

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

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Date: 4/11/78

Project Title: Acquisition of High Resolution Gas Chromatograph - Mass Spectrometer and Data System

Project No: G-33-634

Project Director: Dr. J. Aaron Bertrand

Gr cd

Sponsor: National Science Foundation, Washington, D.C. 20550

Agreement Period: From 4/15/78 Until 9/30/79*
*Includes 6 months flexibility period

Type Agreement: Grant No. CHE78-01594

Amount: \$119,500 NSF Funds (G-33-634)
100,000 GIT Contribution (G-33-322)
\$219,500 Total

Reports Required: Annual Summary Reports; Summary of Completed Project (Form 98A) and Final Technical Report

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Defense Priority Rating: n/a

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GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
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Date: 12/17/80

Project Title: Acquisition of High Resolution Gas Chromatograph-Mass Spectrometer
and Data System

Project No: G-33-634

Project Director: Dr. J. A. Bertrand

Sponsor: National Science Foundation

Effective Termination Date: 9/30/79

Clearance of Accounting Charges: 9/30/79

Grant/Contract Closeout Actions Remaining:

- ☐ Final Invoice and Closing Documents
- ☒ Final Fiscal Report via FCTR
- ☒ Final Report of Inventions
- ☐ Govt. Property Inventory & Related Certificate
- ☐ Classified Material Certificate
- ☐ Other _____

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REPORT TO THE
NATIONAL SCIENCE FOUNDATION
CHEMISTRY INSTRUMENTATION DIVISION

from the

Georgia Institute of Technology
Chemistry Department's
Mass Spectrometry Laboratory

for the partial funding of the

Varian MAT 112 Mass Spectrometer System
Grant No. CHE-78-01594

This report describes the results of the National Science Foundation grant CHE-78-01594 for \$119,500 which was awarded to the Georgia Institute of Technology Chemistry Department to cover partial cost of the Varian MAT 112S mass spectrometer system. This equipment, comprising a reverse Nier-Johnson mass spectrometer-gas chromatograph-data system, was incorporated into our existing mass spectrometry laboratory during the summer of 1978. The operation of this laboratory and all the analytical mass spectrometry equipment in the facility is outlined in this report since much of it was obtained with partial funding from NSF. In addition, many of the research projects supported by the mass spectrometry facility make use of several spectrometers for different measurements in the course of a project.

FINAL PROJECT REPORT
NSF FORM 98A

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PART I-PROJECT IDENTIFICATION INFORMATION

1. Institution and Address Georgia Institute of Technology Atlanta, GA 30332	2. NSF Program Chemical Instrumentation	3. NSF Award Number CHE-78-01594
	4. Award Period From 4/15/78 To 9/30/79	5. Cumulative Award Amount 119,500
6. Project Title High Resolution Mass Spectrometer-Gas Chromatograph and Data System		

PART II-SUMMARY OF COMPLETED PROJECT (FOR PUBLIC USE)

The Chemistry Department of the Georgia Institute of Technology received funds from the National Science Foundation to assist in the purchase of a mass spectrometer-gas chromatograph and associated data acquisition/processing system. This mass spectrometer has been used for the identification of: new compounds synthesized in the laboratory, compounds isolated from natural products, compounds obtained from environmental samples and product compounds from controlled pyrolysis experiments. The chemical ionization capabilities of this mass spectrometer system have been used to great advantage for the identification of compounds that fragment under normal electron impact ionization mass spectrometry. The precise mass capabilities of the mass spectrometer-data system have allowed us to make high speed, exact mass determinations of all the ions in spectra obtained from capillary column gas chromatography-mass spectrometry. This mass spectrometer system has proven to be an invaluable analytical tool for the advancement of chemical research at Georgia Tech.

PART III-TECHNICAL INFORMATION (FOR PROGRAM MANAGEMENT USES)

1. ITEM (Check appropriate blocks)	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses	X				
b. Publication Citations		X			
c. Data on Scientific Collaborators	X				
d. Information on Inventions	X				
e. Technical Description of Project and Results		X			
f. Other (specify)					
2. Principal Investigator/Project Director Name (Typed) Dr. J. A. Bertrand		3. Principal Investigator/Project Director Signature			4. Date 9/2/80

A. MASS SPECTROMETRY LABORATORY EQUIPMENT

The mass spectrometer service in the Chemistry Department of Georgia Tech was initiated in 1966 with the acquisition (NSF partial funding) of a Varian M-66 mass spectrometer. At that time a technician was hired to operate and maintain the instrument. Although the Varian M-66 is no longer manufactured nor are spare parts routinely available, we have rebuilt the mechanical, vacuum and electrical components of the instrument and it is presently operating. The mass spectral facility was upgraded by the addition of a Hitachi RMU-7 spectrometer in 1972 (NSF partial funding). The performance of both these instruments has been maintained throughout the years and still meets the original specifications for the entire mass range. The capabilities of the mass spectrometry lab were significantly upgraded in 1978 by the addition of staff and the Varian MAT 112S gas chromatograph-mass spectrometer-data system combination (NSF partial funding through CHE-78-01594). We have obtained mass spectra on approximately 2500 samples last year and our sample load has increased by 50% over the past year. An outline of the capabilities of equipment in the mass spectrometry laboratory is given below.

Varian MAT 112S

The Varian MAT 112S mass spectrometer that was purchased with the aid of CHE-78-01594 is a medium resolution (10,000) reverse Neir-Johnson instrument with a mass range of 0-1000 AMU. This instrument is interfaced to a Varian 3700 dual column gas chromatograph and a Varian SS200 data system. The 112S is equipped with a combined electron impact/chemical

ionization source. The chemical ionization source is connected to a manifold system which can supply a number of reactant gases such as methane and isobutane. Chemical ionization causes little fragmentation and generally produces a quasimolecular ion at $(M + H)^+$.

The 112S instrument includes a glass-lined batch inlet for introduction of liquids and gases, a direct inlet for introduction of solids, and a gas chromatograph for the introduction and separation of mixtures. The direct probe can be heated from 20°C to 450°C very quickly for the introduction of less volatile substances.

The 112S has provision for single ion detection (SID) for greatly increasing the sensitivity of the system as a specific detector. Also included is a peak matching unit for precise mass determination at high resolution.

The 112S also includes a unit for direct analysis of daughter ions (DADI). This unit allows the identification of metastable decomposition pathways. An ion peak may be examined to determine if it undergoes a decomposition and, if so, to what mass. A peak may also be examined to determine if it is formed from the decomposition of a higher mass ion and, if so, which one.

The 112S may also be used for collisional activation by introduction of a target gas into the field-free region between the magnetic field and the electrostatic sector. The output of the 112S may be recorded on a light beam oscillograph or the SS200 data system.

The following analyses are available:

- (1) normal mass spectrum--scans are recorded at low resolution

- (2) chemical ionization mass spectrum--normal scan using chemical ionization with methane, isobutane or specified reactant gas
- (3) molecular formula determination--measurement of precise mass by computer data evaluation with the instrument at high resolution
- (4) appearance potential measurement--the electron energy is continuously variable from 5 eV to 100 eV
- (5) DADI--determination of metastable decomposition pathways
- (6) SID--single ion detection

Varian 3700 Gas Chromatograph

The mass spectrometry laboratory contains a Varian 3700 gas chromatograph which is interfaced to the 112S spectrometer. The 3700 chromatograph is a dual column unit equipped with a flame ionization detector on one side and a mass spectrometer interface on the other. The interface consists of a glass jet separator for packed columns and a direct connection for capillary columns. The chromatograph is equipped with temperature controlled pneumatics and automatic linear temperature programmers with subambient capability (to -99°C). The GC unit is modified to accept a PyroProbe unit for controlled pyrolysis of substances onto the chromatograph column.

The chromatograph is equipped for use with surface and wall coated open tubular capillary columns for high resolution chromatography.

The gas chromatograph/mass spectrometer provides the following analyses:

- (1) normal GC/MS--strip chart recording of chromatogram--
oscillograph recording of spectra using electron impact
- (2) normal CI/GC/MS--chart recording of spectra as above
using chemical ionization
- (3) pyrolysis GC/MS--using PyroProbe pyrolysis unit
- (4) single ion detection--the mass spectrometer may be used
as a specific ion detector to greatly increase the systematic sensitivity
- (5) high resolution GC/MS using packed or capillary columns
to obtain precise mass determination of each m/z in fast
scan spectra.

The above analyses may be recorded via repetitive scan computer acquisition at speeds up to 0.7 sec/mass decade.

This method allows computer manipulation of data as well as accurate, fast and permanent storage of spectra. Where applicable, capillary column gas chromatography may be used to achieve high chromatograph resolution.

Hitachi Perkin-Elmer RMU-7L

The Hitachi mass spectrometer is a high resolution instrument of the Neir-Johnson geometry equipped for electron impact ionization. The instrument has a glass-lined batch inlet suitable for gas, solid or liquid compounds with an adequate vapor pressure at $\leq 200^{\circ}\text{C}$. For thermally unstable compounds or compounds requiring higher temperatures, there is a direct inlet that is adjustable from ambient to 450°C . Data is recorded on a light beam oscillograph. The mass range is adjustable up to 4000 AMU.

The RMU-7L is used for the following analyses:

- (1) normal mass spectrum--scans are recorded on light beam oscillograph at low resolution
- (2) molecular formula determination--measurement of precise mass by the peak matching technique with the spectrometer at high resolution
- (3) appearance potential measurement--the electron energy is continuously variable from 5 eV to 100 eV
- (4) collisional activation--a collision chamber and target gas inlet system are used to supply a target gas for collisional activation in the field-free regions between the ion source and electrostatic sector and between the electrostatic sector and magnetic field to enhance the production of metastable decomposition via collision induced dissociation
- (5) 2E spectrum--this instrument has been modified to allow the recording of spectra formed by the charge transfer of doubly charged ions to a neutral target gas (a 20/11 charge transfer). Modification of the peak matching unit allows direct measurement of the translational energy involved in the reaction
- (6) isotope ratio measurement--the highly stable batch inlet allows accurate measurement of deuterium labelled compounds. The instrument is slowly scanned over the region of interest and the signal recorded on a strip chart recorder

Varian M-66

The Varian M-66 mass spectrometer is a low resolution (2000) cycloidal instrument capable of analyzing solids, liquids or gases via a stainless steel batch inlet, or solids and liquids of low volatility via direct inlet

probe. The M-66 has a linear mass scale output on calibrated chart paper.

The M-66 uses a Faraday cage for detection. While the M-66 requires a higher sample quantity for analysis than other instruments in the laboratory, the extreme stability of the Faraday cage detection system makes this instrument useful for accurate isotope determinations. Because the analyzing magnet field also acts as an electron beam collimator, the M-66 has no fringe field effects to cause mass discrimination at very low mass. For these reasons the M-66 may be used for very accurate and stable determination of isotopic abundances of mixtures.

The M-66 may be used for the following analyses:

- (1) normal mass spectrum--linear scans are recorded on calibrated chart paper at slow scan rate
- (2) isotopic ratio measurement--expanded scale measurements of the region of interest are recorded on calibrated chart paper

Varian MAT SS200 Data System

The Varian MAT SS200 data system is a password-protected, multi-user, multi-instrument data system for the acquisition and evaluation of mass spectral data. The system allows foreground-background operation and high level programming using FORTRAN IV. The system is based on a DEC PDP 11/34 central processor with an 80K MOS memory and floating point hardware, one 5M word dual disk drive, a Statos 3308 electrostatic printer/plotter, and Tektronix 4010 display terminal. The mass spectrometer interface includes two microprocessors, programmed by the master CPU.

The SS200 allows acquisition and analysis of data taken on the Varian MAT 112S, including GC/MS, electron impact and chemical ionization, high and low resolution.

The following is a brief summary of SS200 applications:

APLOT--analysis plot of total ion current or mass chromatogram

ALIST--a list of analysis information including individual spectrum statistics

SPLIT--a bar graph plot of a spectrum with choice of normalization and mass range

SLIST--a tabulated list of a spectrum with a choice of normalization and mass range

SAVERAGE--average of peak intensities on a peak-by-peak basis for low resolution spectra; an average of peak location (mass) on a peak-by-peak basis for high resolution spectra. Averaging two or more spectra improves intensity and location accuracy

SCOMPARE--displays two bar plot spectra from the same or different analyses for comparison

SSUB--allows subtraction of background spectrum from spectrum of interest

BSEARCH--compares spectrum with the NBS library file according to the Biemann search method described in Analytical Chemistry 43, 681 (1971)

ELEM--interactive calculation of elemental formulae and precise mass

ENLIST--calculates elemental compositions from high resolution spectral data (taken directly from spectrum)

FEDIT--allows editing and modification as well as creation of spectrum files

STABLE--display of spectrum ion series table

All results from the above routines can be presented on the display terminal or the electrostatic line printer.

B. MAINTENANCE AND OPERATION OF THE MASS SPECTROMETER FACILITY

The operation and maintenance of mass spectrometers as service instruments in our Department follow procedures that have been used since the Department purchased its first analytic M-66 mass spectrometer 13½ years ago. Professor T. F. Moran functions as the overall faculty supervisor and day to day operation is handled by experts in the area of mass spectrometry: Dr. B. P. Mathur, a Research Scientist (Dr. Mathur has just recently accepted a corporate position in MS and we are carrying out a search for his replacement); Mr. L. E. Abbey, a Research Technologist in mass spectrometry; and Mr. D. Bostwick, a full-time technician in mass spectrometry.

Our mass spectrometers are in operation each day with service requests for mass spectral fragmentation patterns, exact mass determinations, appearance potential measurements, gas chromatograph-mass spectrometer (GC-MS) separations and identifications, pyrolysis GC-MS runs, etc. Over the last year we have run approximately 2500 samples of which many have been multi-measurement of a non-routine nature. Mr. Abbey and Mr. Bostwick handle the day to day maintenance of the three analytical mass spectrometers, attend to the upkeep of the spare parts stock, and acquaint new post-doctoral fellows and graduate students with the mass spectrometer service that is available in our Department. Mr. Abbey generally handles the mass spectrometric hardware repair and Mr. Bostwick attends to any GC-MS problems as well as software/hardware improvements/maintenance associated with our Varian SS200 data system. Mr. Wilcox, a graduate student employed by the Department, runs mass spectra and aids in certain routine maintenance procedures. Mr. Wilcox works 3 hours each day for 6 days/week.

An undergraduate student is paid by the Department on an hourly basis to continue the analytical service each evening and on the weekend. The responsibility of the latter operator is to handle samples run in conjunction with the undergraduate laboratories.

As noted above the upgrading, maintenance and repair of our mass spectrometer facilities are performed by the excellent full-time technical staff associated with this laboratory. The mass spectrometry group has a combined total of more than 50 years of experience in mass spectrometry. We have the ability and backup services (electronic, machine, glass shops) that are necessary to maintain our instruments at a specification level that is higher than when the mass spectrometer systems were originally delivered. Our staff is fully acquainted with the construction and modification of various spectrometer ion sources, vacuum systems, sample introduction systems, ion beam-neutral beam devices, detection systems, etc. and we are completely capable of repair, modification and upgrading state-of-the-art equipment.

Our Electronics Shop with four full-time technicians helps as needed with electronics maintenance and modifications of existing circuits. Our machinist assists with the manufacture of various stainless steel parts, the fabrication of insulators from machinable ceramics, etc. Our two glassblowers easily handle any glass maintenance problems that arise in the mass spectrometry lab.

During the last fiscal year our budget for the operation, maintenance and updating of our present mass spectral facility was approximately \$69,000. The philosophy of the Department is that the mass spectrometer is a very necessary analytical tool and sufficient funds and manpower are

allocated to keep the service on a level with the increased demands for mass spectral data.

Besides obtaining mass spectra for the Georgia Tech Chemistry Department (free of charge) and other groups on campus, we have aided (free of charge) others in this geographical region in need of mass spectra. For example, in the past year and a half we have obtained mass spectra for investigators at Georgia State University, Clemson University, University of Georgia, Atlanta University, Georgia College at Milledgeville, Bellarmine College, David Lipscomb College, the University of Alabama at Huntsville, the Fernbank Science Center, the University of Alabama Medical School at Birmingham, Emory University Medical School, the Engineering Experiment Station, the Savannah River Plant (DOE), and the Georgia Bureau of Investigation Crime Laboratory and the Mound Laboratory (DOE).

C. AUTOCATALYTIC RESEARCH EFFECTS OF THIS GRANT

The Varian MAT 112S mass spectrometer system has permitted us to upgrade significantly our MS support of existing research programs through the use of specialized mass spectral techniques hitherto unavailable to us, including: GC-MS analysis; Pyrolysis GC-MS analysis; Chemical Ionization MS, Collisional Activation MS and computerized identification routines. This mass spectrometer system has been needed to meet our expanding research activities which have shown steady growth over the past decade. The amount of total funding for chemical research at Georgia Tech was in excess of $\$3.5 \times 10^6$ during the past year. As a direct consequence of the Varian MAT 112S capabilities we have been able to initiate a number of new research projects, such as: "Pyromasschromatography in Disease Diagnosis and Analysis" (NIH funding probable), "Products of the Chlorination and Ozonolysis of Synthetic Dyes" (NSF funding Sept. 1, 1980), "Molecular SIMS Analysis and Laser Desorption MS" (Mobil Research and Development), and others in the area of "Natural Product Separation and Identification." Because of our existing facility and expertise in mass spectrometry we received a 21-110B Mattauch-Herzog geometry spectrometer from Mobil Oil Research and Development to investigate new areas for sample analysis. This system consists of a DuPont 21-110B mass spectrometer, a Grant Mark III comparator-densitometer and a Datex AMS-1 Data System. This is a high resolution (30,000 at 10% valley) instrument which is capable of photoplate or electron multiplier detection. It is equipped with a heated all-glass batch inlet system, as well as a direct insertion probe. The electron energy of the gas ion source is continuously variable from 3 eV to 53 eV with the ion current

unregulated, or may be set at 70 eV or 150 eV in current-regulated mode. The kinetic energy may be varied from 2 KV to 10 KV, in 2 KV increments, and the mass range is 1 to 3000 amu. A peak-matching unit is also connected, for precise mass determination.

The photoplate reading system consists of a Grant Mark III Comparator-Densitometer interfaced with a Datex AMS-1 Data System. When controlled by the data system, the comparator reads any or all of the 30 spectra on a photographic plate. The density and position information is written onto magnetic tape by a Potter MT36 7-track tape drive, for further processing.

The NSF grant for the Varian MAT 112S spectrometer has provided the synergistic effect needed for our facility at Georgia Tech to reach a critical size and thus provide researchers some of the latest techniques in mass spectral analysis.

D. PUBLICATIONS FROM RESEARCH PROJECTS THAT HAVE MADE USE OF GEORGIA
TECH MASS SPECTROMETER FACILITY

1. Published in 1978

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"A Convenient Method for the Stereoselective Reduction of Alkynes to Alkenes by the New Reagents $\text{MgH}_2\text{-CuI}$ and $\text{MgH}_2\text{-CuOBu}^t$," E. C. Ashby, J. J. Lin and A. B. Goel, J. Org. Chem., 43, 757 (1978).

"Photochemical Rearrangements of Cross-Conjugated Cyclohexadienones Related to Epimaalinenone," D. Caine, H. Deutsch and J. T. Gupton, J. Org. Chem., 43, 343 (1978).

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"The Total Synthesis of (-)-Axisonitrile-3. An Application of the Reductive Ring Opening of Vinylcyclopropanes," D. Caine, H. Deutsch, J. Am. Chem. Soc., 100, 8030 (1978).

"Skeletal Rearrangements of Organometallic Compounds of the Alkali Metals," E. Grovenstein, Angewandte Chem. Int. Ed. Engl., 17, 313-332 (1978).

"Phenyl Migration During Preparation of Grignard Reagents," E. Grovenstein, A. B. Cottingham and L. Gelbaum, J. Org. Chem., 43, 3332 (1978).

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"The Effect of Internal Excitation on the Collision Induced Dissociation of $I_2^+(^2\Pi, g, v)$ Ions," Chem. Phys. Lett., **56**, 76 (1978).

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"Use of Dipolar Aprotic Solvents to Alter the Chemoselectivity of Lithium Dimethylcuprate," H. O. House and T. V. Lee, J. Org. Chem., 43, 4369 (1978).

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