Date of Submission of the report: November 30, 2002

BARD Project Number: IS-3022-98

Project Title: Fast Analysis of Pesticide Residues in Agricultural Products

Investigators
Principal Investigator (PI): Aviv Amirav
Co-Principal Investigator (Co-PI): Steven J. Lehotay

Institutions
Tel Aviv University
USDA-ARS Eastern Regional Research Center

Collaborating Investigators:

Keywords not appearing in the title and in order of importance. Avoid abbreviations.

gas chromatography/mass spectrometry, supersonic molecular beam, sample preparation, direct sample introduction, solid-phase extraction, pulsed flame photometric detection

Abbreviations commonly used in the report, in alphabetical order:

DSI = direct sample introduction (or "dirty sample injection")
GC/MS = gas chromatography/mass spectrometry
μECD = micro electron capture detection
EI = electron ionization
M⁺ = molecular ion
PFPD = pulsed flame photometric detection
QuEChERS = quick, easy, cheap, rugged, effective, rugged, and safe
SMB = supersonic molecular beam
SPE = solid-phase extraction

Budget: IS: $133,000        US: $132,000        Total: $265,000

_________________________________  ______________________________________
Signature                              Signature
Principal Investigator                Authorizing Official, Principal Institution
Publication Summary (numbers)

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Postdoctoral Training: List the names and social security/identity numbers of all postdocs who received more than 50% of their funding by the grant.

Michelangelo Anastassiades (Ph.D. Visiting Scientist)      Jitka Zrostliková (visiting graduate student)
Kateřina Mašťovská (Ph.D. Visiting Scientist) Soc. Sec. # 197-80-2262

Cooperation Summary (numbers)

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Description of Cooperation:
Prof. Amirav and Dr. Lehotay have communicated regularly once per week via email letters about research progress in the lab and new events in the analytical field plus short exchanges about specific follow-up items (there have been more than 250 exchanges since Dec. 1999). In many other instances, Prof. Amirav and Dr. Lehotay have discussed specific matters requiring both of their attention over the telephone. Free exchange of information, ideas, and suggestions was given, and all publications related to BARD projects were reviewed thoroughly by the other collaborator. Research results were shared in one of the publications, which warranted co-authorship. Otherwise, an acknowledgment was given if appropriate.

Patent Summary (numbers)

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Abstract

The overall theme of this project was to increase the speed of analysis for monitoring pesticide residues in food. Traditionally, analytical methods for multiple pesticides are time-consuming, expensive, laborious, wasteful, and ineffective to meet critical needs related to food safety. Faster and better methods were needed to provide more cost-effective detection of chemical contaminants, and thus provide a variety of benefits to agriculture.

This overarching goal to speed and improve pesticide analysis was successfully accomplished even beyond what was originally proposed by the investigators in 1998. At that time, the main objectives of this project were: 1) to further develop a direct sample introduction (DSI) device that enables fast sampling and introduction of blended-only agricultural products for analysis by gas chromatography (GC); 2) to evaluate, establish, and further develop the method of simultaneous pulsed flame photometric detector (PFPD) and mass spectrometry (MS) detection for enhanced pesticide identification capabilities; and 3) to develop a new and novel MS pesticide analysis method, based on the use of supersonic molecular beams (SMB) for sampling and ionization. The first and third objectives were successfully accomplished as proposed, and the feasibility of the second objective was already demonstrated. The capabilities of the GC/SMB-MS approach alone were so useful for pesticide analysis that the simultaneous use of a PFPD was considered superfluous. Instead, the PFPD was investigated in combination with an electron-capture detector for low-cost, simultaneous analysis of organophosphorus and organochlorine pesticides in fatty foods. Three important, novel research projects not originally described in the proposal were also accomplished: 1) development of the quick, easy, cheap, effective, rugged, and safe (QuEChERS) method for pesticides in foods; 2) development and optimization of a method using low-pressure (LP) GC/MS to speed pesticide residue analysis; and 3) innovative application of analyte protectants to improve the GC analysis of important problematic pesticides.

All of the accomplishments from this project are expected to have strong impact to the analytical community and implications to agriculture and food safety. For one, an automated DSI approach has become commercially available in combination with GC/MS for the analysis of pesticide residues. Meanwhile, the PFPD has become the selective detector of choice for the analysis of organophosphorus pesticides. Great strides were made in SMB-MS through the manufacture of a prototype "Supersonic GC/MS" instrument, which displayed many advantages over commercial GC/MS instruments. Most notably, the QuEChERS method is already being disseminated to routine monitoring labs and has shown great promise to improve pesticide analytical capabilities and increase lab productivity.

The implications of these developments to agriculture will be to increase the percentage of food monitored and the scope of residues detected in the food, which will serve to improve food safety. Developed and developing countries alike will be able to use these methods to lower costs and improve results, thus imported/exported food products will have better quality without affecting price or availability. This will help increase trade between nations and mitigate certain disputes over residue levels in imported foods. The improved enforcement of permissible residue levels provided by these methods will have the effect to promote good agricultural practices among previously obstinate farmers who felt no repercussions from illegal or harmful practices. Furthermore, the methods developed can be used in the field to analyze samples quickly and effectively, or to screen for high levels of dangerous chemicals that may intentionally or accidentally appear in the food supply.
Achievements

The overall goal to speed and improve pesticide analysis was successfully accomplished even beyond what was originally proposed by the investigators. The six main achievements from this collaborative project included: 1) development and manufacture of a prototype "Supersonic GC/MS" instrument using GC/SMB-MS, which was demonstrated to have several advantages in the rapid and effective analysis of pesticide residues in foods; 2) development of the QuEChERS method and its evaluation in pesticide analysis (including the novel cleanup approach named dispersive-SPE); 3) further development of DSI to enable fast sampling and introduction of rapidly-extracted agricultural products for GC/MS (and GC/MS-MS) analysis; 4) development and optimization of a method using LP-GC/MS to speed the separation of pesticide analytes by at least a factor of three; 5) innovative application of analyte protectants to improve the GC analysis of important problematic pesticides; and 6) development and evaluation of a method of simultaneous PFPD and μECD analysis of organophosphorus and organochlorine pesticides in fatty food matrices. Aspects of only the first two accomplishments will be discussed briefly below.

In the case of Supersonic GC/MS, some of the advantages of the instrument and approach include: 1) the M$^+$ intensity is enhanced in EI and it is practically always exhibited in SMB-MS, which greatly aids identification of the analytes at low levels; 2) high flow rates are possible which allows effective fast and ultra-fast GC/MS with a conventional quadrupole mass analyzer; 3) any column dimensions and any sample introduction device can be used in the approach including DSI; 4) full scan mode is used, thus a virtually unlimited number of analytes can be detected in a single injection; and 5) thermally labile pesticides can be analyzed due to their shorter residence times in the injector and column and lower elution temperatures achieved at high column flow rate. Using GC/SMB-MS, the ability to reliably identify 88 diverse pesticides, including difficult carbamates, was demonstrated in a total procedure less than 30 min in complex extracts such as coriander.

In the case of sample preparation, the QuEChERS approach is a major breakthrough in multiclass, multiresidue analysis of pesticides. Using the method, a single analyst can extract hundreds of pesticides from 6-12 samples in 20-30 min using <$1 of disposable materials and 1 container without generating hazardous waste. In brief, the QuEChERS method entails several unique factors to rapidly and easily provide improved results for the multiclass, multiresidue analysis of pesticides in agricultural food products: 1) minimal sample size that still gives meaningful results; 2) operable in the field or mobile labs; 3)
elimination of solvent evaporation steps; 4) vortexing and centrifuging of the samples to allow batch processing among other benefits; 5) use of 4:1 MgSO₄:NaCl for salting out which yields high recoveries of polar and nonpolar pesticides alike while providing substantial cleanup; 6) development of the dispersive-SPE concept which is greatly advantageous over traditional SPE methods; and 7) development of the analyte protectant concept which masks active sites in the GC system to provide better peak shape, easier integration, and lower detection limits for borderline GC-amenable pesticides.

All of the accomplishments from this project are expected to have strong impact to the analytical community and implications to agriculture and food safety. These state-of-the-art approaches provide exciting advantages over traditional methods and GC/MS instruments used by monitoring labs today. For one, an automated DSI approach has become commercially available in combination with GC/MS for the analysis of pesticide residues. Meanwhile, the PFPD has become the selective detector of choice for the analysis of organophosphorus pesticides. The Supersonic GC/MS instrument is anticipated to become a commercially available instrument in the future. Most notably, the QuEChERS method is already being disseminated to routine monitoring labs and has shown great promise to improve pesticide analytical capabilities and increase lab productivity.

The direct economic benefit to monitoring labs that implement these new approaches are estimated to reduce overall time and cost of multiresidue analysis by a factor of 5-10. Currently, the typical cost of analysis is $1,000 per sample in industrialized countries, which would translate to millions of dollars in savings considering that at least 100,000 samples are analyzed for pesticides in food worldwide every year. The implications of these developments to agriculture will be to increase the percentage of food monitored and the scope of residues detected in the food, which will serve to improve food safety. Developed and developing countries alike will be able to use these methods to lower costs and improve results, thus imported/exported food products will have better quality without affecting price or availability. This will help increase trade between nations and mitigate certain disputes over residue levels in imported foods. The improved enforcement of permissible residue levels provided by these methods will have the effect to promote good agricultural practices among previously obstinate farmers who felt no repercussions from illegal or harmful practices. Furthermore, the methods developed can be used in the field to analyze samples quickly and effectively, or to screen for high levels of dangerous chemicals that may intentionally or accidentally appear in the food supply.
Prof. Amirav and Dr. Lehotay collaborated closely on this research to meet project objectives. They regularly communicated weekly via email exchanges about research projects, and freely shared new information and ideas. Each scientist provided important input on their particular area of expertise, which helped the other's experiments. For example, Dr. Lehotay gave Prof. Amirav much advice on the real-world needs of labs that routinely conduct pesticide residue analysis. Each collaborator extensively and critically reviewed each other's manuscripts related to the project, and co-authorships or acknowledgments were given when appropriate. Undoubtedly, the quality and usefulness of this research to the pesticide and analytical communities would have suffered if not for the collaboration between Prof. Amirav and Dr. Lehotay.

**List of peer-reviewed publications**


### Published papers


### In press and submitted papers


Unpublished data...........................................................................................................