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REGIONAL NETWORK ON PESTICIDES FOR ASIA AND THE PACIFIC

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PEOPLE'S REPUBLIC OF CHINA

Technical report: Gas Chromatography/Mass Spectrometry (GC/MS) Analysis of Pesticides at the Institute for the Control of Agrochemicals, Beijing, P.R. China*

Prepared for the Government of the People's Republic of China
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of F.H. Cottee, consultant in Gas Chromatography/ Mass Spectrometry (GC/MS) Analysis of Pesticides

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Vienna

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* This document has not been edited.

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1. Abstract

This report summarises a one month consultancy in gas chromatography/mass spectrometry (GC/MS) analysis of pesticides at the Institute for the Control of Agrochemicals, Ministry of Agriculture (ICAMA), Beijing, PRC, during the period 22nd September to 21st October, 1988. Details of the training programme and objectives are given, together with recommendations for future training, equipment modifications, additional equipment, safety and Good Laboratory Practice (GLP). In addition, the report addresses the possibility of further assistance under UNDP funding.

2. Summary of Recommendations

2.1 Instrument Modifications

2.1.1 Invest in new valves or pumps in order to allow 24 hour pumping of the instrument.

2.1.2 Provision of an extra floppy disc drive for archival storage.

2.1.3 Have instrument manufacturers rectify several faults and features under warranty.

2.1.4 Modify make-up gas connection.

2.2 Accommodation

2.2.1 Provision of writing space adjacent to the instrument.

2.2.2 Provision of a larger work-bench, with under-bench storage.

2.3 Additional Equipment

2.3.1 Provision of extra CI reagent gases (to be supplied).

2.3.2 Installation of carrier gas purifiers (supplied).

2.3.3 Increase stock of tube fittings and connectors.

2.3.4 Purchase of extra capillary columns for formulation analysis.

2.3.5 Purchase of direct capillary columns link for source.

2.3.6 Future provision of extra columns and autosampler for residue analysis.

2.4 Training

2.4.1 Advanced spectral interpretation course for Mme Ji Ying.

2.4.2 Practical capillary GC course for Mme Ji Ying.

2.4.3 Instrument operation and routine maintenance training for Miss Liu Ping.

2.5 Safety

2.5.1 No food or drink in the laboratory.

2.5.2 Safety glasses to be worn.

2.5.3 Labelling of all containers.

2.5.4 Solvent bottles in catchment trays.

2.5.5 Halocarbon fire extinguishers near door.

2.5.6 Routine safety inspections.

2.6 GLP Requirements

2.6.1 Filing of regular calibration checks and service reports.

2.6.2 Filing of monthly system performance checks.

2.6.3 Recording of GC column usage.

2.6.4 Experimental details in signed notebooks.

2.6.5 Filing of personnel training records.

2.6.6 Compilation of standard operating procedures.

2.7 Maintenance

2.7.1 Weekly replacement of capillary injection line.

2.7.2 Six-monthly replacement of rotary pump oil.

2.7.3 Regular leak checks on gas lines.

2.7.4 Regular checks on electron multiplier gain.

2.7.5 Routine archiving of data.

2.8 Recommended Operating Procedures

Compilation of Operating Manual for the instrument, to supplement that provided by the manufacturer.

2.9 Recommendations for Future Funding

2.9.1 Funding of instrument modifications necessary for continuous operation.

2.9.2 Assistance with funding of MS training courses, particularly for industry.

2.9.3 Funding of practical capillary GC training for Mme Ji Ying.

3. Introduction

The consultancy in GC/MS of pesticides is part of a programme of technical assistance to countries in the Asia Region on various aspects related to the safe production and use of pesticides. To further this aim, a Regional Network on Pesticides for Asia and the Pacific (RENPAP) was established in 1985 with funding from the United Nations Development Programme (UNDP). The Peoples' Republic of China is among the 10 current members of the Network. Under the project, the United Nations Industrial Development Organisation (UNIDO), along with other agencies such as FAO, WHO, World Bank and ESCAP, organises a series of seminars, workshops, training assignments and consultancies covering the whole spectrum of pesticide production and use.

3.1 Pesticides in P.R. China

The population of China is nearly a quarter of the entire world's population yet arable land is only about 7% of the world total. With almost 80% of the population living in rural areas, China is faced with the formidable problem of providing sufficient food and fibre for the country. The government has adopted a two-pronged strategy to tackle this problem, firstly by adjusting rural economic policies to stimulate individual enterprise and secondly by undertaking agricultural research in order to combine the best of traditional agricultural practices with modern science and technology.

Pesticides are clearly an important part of this strategy and great strides have been made in increasing pesticide production, improving their quality and optimising their use. Before 1949, very few pesticides were employed. but during the 1950's a number of organochlorine compounds such as DDT were produced. These have since been replaced by more effective, safer pesticides such as organo-phosphorus compounds, carbamates and pyrethroids. Initially many of these products were imported, but the emphasis is now on local production, both of technical material and formulations.

There are presently 300-400 companies producing over 140 different types of pesticide in China, with a total production of over 180,000 tons of active ingredient. Of this production, about 70% is insecticides, with the remainder being equally divided between fungicides and herbicides. At present the use of rodenticides and plant growth regulators is at a very low level. A small proportion of about 20 of these pesticides is exported, but China also imports considerable quantities of the newer pesticides, particularly herbicides and fungicides.

3.2 ICAMA

The explosive growth in the manufacture and use of pesticides in China coupled with the short history of pesticide management have caused the pesticide management authorities and manufacturers to strengthen the quality control and registration requirements for pesticides in recent years. ICAMA was established in 1963 under the jurisdiction of the Ministry of Agriculture. Its functions are:

i) The approval of production and utilisation of new pesticides.

ii) Review of registered pesticides.

iii) Establishing of registration requirements for imported and exported pesticides.

iv) Supervision and inspection of quality and safe use of pesticides.

v) Training of personnel in pesticide analytical methods.
The organisation chart is enclosed as Appendix I.

The GC/MS equipment for which I was to provide consultancy is located in the Pesticide Analysis Division under the supervision of Mr. Zhang Baizhen. This Division has the following responsibilities.

i) To evaluate and examine pesticide specifications and analytical methods supplied for registration purposes.

ii) To undertake arbitration analysis of pesticide quality.

iii) To supervise and examine the quality of agrochemical products.

iv) To undertake research work on pesticide analytical methods and to provide technical exchange and personnel training on pesticide analytical technology.

The Institute therefore has both an arbitration role and an industrial training role, of which the latter is particularly appropriate for UNIDO support. Some idea of the need for quality control training in the pesticide manufacturing industry can be gained from the fact that some 40% of industrial production fails to meet National specifications for quality.

In addition to the central ICAMA laboratory in Beijing there are at present 14 regional laboratories, of which perhaps four are satisfactorily equipped and trained. Ultimately it is intended that each province should have its own institute.

4. Training Programme

The following programme was drawn up by the Deputy Director of ICAMA, Mme Zhang Chunjuan:

Duties: The consultant in association with the project authorities at the Institute for Control of Agrochemicals, Ministry of Agriculture, Beijing is expected to assist them in the use of GC/MS for analysis of pesticides at the institute which has recently installed a Shimadzu QP-1000A GS/MS. His duties would involve:

- Optimization of applying conditions GC/MS instrument and give lectures on practical applications of mass spectrometry of pesticide and pollutant analysis (1 week).

- Identification methods of mass spectra for major classification of pesticides (e.g. Organophosphorus compounds, Carbamates, Pyrethroids, etc. (1.5 weeks).

- Separation and structural identification of intermediates and impurities in the pesticide formulations e.g. Butachlor, Acephate, Phoxim, Fenvalerate, etc. (1.5 weeks).

- Submitting a report on his findings and recommendation, covering training requirements for institute staff, additional equipment needed, improve safety aspects in the laboratory and adopting GLP standards.

The following specification was provided for the instrument:

Mass range, M/Z - 10 - 1000
Resolution M/M - 2M (2000 Max)
Ionization method, EI/CI
Analyzer rods, Molybdenum hyperbolic quadrupole type
Standard mass Spectra for library search NBC/NIH/EPA
Library 39,750 mass Spectra

Before arrival in Beijing, it was established by telex that the instrument was equipped with both packed and capillary GC columns and a split/splitless injector.

4.1 Staffing

On the first two days of the assignment I was introduced to the staff of the Pesticide Analysis Division and was briefed on the project by Mme Zhang Chunjuan and Mr. Zhang Baizhen. I also had discussions with the acting Deputy Director, Mr. Zhu Tianzhong and the head of the Foreign Affairs Section, Mme Li Bin.

The GC/MS instrument is run by a graduate of the Shandung University, Mme Ji Ying, assisted by a younger graduate from the Beijing Agricultural University, Mr. Ye Jiming, and by a technician Miss Liu Ping. Their current qualifications and training are summarised in Appendix III. Mr. Zhang Baizhen had previously spent 18 months working at ICI, Jealots Hill, England and had gained an M.Sc. at Chelsea College on a GC/MS topic. He was therefore fully aware of the capabilities of GC/MS. A full list of staff met at ICAMA is included as Appendix X.

4.2. Instrumentation

The GC/MS instrument was well located in an air-conditioned, clean laboratory. A glass partition separated it from the corridor, thus providing a relatively clean atmosphere. A stable voltage supply was provided by a Chinese-manufactured constant voltage transformer, which unfortunately could only be used for eight hours at a time. A formica-topped desk provided a work bench, and there was a cupboard for storage of manuals, spares and chemicals.

The Pesticide Analysis Division was well equipped with chromatographic and spectroscopic instruments and ancillary equipment, which are summarised in Appendix III.

4.3 Training Programme Implementation

On arrival I found that the instrument had been little used in the six months since it installation. However, the staff had recently started to analyse a complex organophosphorous (OP) insecticide formulation and it was therefore decided to use this analysis as a vehicle to demonstrate the various operational modes of the GC/MS and the strategy for their use. The formulation itself had originated from a small factory in Sichuang Province and was labelled as methamidophos EC. It had been submitted to ICAMA for analysis because it had caused severe phytotoxicity to cotton crops, and was therefore suspected of being contaminated with a herbicide. From the symptomology of the damage 2,4-D butyl ester was suspected.

4.4 Practical and Theoretical Training

4.4.1 Electron Impact

The use of the instrument in electron impact (EI) mode was demonstrated using splitless injection onto a 25m 0.2mm OV17 capillary column as the sample introduction system. The following topics were covered:

i) Capillary injection techniques, including split, splitless, and the principles of on-column injection.

ii) Instrument tuning and the effect of instrument parameters on resolution and sensitivity.

iii) The electron impact process.

iv) Collection and storage of data.

4.4.2 Interpretation

Using the resulting data the principles of data manipulation and spectral interpretation were discussed, covering the following steps:

i) The organisation of data storage on the data system.

ii) Principles of spectrum subtraction.

iii) The role and limitations of library searching.

iv) The use of mass chromatography (MC) for simplifying complex GC/MS analyses and identifying minor components.

v) The interpretation of OP spectra.

vi) Identification of intermediates and impurities.

At this stage it was possible to identify many of the major components in the formulation, as shown in Appendix IV. Methamidophos was absent, the major OP being malathion.

4.4.3 Selected Ion Monitoring

The next stage was the detection of the suspected 2,4-D butyl ester impurity, which was achieved using selected ion monitoring (SIM) - also known as mass fragmentography (MF).

The following topics were demonstrated:

i) The reasons for the enhanced sensitivity of SIM.

ii) The choice of ions for monitoring and their effect on the sensitivity and reliability of the results.

iii) External standardisation techniques.

iv) Standard addition.

v) The difference in precision between MC and SIM and the appropriate role for the two techniques.

Using this methodology 2,4-D butyl ester was successfully identified at the 20 p.p.m. level. At this stage the use of chemical pre-treatment to simplify a complex formulation was discussed. The advantage of solvent extraction and derivatisation was explained particularly for polar components. Unfortunately, owing to lack of time it was not possible to carry out these experiments.

4.4.4 Chemical Ionisation

After obtaining a missing component from the instrument manufacturers the instrument was converted to chemical ionisation (CI) operation and the following topics demonstrated:

i) Installation of reagent gas.

ii) The range of reagent gases and their most appropriate use.

iii) Tuning of the instrument in CI.

iv) The differences between CI and EI operation.

v) Interpretation of CI spectra (only briefly discussed).

The resulting CI GC/MS trace is shown in Appendix V, and the spectra will be used as an interpretation exercise by Mme Ji Ying.

A number of reference compounds and useful items for gas chromatography were left with the Institute. These are summarised in Appendix IX.

4.4.5 Maintenance

The following items were covered:

i) The need for weekly tuning and calibration, and proper filing of the results.

ii) Weekly cleaning of the GC inlet.

iii) The use of standards to check performance.

iv) Record keeping for GC column use, and the need to reserve columns for particular compound classes.

v) Care and regeneration of capillary columns.

vi) The principles of fault-finding.

4.4.6 Seminars

Two half-day seminars were given to members of the Institute. The first of these was entitled "The Theory and Practice of Mass Spectrometry in Pesticide Analysis". A summary is given in Appendix VI, and a shortened version of the seminar is to be published in the Institute's journal which receives wide circulation in the Agrochemical industry.

The second seminar was given to members of the Pesticide Residue Division and concentrated on applications of mass spectrometry in residue analysis. A summary is given in Appendix VII.

In addition, several informal discussions were held with members of the institute, for example on problems with fluorescence detection in HPLC.

5. Detailed Recommendations

The following recommendations have been discussed and agreed with Mr. Zhang Baizhen.

5.1 Instrument Modifications

i) The instrument is extremely under-utilised because it is necessary to turn it off every night. The reasons for this are concern over continuity of mains electricity supply and the fact that the constant voltage transformer, although never used at more than half its rated output, overheats after eight hours use. Such intermittent use is extremely bad practice for high vacuum equipment and has a disastrous effect on sensitivity and stability. Consequently, it was necessary for the MS staff to come in late at night to shut the instrument off and very early in the morning to turn it on again in order to get even a short working day out of the GC/MS during my assignment.

As this is the most serious limitation to the effective use of this powerful and expensive piece of equipment, it is recommended that urgent consideration should be given to continuous operation of the vacuum system. The following actions are necessary:

a) Replacement of manually operated butterfly valves on the diffusion pumps by pneumatically operated ones.

OR

Replacement of the diffusion pumps by turbomolecular pumps. The manufacturers would be able to provide information on either course of action.

b) Replacement of the constant voltage transformer (CVT) with one rated for continuous use.

OR

Provision of a changeover switch between the CVT and raw mains to enable the pumps to be left running overnight.

ii) Archival data storage is at present on the same floppy disc that contains the system software. This is inefficient, as storage capacity on the disc is limited by the presence of the software and changing the disk upsets the instrument operating parameters. A second floppy disc is recommended for storage.

iii) Several features of the instrument are unsatisfactory and should be changed under warranty by the manufacturers.

The include:

a) Collapsed flexible vacuum tubing should be replaced by reinforced nylon tubing.

b) Water hoses are only push-fit and one is already leaking. This constitutes a safety hazard, and a flood would severely damage the instrument. Screw clips should be fitted.

c) A split nut is supplied for the capillary column detector, which cannot be properly tightened. This should be replaced by a fitting containing a complete nut.

d) The isobutane cylinder supplied for CI appears to be empty and required replacement.

e) The isobutane pressure regulator supplied with the instrument is too coarse. A 0-4 bar gauge would be appropriate.

iv) Make-up gas for the jet-separator is supplied via the packed column injector and is prone to leaks. A fitting should be obtained from the manufacturers to enable direct connection.

5.2 Accommodation

i) A large desk or table adjacent to the spectrometer is required for writing space. At present spectra, notebooks, etc. are spread over the work bench and the instrument and constitute a safety hazard.

ii) A larger chemical bench with proper underbench storage facilities is required. The existing desk would probably fulfil requirement i).

5.3 Additional Equipment

i) The existing CI reagent gas is not the most appropriate for pesticide analysis, and will lead to rapid instrument contamination. Ammonia and methane are recommended. The local office of the author's company has agreed to supply these, as purchase in China is difficult.

ii) Capillary column life will be greatly extended by the use of carrier gas purifiers. Suitable units were supplied by the author but a suitable mounting board will have to be made.

iii) A greater range of tubing fittings and couplings should be stocked. These would be shared with the GC laboratory.

iv) The Division stocks a wide range of packed GC columns, but has only the two capillary columns supplied with the GC/MS. The capacity of these is not sufficient for product and formulation analysis. Specifications for suggested extra columns (0.3 mm diameter) have been supplied to the Institute.

v) It is not necessary for GC/MS analyses to use published GC methods and therefore packed columns could be dispensed with. It is recommended that the instrument should be converted to capillary column use only, which will extend the range of compounds amenable to GC/MS analysis and increase sensitivity.

vi) The instrument would be a valuable aid to pesticide residue analysis. Extra columns would have to be purchased specifically for this purpose and a GC autosampler would increase throughput and repeatability.

5.4 Training

i) Mme Ji Ying has a basic grounding in spectral interpretation. It is recommended that after another six months or so of practical MS experience at ICAMA she should attend a suitable course on advanced spectral interpretation either in China or abroad.

ii) Mme Ji Ying is at present the only person in ICAMA with practical experience of capillary GC techniques. It is recommended that the Institute should regard her as the focal point for this major advance in gas chromatography by sending her on a practical course on capillary GC.

iii) Assuming that the recommendation to leave the instrument turned on is carried out, the interpretation work-load will increase very rapidly. It is therefore recommended that Miss Liu Ping should be fully trained in the use and maintenance of the instrument in order to relieve the work-load on Mme Ji Ying and to provide continuity of expertise should she leave.

5.5 Safety

Safety standards were generally adequate. However, the following detailed recommendations are made:

i) The rule on no food or drink in the laboratory should be strictly enforced.

ii) Safety glasses (prescription if necessary) should be worn at all times except when seated at a desk or the MS console.

iii) All tubes and flasks should be clearly and indelibly labelled.

iv) Solvent bottles should be kept in a tray and segregated from flammable materials.

v) A halocarbon fire extinguisher should be available near the exit into the corridor.

iv) Staff at all levels should participate in periodic safety inspections of the Division on a rota basis, and the reports discussed with the Directors.

5.6 GLP Requirements

The laboratory is not at present required to work to formal GLP standards, but it should work towards meeting these requirements in the future. Immediate recommendations are:

i) Print-out from weekly instrument calibration should be dated and filed in a ring-binder. Service engineers reports should be stored in the same file.

ii) Periodic (e.g. monthly) checks on the complete system performance should be made using the GC test mix provided by the author. Results should be filed with the calibration data.

iii) The existing instrument log-book should be modified to include a record of GC column usage.

iv) All experimental details (including weighings) should be made in a laboratory notebook and counter-signed by the laboratory supervisor.

v) A written record of personnel training should be kept on file.

vi) A manual of standard operating procedures should be compiled for routine laboratory tasks, e.g. extractions.

5.7 Maintenance

i) Weekly replacement of the capillary injection liner is required for formulation analysis. A hundred-fold improvement in sensitivity was obtained when the liner was replaced during my assignment.

ii) Six-monthly replacement of rotary pump oil is recommended if CI is routinely used. Pumps should be gas ballasted after CI use.

iii) Regular leak checks on gas lines should be carried out using detergent (not toilet soap) solution.

iv) The recommended procedure for checking electron multiplier gain on this instrument should be obtained from the manufacturer.

v) Valuable data on the hard disc should be backed up on to floppy disc at the end of a day's work.

5.8 Recommended Operating Procedures

A number of recommendations specific to the instrument are summarised in Appendix VIII. These should be expanded with increasing operational experience and compiled in the Division's own operating manual.

5.9 Recommendation for Future Funding

The addition of GC/MS to the range of analytical techniques available at ICAMA will benefit China's agrochemical industry in two ways. Firstly it will provide rapid, unambiguous information on product quality and secondly it will support the development of analytical methods for registration and quality control purposes. In addition, there are many other similar instruments in China which are used in support of industry, for example at the Scientific Instrument Factory of the Chinese Academy of Sciences or at the Industrial Health and Safety Laboratory in Beijing. Thus any assistance provided under UNDP funding would benefit not only the agrochemical industry, but by sharing of experience and expertise would also benefit other industries which utilise this technology.

Three specific recommendations are made:

i) Apparently most MS instruments in China suffer from the constraint of being turned off every night and thus a heavy investment in equipment and expertise is being wasted. This report contains suggestions for modifications which will enable safe operation when power supply is intermittent. To put the power supply "problem" into perspective, there was not a single power cut during my four week assignment in Beijing. UNDP should consider funding the necessary modifications to the ICAMA instrument as a test-case.

ii) The professional body for mass spectroscopists in China, the Chinese Mass Spectrometry Association, has a valuable role to play in training, but at present only holds biennial meetings. A local Association also exists in Beijing which holds annual meetings. Neither organisation at present holds training courses. The author intends to initiate contacts between the British and Chinese MS Societies.

The value of such inter-society contact will be greatly enhanced if the UNDP could assist in funding industrial courses of the type already organised by societies in Western Europe and America.

iii) Capillary GC, with or without MS detection, is leading to dramatic advances in product and formulation analysis and in residue analysis. Funding of suitable training for Mme Ji Ying would greatly benefit the work of the Institute.

6. Conclusions

The GC/MS equipment installed at ICAMA has an important role to play in pesticide analysis in three areas:

i) Confirmation of compounds detected by chromatographic methods.

ii) Structure determination of unknown compounds.

iii) Specific detection of target compounds in a mixture at low levels.

The training programme undertaken at ICAMA has demonstrated these three aspects of GC/MS using a problem formulation submitted to the Institute as an example. The MS staff at ICAMA have been able to apply the various operational modes available on their equipment in order to answer questions about a typical formulation.

The biggest limitation to the effective use of the equipment is the drift and limited availability resulting from having to turn it off every day. Further investment will be necessary to overcome this and it is recommended that special funds be allocated to make the necessary modifications.

The GC/MS equipment, and the allied capillary GC technology, also have enormous potential for pesticide residue analysis. It is therefore recommended that further training of the existing GC/MS staff should be undertaken so as to increase the efficiency of use of the instrument and to allow the staff to act as a focal point in the Institute for training in capillary GC methods.

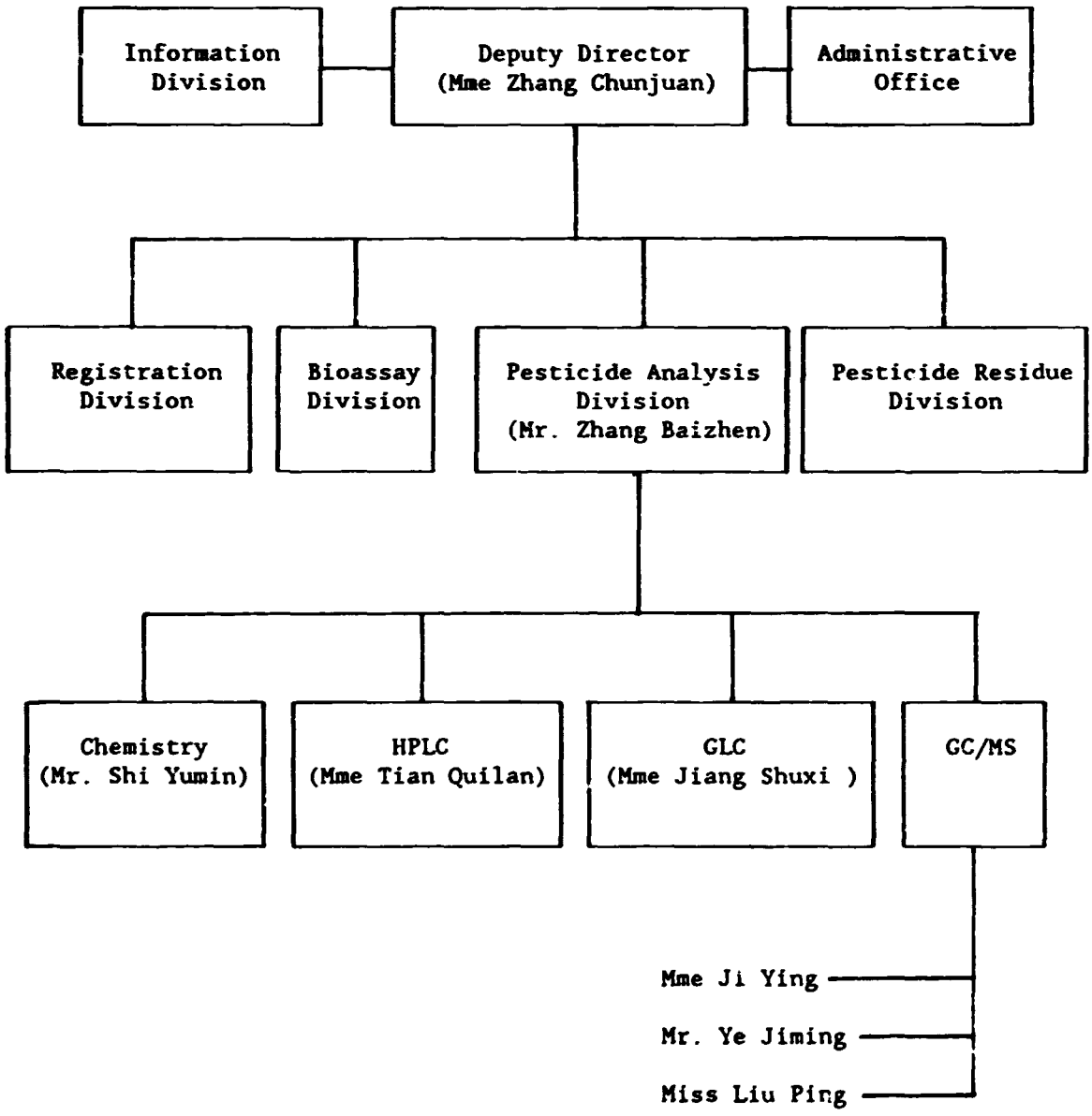
7. Acknowledgements

The author owes an enormous debt of gratitude to all those staff at ICAMA who contributed to making this consultancy such an enjoyable and profitable experience. Mr. Shi Yumin acted as a guide, interpreter and fund of information throughout. I wish to thank Mme Zhang Chunguan for organising the consultancy and making the necessary facilities available.

Mr. Zhang Baizhen was always at hand to provide practical assistance and information. Others too numerous to name have contributed to this consultancy in many ways. However, I wish to reserve special thanks for the GC/MS staff who have worked so hard during my stay in China. Liu Ping, Ye Jiming and particularly Ji Ying have worked long hours and I hope they have profited from this consultancy as much as they deserve to.

Appendix I

Organisation of ICAMA



Appendix II

GC/MS Staff Training

Ji Ying

Degree in Analytical Chemistry - Shandung University	1979 - 1983
Joined ICAMA	1983
6 - month English Training Course	
1 - month Pesticide Quality Control Course, India	1987
1 - month Instrumentation Training Course	1987
3 - week Shimadzu GC/MS training course	1988
Member of Beijing MS Association and Chinese MS Association	

Ye Jiming

Degree in Pesticide Chemistry - Beijing Agricultural University	1981 - 1985
Joined ICAMA	1985 - 1987
English Course - Beijing Forest University	Nov. 1987 - July 1988

Liu Ping

[illegible] School Training (General Education)	
Joined ICAMA	1979
Nanjing University	1979 -1982

Appendix III

Summary of Analytical Equipment in Pesticide Analysis Division

Gas Chromatography

Shimadzu GC 7AG + FPD

2 SPS01's of Chinese manufacture + ECD

All instruments used packed columns only

Liquid Chromatography

3 Waters 300 series instruments with UV and fluorescence detectors

One GPC chromatograph

Polarography

2 Chinese manufactured instruments

IR Spectroscopy

Shimadzu IR - 400

One Chinese-manufactured instrument

UV Spectroscopy

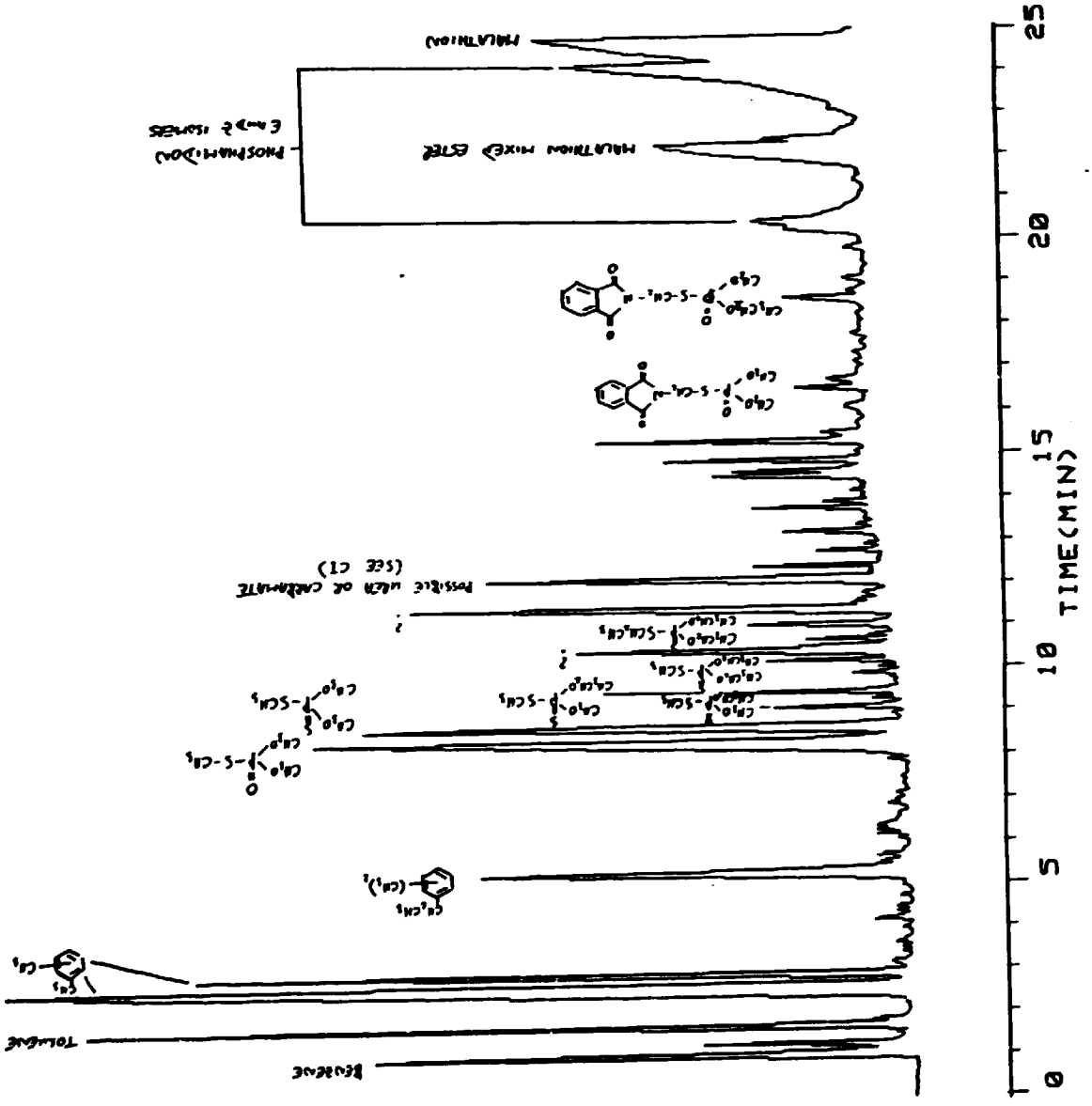
2 Chinese-manufactured instruments

GC/MS

Shimadzu QP 1000 A

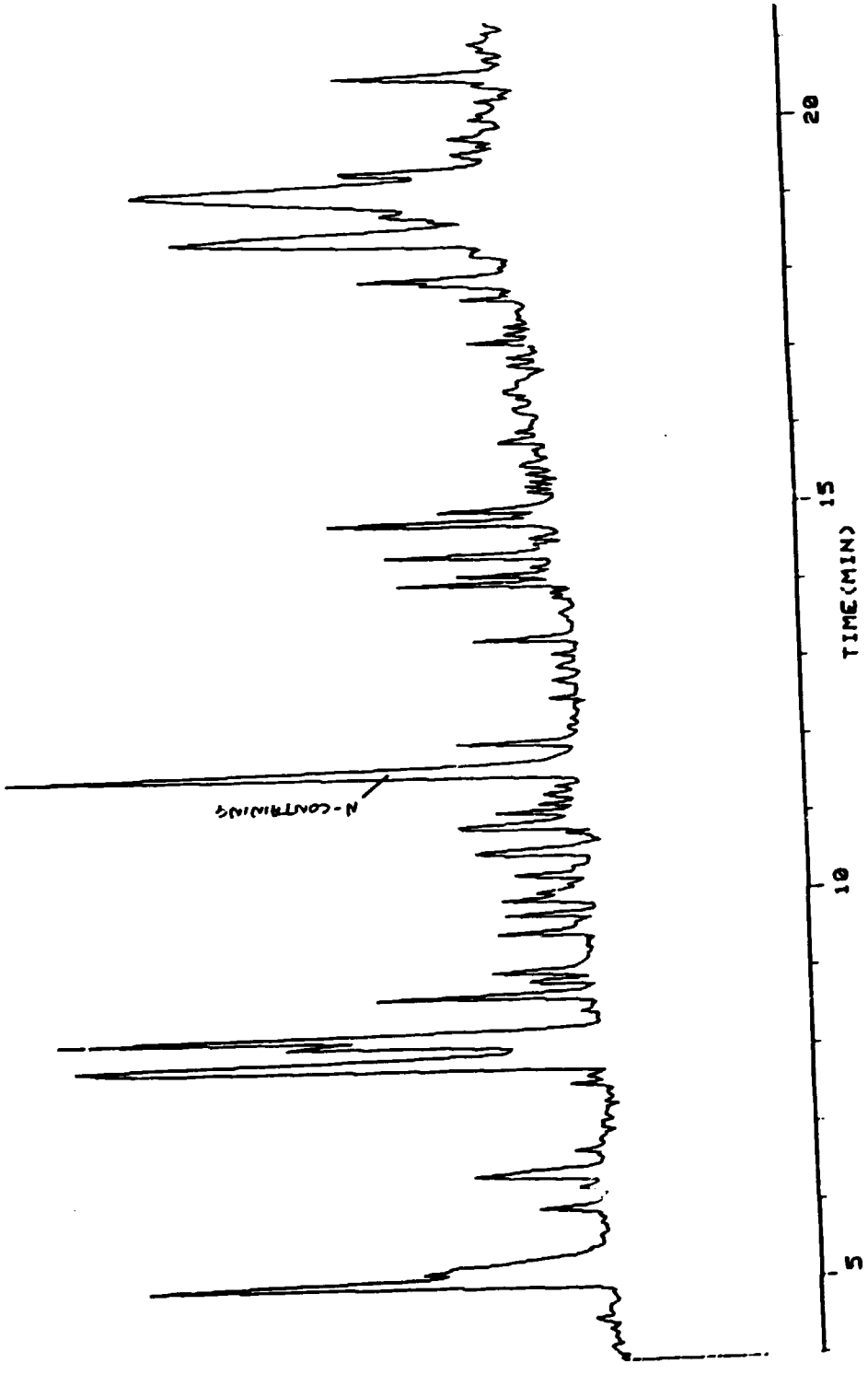
Appendix IV

EI TIC Trace of OP Formulation



Appendix V

Isoputane CI TIC Trace of OP Formulation



Appendix VI

The Theory and Practice of Mass Spectrometry in Pesticide Analysis

Abstract

Mass spectrometry is one of the best established spectroscopic techniques, having seen continuous development for over 50 years. This seminar traces the history of the technique and then goes on to describe the most common components of a modern mass spectrometer and how they are applied in pesticide analysis.

Some of the many applications in pesticide analysis are then described, illustrating the variety of techniques which can be used to extract information from a complex mixture. The control role of the data system is emphasised and particular reference is made to techniques available on the ICAMA instrument.

Finally, a selective view of future development is presented. Foremost amongst these is combined LC/MS, which will eventually play as important a role as GC/MS does at present.

Appendix VII

Applications of Mass Spectrometry in Pesticide Residue Analysis

Abstract

The purpose of this seminar is to illustrate the features of combined GC/MS which are of value for residue analysis. The GC/MS combination has three very desirable properties; it is extremely sensitive, highly specific and readily adaptable to different analyses.

The reasons for these properties are described and their use in residue analysis illustrated. Particular emphasis is placed on the use of capillary GC in combination with the spectrometer, as capillary columns represent a dramatic advance in GC technology.

The seminar also looks at GC/MS techniques not available on the ICAMA instrument, but accessible on other instruments in Beijing, which can result in detection of trace materials in complex mixtures at the femtogram level.

Appendix VIII

MS Operation Procedures

1. The Data System

i) The capacity for data storage and manipulation on the floppy disc is limited. It is recommended that data are acquired directly onto the Winchester disc and only transferred to floppy discs for archival storage.

ii) For acquisition of capillary GC data a minimum scan rate of 2S/scan is recommended. 1S/scan is preferable, particularly with 0.2 mm i.d. columns.

iii) The peak selection routines available on the data system will acquire fewer spectra, thus saving disc space. However, where minor components in a mixture are important it is recommended that all scans are acquired.

2. Turning On

i) Turn on solvent cut valve whenever data are not actually being acquired, in order to reduce source contamination.

ii) Ensure carrier gas flow is established before heating GC oven.

iii) Set data system to write to HDØ.

iv) Don't forget to turn on Winchester drive.

v) The source will heat up faster if the filament is turned on.

vi) The source temperature does not have to be above the GC oven temperature. 150° is usually best for CI and 200° for EI.

3. Turning Off

i) Leave a low flow of carrier gas through the columns, i.e. cylinder and GC gas control knob must both be left on. Alternatively, remove the detector end of the column and seal it and the jet separator.

ii) Column caps placed on the split and vent outlets of the injector will prevent gas flow in the event of a power cut.

iii) Turn off the CI reagent gas cylinders.

vi) Turn off the make-up gas.

v) The ends of GC columns must be sealed when they are removed from the instrument.

vi) Contamination in the injection end of a capillary column is best removed by breaking off the end of the columns. Alternatively, use a 1 m retention gap of uncoated column using the coupling supplied.

Appendix IX

Equipment and Standards Donated to ICAMA

1. Equipment

1.1 Lengths of uncoated 0.5 and 0.3 mm i.d. capillary tubing for retention gaps, plus suitable glass knife.

1.2 Low dead-volume fittings for joining capillary tubing. Stainless steel and silica versions.

1.3 Mixed sizes of silicone tubing.

1.4 Spare floppy discs.

1.5 Carrier gas purifiers.

2. Standards

2.1 Chrompack standard GC test-mix for assessing columns and interface performance.

2.2 Mixture of hydrocarbon standards to assess molecular weight discrimination in injector.

2.3 Heptacosafluorotributylamine MS calibration standard.

2.4 Cypermethrin to assess CI and GC performance.

Appendix X

Staff Met at ICAMA

Mr. Zhang Shixian	-	Deputy Director, Bureaux of Agriculture
Mme Zhang Chunjuan	-	Deputy Director, ICAMA
Mr. Zhu Tianzhang	-	Deputy Director, ICAMA
Mr. Li Benshang	-	Pesticide Residue Division
Mr. Zhang Ziming	-	Director, Registration Division
Mme Li Bin	-	Head, Foreign Affairs Section
Mr. Ma Guangming	-	Registration Division
Mr. Yu Tao	-	Registration Division
Mr. Zhang Jidong	-	Deputy Director, Information Division
Mr. Zhang Baizhen	-	Director, Pesticide Analysis Division
Mr. Shi Yumin	-	Deputy Director, Analysis Division
Mme Tian Qiulan	-	Deputy Director, Analysis Division
Mme Jiang Shuxin	-	Analysis Division
Mme Ji Ying	-	Analysis Division
Mr. Ye Jiming	-	Analysis Division
Miss Liu Ping	-	Analysis Division