at the shop floor in the industries. Linking these guidelines at the production level with FAO Code of Conduct on Distribution and Use of Pesticides, it should be possible to vastly improve overall safety and minimize or eliminate environmental risks associated with production and use of pesticides.

In all these, he emphasized that the quality plays an important role especially when dealing with toxic/hazardous chemicals. Quality control at the production end is of vital importance because it is controlled during the production and would reduce mishaps happening at the regulatory end. Therefore, he said, that this workshop will be useful to avoid impurities in technical materials at the production stage by increasing management/worker responsibility to quality control/quality assurance.

While welcoming the delegates Dr. Park, Director General, Agricultural Chemical Research Institute, Rural Development Administration, Ministry of Agriculture, Forest & Fisheries, Govt. of Republic of Korea, said that he was glad to know that UNIDO/RENPAP has fruitfully set in motion the Regional Pesticide Network Programme to promote development of pesticide and their control in this region of the world.

He said that the dependance of pesticide in agriculture is of great need since agricultural productivity and quality which are firmly linked to pest in modern agriculture is essential for sustaining food production. Exploitation of cash crop resources and potential crops to tackle trade liberalization of agro-products requires further pesticide demand to protect the crops.

While the outcome from pesticide use are quite apparent, one has to keep in mind the potential adverse impacts due to the wide use of these chemicals. Although R&D, safe use and control of pesticides

have been progressed at a great pace the world over, he said, it is still necessary to harmonize a balance between maintenance of pollution free environment and use of modern technologies.

He said that some countries of the region have made progress in manufacturing pesticide technicals to some extent. However, most regional countries place main reliance on developed countries for the most part of their required quantity of pesticides. Pesticide industry is a rapid growing one, therefore, without provision that developing countries close up to the advanced pesticide technology, they will always find themselves far from self-reliance. Against this framework, the magnitude of such an inequality could be minimized through mutual cooperation and integral efforts.

From these points of view, he said, that he was glad this valuable Regional Workshop is held in his Institute. He highlighted that some impurities in pesticide technical grade material proved to be more hazardous than active ingredient, may cause to catalyze degradation of a.i., and may induce phytotoxicity, those critical impurities in technical grade materials should be identified and regulated to upgrade pesticide safety.

He expected that the Workshop will go far toward elevating pesticide quality among the regional countries and encourage further inter-cooperation and dependance in all sphere of pesticide utilization with this relevant workshop as momentum.

Dr. Dhua presented the activities of the RENPAP in the Asia and the Pacific region with the help of slides. He highlighted the focus of the project which is sharply on the promotion of safe pesticides which are environment and user friendly. The various activities of the current phase of the project has been designed to promote "clean" technologies, production of environment and user friendly pesticides including the bio-botanical group of pesticides. Appreciating the relevance of the RENPAP project activities the member countries of the network are now extending greater support than ever before and the membership is on the increase.

IV. DESIGNATION OF OFFICERS

Dr.Byung-Youl Oh, Head of Formulation Laboratory, Agricultural Chemicals Research Institute, Rural Development Administration, served as the Chairman. Mr.Vinay Kolhi, Joint Secretary, Department of Chemicals and Petrochemicals, Ministry of Chemicals and Fertilizers, Govt. of India served as Co-Chairman and Ms.Bella Fe D.Carmona, Fertilizer and Pesticide Authority, Govt. of Philiphines as the Rapporteur.

V. ADOPTION OF AGENDA

The Meeting adopted the Agenda as presented in Appendix-II.

VI. TECHNICAL SESSION

A.Key note session

The workshop started with a keynote paper from UNIDO, Vienna. The paper gave a broad coverage of developments in chemistry R&D that took place since the introduction of DDT almost 50 years ago. During the last 20-25 years there has been a revolutionary changes in the introduction of new pesticides which reduce the amount used per hectare from 3-5 Kg to as low as 20-100 gm and at the same time reducing mammalian toxicity.This happened practically in all areas such as herbicides,fungicides and insecticides.This is also one of the reasons for an average increase of 20% in the yield of various major crops during 1980-1987.

The paper described a number of strategies used by chemists to find new pesticide and how the chemistry becoming more complex due to presence of double bonds and asymmetric carbon atoms and how companies are using mode of action studies and computer graphics to make specific compounds which would be perfect fit for interaction with enzyme systems.Example of azole fungicides are ergosterol inhibitors was given and how they exhibit both fungicidal and plant growth regulatory activity. Example is given as to how the fungicidal activity could be separated from plant growth regulatory activity.

The paper explained how developed countries are moving towards low-volume-high value pesticide taking advantages of the development in the R & D of the chemistry of pesticides. Developing countries still use old pesticides and they should be encouraged to move towards user and environment safe pesticides, their formulation and application methods

Importance of Integrated Pest Management(IPM) was emphasized and their role of pesticides in the IPM was highlighted. He said that it is essential for the industry and the governments to strive towards IPM to reduce overall pesticide consumption in agriculture

Development of registration requirements over the last three decades was described and he emphasized the role of the companies for moving towards more pure compounds thereby avoiding impurities including unwanted isomers to remove any undesired effects on the bio-efficacy, ecosystem, and the user.

B. Country paper presentation

Country papers highlighting the status of the pesticide industry in general and their regulations specifying maximum limits of impurities permissible in the technical grade materials was presented by the delegates. The summary of each paper is presented below;

1.Bangladesh

The report of Bangladesh was presented by Mr. Karim. He stated that at present in Bangladesh there are 260 different brand of pesticides registered for agricultural use and 49 for public health. He stated that 80% of the farmers use insecticides 5% use of herbicides and 60% use of fungicides. The total consumption of pesticides is about 7,000M/T annually. Some of the pesticides are locally manufactured and some are imported from other countries.

The registration of pesticides is governed by Pesticide Ordinance 1971 and its Rules 1985. The Ordinance is administered by the Plant Protection Wing, Department of Agriculture Extension, Ministry of Agriculture. The process of registration of pesticides is based on the results of physical and chemical properties determined by the quality control laboratory and through field trials in the different research institute.

Pollution control and environment protection methods are being used by the pesticide industry and in accordance with the procedures laid down by the environment protection agency(EPA) of U.S.A.

The success of pesticide management and for the detection of impurities in technical materials depends on the well-established pesticide laboratories equipped with modern sophisticated equipments and experienced manpower. The establishment of such laboratories in Bangladesh would need external financial support and assistance.

2. Peoples Republic of China

Ms. Ying presented the paper for P.R. China. She said that China is big agricultural country. The amount of pesticide produced and used is quite large in the world. Almost 2.000 pesticides production factories are in operation and can produce more than 150 kinds of pesticides. The annual output pesticide technical product is over 2,000M/T, most of which are insecticides. Out of the insecticides 78% are organophosphorus compounds, carbamates, and synthetic pyrethroids. Fungicides accounted for 9% and herbicides 10% of the total pesticide usage in the country. Besides, rodenticides and plant growth regulators are also produced.

In the production process of technical material, impurities are mostly by-products from reaction and unreacted products / intermediates.

China attaches great importance to the quality of pesticide products. There is a comprehensive registration, examination and approval system for production and sale of every pesticide. In the past,in the pesticide quality only the active ingredient used to be tested and not impurities. In recent years, with the strengthening of the pesticide management, China has started to attach more importance to the impurities present in the technical grade pesticide materials. For example, in the standard of formulating quintozene, the content of hexachlorobenzene has been limited.

China's pesticide industry had a late start. There are still some problems that need to be solved. To learn advanced experiences, efforts are being made to interact with the countries advanced in this regard so as to make greater efforts towards the development of the pesticide industry.

3. India

The country paper of India was presented by Mr. Kohli. He said that India is major producer of pesticide-technical as well as formulation. In 1990 the installed capacity was 118,500M/T. Production in this year was 67,370M/T. Fifty-four basic pesticides were produced. Considering that the pesticide industry started in 1952-1953, this is no mean achievement. In fact, total import in 1990 were about 1,389M/T and only technical material was imported of the value of US$ 7,066,000. Export in the same year were valued at US$ 10,500,000.

So far as formulations are concerned, these are produced in as many as about 600 units and although only 30% of the capacity is utilized as against a production of 430,937M.T./K.L., exports were valued at US$ 77,635,000. Most of the technology for analysis of the chemical structure, impurities, and contaminants including toxic substances is available and installed in the country.
The intensity of the available analytical capability needs to be densified. Standardization has to a large extent progressed well. Pesticides available in the country started with the organochlorine group, organophosphorus group, carbamate, synthetic pyrethroid, and include the latest available highly potent, bio-degradable products.

4. Indonesia

Ms. Hidayati presented the country paper of Indonesia. She stated that pesticide formulation industries in Indonesia produced

about 60% insecticides ,15% fungicides, 15% herbicides, and 10% others. The type of pesticide produced are granules, dusts, WP, OC, WSC, EC, and ULV. For the manufacture of technical grade material in Indonesia, the present licensed capacity is 14,500M.T./K.L. per year of diazinon, monocrotophos, ethepon, glyphosate, carbofuran and carbaryl.

Production of active ingredients is done to conform to Standard Industries of Indonesia(SII) specifications. The identification of impurities have not yet been included in the SII and are causing difficulties of identification and enforcement.

The investigation of impurities in active ingredients is very important because these can affect the formulated products and may result in degradation and also causing environmental pollution.

5. Republic of Korea

The report from Republic of Korea was presented by Dr. Byung-Youl Oh. He said that a total of 26 pesticide firms are being involved in pesticide production, which comprised of 12 formulators and 14 technical manufacturers. These firms produced 16,332M/T of technical and 25,286M/T of formulated materials on a.i. basis in 1990. Domestic formulators also imported 8,400M/T of technical and 1,324M/T of formulated products, which was 66% and 95% of local production of technical and finished product respectively. Major groups of consumed pesticides are ogranophosphorus, carbamate, synthetic pyrethroid, urea and antibiotic. Conventional types of formulations are widely used as a total of 501 formulations with 270 registered a.i..

Classification and the restricted use of pesticides are in accordance with the FAO/WHO guidelines. The target impurities to be regulated in the Republic are hexachlorobenzene in chlorothalonil, DDt related compounds in dicofol, hydrazine in maleic hydrazide ethylene thiourea in mancozeb, perchloroethylene in oxyfluorfen, and n-dinitro-di-n-propylamine in trifluralin. Regulation limits of the declared impurities are in legal action including routine counter-measure by the authorized agency(National Agricultural Material Inspection Office)

In addition, he stated, that improvement of application technology of pesticides and development of easy-to-apply formulation are some of the immediate obstacles encountered in the Republic so as to tackle the current situation of rural community.

6. Malaysia

The Malaysian country paper was presented by Mr. Fauzan Bin Yunus. He stated that evaluation of impurities in technical grade pesticide material is limited to comparing the level of impurities provided by the applicants during registration application to the limit in Malaysian/FAO/WHO specification. Pesticide industry in the country if based on formulation of pesticide from imported technical grade material. Very often, local formulators are not informed of the impurities in a particular batch of technical material imported because overseas suppliers often procure their product from different manufacturers resulting in import of technical material which differ from those registered by the Pesticide Board of Malaysia. Pesticide Board is now taking steps to restrict the source of registered pesticides. He stated that it will be beneficial to the regulatory authority in particular those with limited resources if the workshop addresses this issue to identify the pesticides that contain the impurities.

7. Myanmar

The presentation from Myanmar was made by Mr. Sein. He stated that in 1989 formulation plant was established jointly by the government, UNDP and UNIDO. The formulation plant set up recently has a capacity to produce 1.08 million liters per year and this quantity is not adequate to meet the requirements of the Myanmar agricultural services; therefore, pesticide still being imported to meet the requirements

The government has now introduce the pesticide law. The pesticide specification adopted in Myanmar are based on FAO/WHO guidelines and methods of analysis are based on CIPAC method.

All the waste are stored systematically awaiting incineration. Myanmar needs technology and equipments for the identification of impurities in technical grade material to ensure delivery of good quality of pesticide to the farmers.

8. Pakistan

The country paper for Pakistan was presented jointly by Mr. Mumtaz and Mr. Mushtaque. They informed the meeting that over 300 brands of pesticides are registered for pest management in agriculture mainly for cotton, rice, sugar cane , maize, and horticultural crops. With banning of BHC and DDT, the manufacturing unit have been closed down and no other unit so far has been set up for the basic manufacture of pesticide. There are however 14 formulation plants and these are working at 40% capacity. Hence,

there is total reliance on the imported pesticide products. Provisions exist in the Pesticide Act for the safety of the workers, but the arrangement for the implementation are lacking. Poisoning cases due to improper handling do sometimes occur specially during the extreme summer conditions. Due to impurities of isomalathion in malathion, 2,500 cases of poisoning took place in 1976.

Use of pesticide has increased from 1981 at 905M/T a.i. to 4,460M/T of a.i. in 1990 mainly because of cotton and other crops,where cost/benefit has become more favorable to the farmers. Because of development of insect resistance, the insecticide dosages have been increased, but this is a limited solution because of obvious economic and toxicological factors.

In quality control and residue analysis, GLC and HPLC are being used following AOAC, CIPAC, and other methods modified in the laboratory.

Problems in respect of degradation and impurities in toxicants require upgradation of equipment and expertise.

9. The Philippines

Ms. Carmona presented the country paper of the Philippines. She stated that the Fertilizer and Pesticide Authority(FPA) requests that registrant declares impurities and/or possible impurities which may be found in their products and the conditions under which such impurities may occur in the manufacturing process, however compliance leaves much to be desired. Availability of analytical methods for identification of such impurities and analytical methods for detection are very limited. Information provided pertaining to the toxicological implications of some of the impurities range from nil to very minimum. In such cases, FPA relies on studies and information available from international organizations like the USEPA, FAO, WHO with regard to the identity of the suspected impurity in the manufacture of particular pesticide and if available the toxicologically acceptable level thereof. Certificate of analysis from international independent laboratory showing acceptable level or absence of such impurity is required.

For pre-registration, confirmatory analysis of the a.i. and formulation is done through BPI-Pesticide Residue and Formulation Laboratory and PIPAC. On post-registration, counter checking of product quality is done by sampling from dealer shelves. Monitoring of the quality control programme of pesticide formulations is likewise undertaken. BPI in collaboration with CIPAC undertakes standardization of methods of pesticide analysis and quality control.

10. Sri Lanka

The country paper of Sri Lanka was presented by Mr.Wettasinghe . He said that as in many other countries food production in Sri Lanka has been increased by various methods such as the introduction of high yielding varieties, improved irrigation systems, high cropping intensity and increased inputs of chemicals and organic fertilizers and pesticides.

The average yield now lost due to pests, weeds and diseases is about 30%. Crop protection programme has been strengthened to control these problems through improved farming systems, introduction of IPM for rice and through the use of biological and chemical methods. However, pesticides still play an important role in reducing the problems.

In the past two decades flowable, microgranular soluble powders and controlled release capsules have been introduced. Among the thirteen major companies 5 carry out formulations using imported technical materials from other countries. The quality of the technical materials is important for the products to be safe and effective. The pesticide industry is fully dependent of the data submitted by the parent companies. Only a few pesticides are currently being formulated locally. Example in analytical facilities are limited and use of pollution control methods are necessary.

11. Thailand.

The country paper of Thailand was presented jointly by Ms.Sriplakich and Ms.Nuetrakod. They stated that the pesticide problem in Thailand include harmful effects to the agricultural workers and in the formulation plant, residual effect to the consumer and the environment mainly arising out of the lack of awareness, misuse, overuse, shortage of protective equipment, accident, improper waste disposal, social irresponsibility and suicide. The government policy has been to search for alternative pest control means and good agricultural practices for sustainable agriculture.

Over 200 active ingredients and 350 formulations are registered in Thailand. There are many trade names for each formulation and there are as many as 246 trade names for methylparathion 50EC. The registration scheme is being strengthened for safe and effective use of pesticides through detailed data requirement of trial efficacy, toxicology, risk assessment and certificate of product analysis of active ingredient content. The use of specification is required for the quality control of 18 pesticides and 32 formulations. The presence of impurities in technical grade products are limited. So far, impurities analyzed are water, acidity/alkalinity, material

insoluble in specific solvent, arsenic, lead, cadmium,DDT related compounds, BHC isomers, trimethyl phosphate, omethoate,and 4,4'-bipyridyl. Analytical methods conform to CIPAC using TLC, GLC and HPLC.

12. Vietnam

Ms.Dung presented the country paper of Vietnam. She informed the meeting that an advisory council for pesticide was established in 1991 to consider all aspects of pesticide production, research trials and public health usage. The active ingredients for the formulation of EC, WP and granule for agricultural production are imported.

The Ministry of Agriculture and food industry and the pesticide industry have established a center for quality control . This center is equipped with TLC, GC, and HPLC.

Research on pesticide residue present in agricultural products and the environment has been done during the last few years. Standard method for residue analysis of the following pesticides have been established;

-BHC and methylparathion in paddy and soyabean
-Methylparathion, methamidophos, dimetoate and BHC in tea products

She urged that the government of Vietnam would need assistance from the international organizations in order to set up laboratories equipped with necessary facilities and expertise.

C. Presentation of Technical Papers

a. Mr. Gimeno in his presentation entitled "New Trends in Pesticide Formulation" mentioned that devising new ways of controlling pest at the right time and with the smallest amount of active ingredient is a challenge for the formulation chemist. Formulation are developed to optimize the biological activity of the active ingredient and at the same time reduce or remove adverse effects on non-target organisms and the environment. In addition it is aimed to improve product handling so that the product poses no problems to the end user.

He emphasized that it costs around $100 million(1989) and takes around 10 years to develop a new pesticide. The lecture gave in detail factors involved in the development of microencapsulation, water soluble packaging for water dispersible powders as user friendly formulations. In the majority of cases the development of a

safer product is driven by commercial pressures, regulatory pressures and political pressures. Today the US EPA, and the German regulatory authorities have introduced legislation for the control of the so called inerts used in various pesticide formulations. Countries such as France are introducing safer formulation and slowly moving away from dusts and emulsifiable concentrates. The various advantages to move away to safer formulations were discussed. Various methods used in microencapsulation by interfacial polymerization methods were described.

b. Mr. Gimeno in his presentation lecture dealt with the "Effect of Impurities on the Cost of Synthesis, Formulation, Registration, Quality and Assurance". With 17 million tones of pesticides made at a cost of $22.3 billion there is a great concern from the environmentalists and the registration authorities regarding the impact of impurities on the environment. Accordingly for registration and registration of pesticides chemical companies will have to generate complex mixture of data which is proving very costly.

The main aim of formulation is to reduce the amount of active ingredient per unit area, reduce risks to potential end user, lower formulation costs by automation of the quality control programme. Various methods are described to improve packaging and handling during formulation and usage. In addition examples are given to reduce phytotoxicity and reduce quality control and quality assurance costs.

Examples of impurities in active ingredients such as dicofol, malathion, captan, and napropamide, and how purification could be affective were given.

c. In his presentation on the "Introduction to Mass Spectrometry and Interpretation of Mass Spectrum", Dr. Oh stated that the recent advances in instrumental analysis was focussed on mass spectrometry interfaced with GLC or HPLC for the molecular confirmation of impurities in technical grade pesticides.

Sample introduction to mass spectrometer(MS) can be made by GLC with packed column or capillary column. Interfacing orifices for GLC widely being used are porous diffusion, permeable membrane, and jet separator. Commercially available interfaces for HPLC are moving belt or thermospray system. Another introduction methods involve direct exposure probe technique and pyrolysis.

Ionization method of the compound is done by means of electron EI(impact), CI(chemical ionization), DISIMS(discharged ion secondary ion MS), or FAB(Fast atom bombardment). In order to

separate ionized fragments or molecular ion, quadrupole mass filter and ion trap MS are most commonly used. As an ion detector of MS, continuous dynode electron multiplier or PPINICI(Pulsed positive ion negative ion CI) is generally adopted in most MS.

To avoid chemical reaction among fragmented ions and burning out the filament, Dr. Oh said that high vacuum condition has to be maintained during MS work. Diffusion pump by using heated oil (polyphenylether) is common for vacuum generation.

A brief interpretation theory on mass spectrum was also given by Dr. Oh illustrating natural abundance of common elements, combination of major elements, rules for rings and double bonds, molecular ion identification techniques, and nitrogen rule. Some of the basic compounds involving aliphatic and aromatic were demonstrated with their mass spectra. In addition, fragmentation pattern of typical chemicals was interpreted by Dr. Oh during his presentation.

d. "Analytical Methods for Impurities" discussed during the workshop were hexachlorobenzene in chlorothalonil, DDT related compounds in dicofol, hydrazine in maleic hydrazide, ethylene thiourea in mancozeb, and N-nitro-di-n-propylamine in trifluralin.

Proposed analytical methods for the impurities by GLC, HPLC and spectrometry were given by Dr. Oh as attached in Appendix-III.

D. Laboratory Work for Identification of Impurities in Technical Grade Pesticide

Chlorothalonil technical was chosen as a sample to identify, confirm the molecular structure, detect quantitatively the impurities. Technical grade chlorothalonil was dissolved in acetone at about 1% concentration. A total of 0.5ml of the acetone solution which was equivalent to 5mg of the technical was loaded on TLC plates(20X20cm) of silica gel G60 by using a micro-applicator. The plates were placed in the development solvent(n-hexane:ethyl acetate:methanol 8:3:2) in a TLC chamber. The development of the tlc plates took 30 minutes and then the isolated bands confirmed under UV lamp. The band corresponding to the impurity were scrapped from the plates, extracted with solvent with 40ml of acetone using an ultrasonic equipment. The dissolved impurity was filtered by passing through a layer of anhydrous sodium sulphate. The dissolved impurity was filtered by passing through a layer of anhydrous sodium sulphate. The filtrate was evaporated using a rotary evaporator at 40C to dryness. The dried impurity was again dissolved in deteuriated acetone for analysis by C-NMR. At the same time, 10 fold diluted

solution of chlorothalonil stock solution in acetone was subjected to GC/MS work. Acetone diluted chlorothalonil technical was injected to GC installed with 25m capillary column(DB-1) which was programmed from 80 to 260C at the rate of 10 C/minute. Injection temperature was maintained at 260C and transfer line was 270C.
The split mode was adopted with a velocity ratio of 30:2 of helium as carrier gas. The condition of mass spectrometer was EI 90ev, 1300 voltage on the detector. Quadruple was used as mass analyzer. Scan rate of the data was adjusted to one scan/second. Typical peak was recorded on the chromatogram with a scan time of 810 seconds. After completion of GC/MS work, the mass spectrum of the impurity showed that the highest intensity of molecular ion was clustered around 262-268 M/Z, which illustrated aromatic compounds. The mass spectrum also showed six logical fragment losses from the molecular ion was 35 which meant that the impurity contained 6 chlorine atoms.

FT-NMR spectrum for C showed only single peak appeared with 205ppm of shift value which was the typical value for C-Cl linkage. From the interpretation of the MS/NMR spectrum, the impurity was found to be hexachlorobenzene(HCB). In addition to that, the obtained mass spectrum was searched by using NBS(National Bureau of Standards) library which was installed in the instrument. The searching results showed that the impurity was HCB with a probability of 98%.

For the quantification of the HCB in technical, GC/ECD(electron capture detector) was used. A chromatographic column clean-up was done in order to eliminate the high amount chlorothalanil and not to saturate the detector. The clean-up column was packed with activated florisil and anhydrous sodium sulphate was placed at the top of the packing. The column was washed with n-hexane and then 8ml of technical stock solution was added. In order to elute the HCB from the column, 40ml of dichloromethane:n-hexane(2:8) was used. The eluate was concentrated to 5ml using a rotary evaporator at 40C. The final solution was injected to the GC/ECD. The GC conditions were 220C in the injection block, 280C in the detector with the column temperature 190C, The column used was borosilicate glass 3mm internal diameter and 200cm length packed with 3% of the OV-17 on chromosorb HP-100/200 mesh. The calibration curve of HCB standard was linear between 0.02ng-0.4ng.

The retention time of HCB under the above condition was 3.2 minutes. The sample was calculated in terms of concentration against standards.

VII. Report on Field Visits

A. The Toxicology Research Centre, Daejeon ; A visit to the Toxicology Research Centre of the Korean Research Institute of Chemical Technology Institute(KRICI) located in Daejeon was arranged to provide the participants an idea about the modern facilities needed to carry out toxicological evaluation of pesticides and their formulations. The Director of the Institute, Dr. Roh took the participants around the laboratories. He explained as to how UNDP/UNIDO provided the important financial and technical assistance during the first phase to set up the Centre which according to Dr. Roh is the best equipped Toxicology Centre with trained staff in Asia experts they managed to adapt the design of a Japanese Toxicology Laboratory to suit South Korean conditions.

The Centre is now doing all basic toxicology tests, 90 day feeding trials, breed SPF rodents for testing and are in the process of expanding to cover experiments with dogs. He said that the Centre carries out eco-toxicology studies for effects of pesticides to fish, daphnia, algae etc. The participants were shown the breeding facilities for SPF animals, quality control laboratories, SOP, studies with radio-labelled compounds, how data are entered in each laboratory and sent to central data control unit where reports are prepared and quality assurance is checked.

Dr. Roh mentioned that the Toxicology Centre has already been cleared for Korean and Japanese GLP and are doing contract work for Korean and Japanese companies. They are aiming to get European and US. EPA GLP regulations. He kindly agreed to provide any training to RENPAP member countries if requested through UNDP/UNIDO

B. The Honnong Central Research Institute ; Following the visit to the Toxicology Centre, a visit was made to Hannong Central Research Institute near Suweon. It is one of the biggest chemical producers in the participants. Their small but compact pilot formulation plant gave an idea to the participants.

The two visits in South Korea clearly indicated to the participants of the workshop the availability of highly equipped institutions with in the RENPAP member countries.

VIII. RECOMMENDATION

1. All member countries should endeavour to adopt within a specific time frame limits of impurities permitted in technical material prescribed in the FAO/WHO specifications.

2. The methods of analysis need to be standardized and in the first phase, utilizing the mechanism of RENPAC, the six participating laboratories in P.R. of China, India, Indonesia, Rep. of Korea, the Philippines and Thailand should adopt these in close association with CIPAC. Other countries should also join as when they upgrade their analytical laboratories.

3. Having recognized that all member countries should have analytical facilities for determining impurities in technical material and having appreciated the offer made by Rep. of Korea and India to use their analytical facilities, and having felt the need that all countries will have to have a basic minimum analytical facilities in order to facilitate, it is recommended that respective Government will require to provide the basic minimum analytical facilities.

4. Having approved paucity of necessary equipments and trained manpower, the workshop recommended that the relevant efforts of nation states in this regard needs to be supplemented by international agencies including UNDP/UNIDO/RENPAP, etc..

5. Having appreciated the good analytical work being done in some laboratories in the region and having felt the need for identifying impurities and problems they cause, it is recommended to make efforts to carry out coordinated research according to the specialized areas of work of the participating laboratories using RENPAC mechanism.

6. Having recognized the lack of information in the region on impurities, metabolites and degradation of the pesticides with regard to toxicity and hazards of the pesticides and taking into account the capacities of RENPAP/RENPAC to generate and obtain data in these areas, it is recommended that member countries should make use of the network for regular exchange of data and information.

Appendix I

LIST OF PARTICIPANTS

COUNTRY REPRESENTATIVES

Bangladesh

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	Ms. Nunchana Neutrakod Ditto
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RESOURCE PERSONS

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	Dr. Byung-Youl Oh Head of Formulation Lab Pesticide Chemistry Department Agricultural Chemicals Research Institute Rural Development Administration Suweon 441-707, Republic of Korea

Assistant for Lab Work	Mr. Jin-Hwa Kim ditto
	Mr. Seung-Soon Park ditto
	Mr. Hee-Sam Lee ditto

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Appendix II

AGENDA

Workshop on Impurities in Technical Grade Pesticide Materials
Suweon 441-707, Republic of Korea, October 11-18, 1992

October 11 (SUN)

Arrival of participants

October 12 (Mon)

09:00-10:00 Registration

10:00-10:30 Opening Ceremony
* Opening Address - Dr. B. Sugavanam
* Welcome Address - Dr. Young-Sun Park
Dr. S.P. Dhua

10:45-12:30 Election of Chairman
Appointment of Rapporteur
Adoption of Agenda
Plenary Lecture
* New Chemistry in Agrochemical Products - Dr. B. Sugavanam

13:30-15:00 Slide Presentation for RDA Projects

15:00-17:00 Presentation of Country Paper
* Bangladesh
* India
* Indonesia
* Republic of Korea
* Malaysia

October 13(Tue)

09:00-10:30 Presentation of Country Paper
* Myanmar
* Pakistan
* Philippines
* Sri Lanka
* Vietnam

10:45-12:30 New Trends in Pesticide Formulation - Dr. Miguel Gimeno
* Regulation Pressure
* Microencapsulation
* Water-soluble Packaging
* Open for Discussion

13:30-15:00 Advances in Instrumental Analysis - Dr. Byung-Youl Oh
* Introduction to MS
* Interpretation of mass spectra
* Open for Question

15;15-17:00 Impurities Level Content in Technical Products and Their Significance - Dr. Miguel Gimeno
* Formulation & Synthetic Cost
* Registration
* QC/QA Cost & Phytotoxicity
* Self-life of Formulation
* Packaging & Handling
* Open for Discussion

October 14(Wed)

09:00-10:30 Country Paper Presentation-China
Analytical Methods of Impurities in Technicals - Dr. Byung-Youl Oh
* Dicofol, Mancozeb, Chlorothalonil, MH, Trifluralin

10:45-12:30 Experimental Practices - Dr. Byung-Youl Oh
* TLC, GC, HPLC, GC/MS, FT-NMR

13:30-15:00 Continue Experimental Work

15:15-17:00 Continue Experimental Work

October 15(Thu)

08:00-10:00 En Route(Hotel-Taijon)

10:00-12:00 Toxicology Lab

13:00-16:00 En Route(Taijon-East Suweon)

17:30-19:00 Hannong Research Institute

October 16(Fri)

09:00-10:30 Interpretation of Experimental Results

10:45-12:30 Collaborative Tests(Round Robin Studies) - GLP Protocols

Standardization of Analytical Methods

October 17(Sat)

09:00-10:30 Open Forum-Discussion in Reports, Recommendation for Future Work, etc.

10:30-11:30 Workshop Conclusion and Comments
Dr. B. Sugavanam, Dr. S. P. Dhua

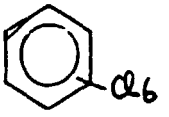
Appendix III

PROPOSED ANALYTICAL METHODS OF IMPURITIES IN TECHNICAL GRADE PESTICIDES

1. Hexachlorobenzene(HCB) in chlorothalonil technical

A. Formula

o Chemical structure



o Molecular weight : 284.78

B. Outline of analytical method

Acetone-soluble HCB is directly injected to GLC attached with ECD.

C. Reagents and apparatus

1. Reagents
   o Hexachlorobenzene standard
   o Acetone

2. Apparatus
   o GLC attached with ECD

D. Procedure

1. Preparation of Standard solution
   Weigh out precisely 10mg HCB standard, transfer to 100ml volumetric flask and make up volume with acetone. Pipette 1ml of the dissolved standard solution on 100ml volumetric flask and make up volume with acetone.

2. Preparation of sample solution
   Weigh out precisely 20mg sample, transfer to 100ml volumetric flask and make up volume with acetone. Inject to GLC.

E. Conditions of instrumental analysis

o Column : 50m SE-30 capillary column
ID 0.32mm, 0.5mm film thickness
o Temperature : column initial temp. 150 (program rate 60c/min)
detector 280c

F. Calculation

$$HCB(\%) = \frac{A*1/100*1/100*\text{sample peak area}*\text{standard purity}}{B*1/50*\text{standard peak area}}$$

in which a: weight of HCB standard(gram)
b: weight of sample(gram)

2. DDT related compounds in dicofol technical

A. DDT related compounds

O,P'-DDD, P,P'-DDD, O,P'-DDE, P,P'-DDE, O,P'-DDT, P,P'-DDT, O,P'-ER-8, P,P'-ER-8

B. Outline of analytical method

Methanol-soluble DDT related compounds are determined by HPLC at 205nm of UV detector.

C. Reagents and apparatus

a. Reagents
- o Acetonitrile HPLC garde
- o Methanol HPLC grade
- o Methylene chloride HPLC grade
- o Water HPLC grade
- o standards of DDT related compound

b. Apparatus

- o HPLC attached with UV detector(203nm)

D. Procedure

a. Preparation of standard solution
- o Weigh out precisely each of standard in Table 1, transfer to 25ml volumetric and fill up to the volume with methanol.
- o Working standard stock solution
  Pipette 1ml of standard stock solution into 25ml volumetric flask and make up to the mark with methanol.
- o Working standard solution
  Pipette 5ml of working standard stock solution into 25ml volumetric flask and make up to the volume with methanol.

Table 1. Weight of standards to be measured

Standard	Weight(mg)
P,P'- DDD	5.0
O,P'- DDD	5.0
O,P'- DDE	7.0
P,P'- DDT	1.5
O,P'- DDT	1.5
P,P'- DDE	5.0
O,P'- ER - 8	10.0
P,p'- ER - 8	12.0

E. Conditions of instrumental analysis

- o column : ODS column 5um
- o Mobile phase(gradient program) : A-H2O, B-Acetonitrile
- o Gradient programme of mobile phase

Time(minutes)	%
0	60
9	60
19	75
25	90
28	90
29	60
33	End

Flow rate : 3ml/min, Temperature : 40C

* Retention time of DDT related compounds are as follows.
P,P'- DDD - O,P'- DDD - O,P'- DDE - P,P'- DDT - O,P'- DDT - P,P' - DDE - O,P'- ER - 8 - P,P'- ER - 8

F. Calculation

Content of each DDT related compounds(Wt%) is calculated by

$$\frac{\text{Standard Wt.}}{\text{Sample Wt.}} \times \frac{\text{Sample area}}{\text{Standard area}} \times \text{standard purity(\%)}$$

3. Hydrazine in maleic hydrazide(MH) technical

A. Formula

o Chemical structure

$H_2N = NH_2 \cdot H_2O$

B. Outline of analytical method

Hydrazine forms a orange coloured compound with p-dimethylamino-benzaldehyde in diluted HCL. The concentration of hydrazine is measured calorimetrically and compared with a standard series and blank.

C. Reagents and apparatus

a. Reagents
- o p-Dimethylaminobenazaldehyde
- o Hydrazine hydrate
- o Hydrochloric acid, concentrated

b. Apparatus

UV Spectrophotometer

D. Preparation of reagent and standard solutions

a. Preparation of colour reagent
Dissolve 1g of p-Dimethylaminobenzaldehyde in 10ml of concentrated hydrochloric acid and make up 100ml with water. Prepare this solution just before use.

b. Standard stock solution
Dissolve precisely 2.0g hydrazine hydrate standard in a 1,000ml volumetric flask and make up to the mark with water.

c. Working standard solution
Pipette 10ml of the standard stock solution into 1,000ml volumetric flask and fill up to the mark with water.

o Calculation of hydrazine concentration in diluted standard solution

Hydrazine(ppm)=weight of H.H.(g)*purity of H.H*10*0.6404

in which, 0.6404 = $\frac{\text{Molecular weight of hydrazine}}{\text{Molecular weight of hydrazine hydrate}} = \frac{32.06}{50.06}$

d. Calibration of standard solution

Pipette 2, 4, 6, 8, 32ml of working standard solution into individual 1,000ml volumetric flask and make up to the mark with water. Take 2ml of colour reagent into 100ml volumetric flask and Allow these solutions to stand for 10 minutes.
Measure the absorbance of the standard series and blank at 458nm. Blank solution is made by adding 2ml of the colour reagent into 100ml volumetric flask and making up to the mark with water.

E. Procedure

a. Standard solution
Pipette 4ml of the working standard solution into 1,000ml volumetric flask and make up to the mark with water. And then measure the absorbance in the same way as the calibration.

b. Sample solution
Weigh out precisely 1.0g MH technical, transfer to 250ml volumetric flask and make up to the mark with water. Measure the absorbance in the same way as the calibration.

F. Calculation

Hydrazine concentration(ppm) in MH technical

$= \frac{\text{absorbance of the technical solution}}{\text{absorbance of the standard solution}} * \frac{4}{\text{weight of MH technical}}$

$* \frac{250}{1{,}000} *$ hydrzine concentration(ppm) in working standard solution

4. Ethylene thiourea(ETU) in mancozeb thchnical

A. Formula

o Chemical structure

o Molecular weight : 102.17

B. Outline of Analytical method

Water-soluble ETU is directly determined by HLPC at 233nm of UV detector.

C. Reagents and apparatus

a. Reagents
- o Acetonitrile HPLC grade
- o Methanol HPLC grade
- o 4% zinc chloride solution
- o Ethylene thiourea standard

b. Apparatus
- o HPLC attached with UV detector(233nm)

D. Procedure

a. Preparation of external standard solution
- o Stock solution
  Weigh out precisely 0.025g of ethylene thiourea standard, transfer to 50ml volumetric flask and make up to the volume with water.

- o Working standard solution
  Pipette 5ml of the stock solution into 100ml volumetric flask, make up to the mark with 4% Zinc chloride solution and mix well.

b. Preparation of sample solution
Weigh out precisely 0.1 to 0.2g of technical or wettable powder, transfer to 50ml Erlenmyer flask and add 10ml of 4% Zinc chloride solution. Shake mechanically for 30 minutes and filter off insoluble.

E. Condition of instrumental analysis
- o HPLC column : ODS 10um 30cm X 7.9mm
- o Mobile phase : Pipette 10ml acetonitrile, 13ml methanol into 1L volumetric cylinder and fill up to the volume with water.

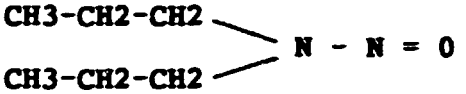
F. Calculation

$$ETU(\%) = \frac{A \times C}{B \times D \times 10}$$

in which : A - Peak area of sample
B - Peak area of working standard
C - Concentration of working standard(ppm)
D - Weight of sample(gm)

5. N-Nitroso-di-n-propylamine(NDPA) in trifluralin technical

A. Formula
o Chemical Structure



o Molecular weight : 130.2

B. Outline of analytical method
Trifluralin technical is distilled under steam current to co-distillate DNPA into water. The distilled NDPA is determined by HPLC at 254nm of UV detector

C. Reagents and apparatus

a. Reagents
o N-Hexane HPLC grade
o Anhydrous sodium sulfate
o Distilled water HPLC grade
o Methanol HPLC grade
o N-Propanol
o Saturated sodium chloride solution
o Standard solution of NDPA lul/ml in N-hexane

b. Apparatus
o Steam distillation apparatus attached with vacuum line and steam current insertion
o Oil bath and ice bath
o HPLC attached with UV detector(254nm)
o HPLC column : ODS type 10um 25cm X 4.6mm
o Separatory funnel with teflon cock and stopper

D. Extraction of NDPA from technical
o Weigh precisely 10 to 15g of technical, transfer to the distillation unit, add 25ml of saturated NaCl solution and connect the joints tightly.

o add water into the receiver and connect it to the condenser. Take care that the end of the condenser is immersed in the water.

- o Connect cooling water line to the condenser and put receiver in the ice bath.
- o Put distilling flask in the oil bath which is preheated at 110c.
- o Connect receiver to the vacuum line. The pressure should be 20mmHg.
- o Connect distillation flask to steam generator to distillation flask and adjust the steam flow. Continue distillation vigorously until the distilled volume of the receiver is reached about 150ml
- o Disconnect the receiver from the apparatus. Transfer distilled solution to separatory funnel. Add n-hexane, shake, and separate the n-hexane layer from the funnel. Repeat the procedure three times.
- o Dehydrate the n-hexane layer by passing anhydrous sodium sulfate pad, add 0.2ml of n-propanol, and evaporate the n-hexane under rotary evaporator below 20C until the final volume is to be precisely 5ml.

E. Instrumental analysis

Condensed sample solution and standard solution of DNPA are purified by passing microfilter before injection to the HPLC.

- o Analytical condition

Mobile phase : methanol/water = 35/65(U/V)
Column temperature : 40C
Flow rate : 3.3ml/min
Wave length : 254nm

F. Calculation

$$\text{NDPA content(ppm)} = \frac{Ac \times Ps \times Vf}{As \times Pc \times Vi}$$

in which ; Ac - Peak area of sample
As - Peak area of standard
Ps - Standard amount injected(ng)
Pc - Weight of sample(gm)
Vf - Final volume of sample(ml)
Vi - Injected volume of sample(ul)

UNIDO COMMENTS

The workshop on Impurities in Technical Grade Pesticide Material dealt with an important topic of impurities in technical active ingredients. The topics covered in the workshop included state of the art technology used in determining impurities and break-down products on storage.

The counterparts of the workshop clearly demonstrated their capability to organize the workshop and also provided high level demonstration work for the benefit of the participants. Such a workshop should be followed by in-depth training to selected candidates in the laboratories of the Agricultural Chemicals Research Institute, Rural Development Administration, Suweon, Republic of Korea.