DOE/MC/29467 -- 5319
(M97002067)

Continued Development of an Atmospheric Monitoring Mass Spectrometry System - Task 2.2

Topical Report
January 1 - December 31,1 995

By
F. L. King

Work Performed Under Contract No.: DE-FC21-92MC29467

For

U.S. Department of Energy
Office of Environmental Management
Office of Technology Development
1000 Independence Avenue
Washington, DC 20585

U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

MASTER

By
West Virginia University
Department of Chemistry
Morgantown, West Virginia 26505-6045

HH

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Disclaimer

ABSTRACT

The objective of this project was the development of a mass spectrometric methodology applicable to the field determination of Volatile Organic Compounds (VOC's), such as BTEX components (Benzene, Toluene, Ethylbenzene, and Xylenes. A combination of chemical ionization, selective ion storage, and tandem mass spectrometry was planned to be employed with an ion trap mass spectrometry system. The Gas Chromatography Mass Spectrometry (GC-MS) interface on the ion trap system was modified to permit direct atmospheric monitoring. Through the use of tandem mass spectrometry methods the need for chromatographic separation would be eliminated reducing the overall size and complexity of the system.

TABLE OF CONTENTS

EXECUTIVE SUMMARY

Although this project had a starting date of 1-1-95, funds were not made available until 3-13-95. The work beagn in the first quarter limited to unfunded research conducted by undergraduate students. These students has worked since the beginning of the Spring 1995 semester on preliminary development of tandem mass spectrometry (MS/MS) methods. A small allotment of BTEX standard material was obtained with the assistance of the NRCCE at WVU.

During the second quarter water chemical ionization methods were developed for benzene, toluene, ethylbenzene and xylenes. Standards for calibration of the instrument were successfully formulated during this quarter. Experiments to determine conditions under which ethylbenzene and xylenes can be determined by tandem mass spectrometry began. A new molecular beam sampling interface was designed and installed in the middle of the beginning of the third quarter. Necessary modifications for field operation were evaluated. A laptop computer and natural gas powered electric generator were acquired by the NRCCE for use in eventual field tests of the system.

Collaboration with Varian continued, however, the ion isolation software was tested and found to lack needed flexibility. Varian has been apprised of the needs for future software. Difficulties with instrument control in the software have prevented the further development of methods. The NRCCE has provided additional support of this project in personnel and supply.

During the final quarter work shifted back to restoring the ion trap system to reproduce chemical ionization of benzene, toluene, and xylenes with water. For this last quarter of the project the personnel working on the project consisted of one part-time technician. Originally the technician was supposed to work full time through the end of November, but he decided to continue his education and returned to full time student status. Because there was no time to hire replacement personnel and because of technical problems with the trap, it was decided to complete the project with this person working half-time. The technician ceased working on the trap at the contracted close date of November 30, 1995. At the end of the project approximately $12,200 remained in the account and reverted to the funding agency. Effectively only the months of October and November were available for work during the final quarter.

1.0 Introduction

In the general area of Characterization, Sensors, and Monitoring, analytical systems are needed that can provide near real-time measurements of hazardous materials and their degradation products at sites where contamination is suspected. Of particular interest are the volatile organic compounds (VOC'S) associated with petrochemicals. Presently, we are investigating the utility of atmospheric sampling mass spectrometry for the determination of benzene, toluene, ethylbenzene, and xylenes in ambient air. Preliminary methods relying on chemical ionization (CI) and/or tandem mass spectrometry (MS/MS) were identified in a survey of the literature. It was proposed to continue this work by developing methods that employ a combination of CI and MS/MS techniques with the ion trap mass spectrometer for the identification of components in mixtures.

2.0 Purpose

The overall objective of this project is the development of an atmospheric monitoring ion trap mass spectrometry system and associated methods for determination of volatile organic compounds. One of our ultimate goals is to develop methods that can be employed by technician level operators. We believe that this is an essential first step toward the development of truly field portable mass spectrometry systems.

3.0 Background

During 1994, the NRCCE acquired an ion trap mass spectrometry system for use in atmospheric monitoring. Through funding of a project entitled "Evaluation of IR and Mass Spectrometric Techniques for On-Site Monitoring of Volatile Organic Compounds" mass spectrometric methods for separation and determination of the principal components in BTEX, (Benzene, Toluene, Ethlylbenzene, and Xylenes) were identified in the literature. The literature methods indicate some interference problems that must be considered to obtain accurate data, ie. the separation of xylenes and ethylbenzene. In the 1995 project year it is proposed to develop complete methods for the speciation of 10 components in an environmental petroleum standard and the speciation of 9 components in an environmental halogenated hydrocarbon standard. Our interest in the petroleum standard is to test the ability of the system to identify components in the atmosphere near a leaking petroleum tank; whereas, the interest in the halocarbons stems from a desire to develop monitoring for off gas from hazardous waste incinerators. During the course of the work potential interferences arising from both the sample and the monitoring environment will be identified. The original methods will then be modified by employing selective reagent chemical ionization and/or tandem mass spectrometry to selectively identify the species of interest and to eliminate the influence of the inteferent species.

4.0 Methodology

Water chemical ionization was found to provide strong, characteristic molecular ion signals for the analytes. It was hoped that selective ion storage software would enable parent ions corresponding to the individual sample components to be monitored and quantified. This was attempted with the GC inlet so as to avoid problems that might arise from the atmospheric interface. The nature of the software precluded independent control of ionization, mass scanning, and detection. An additional problem was that the software for selected ion storage precluded the use of tandem mass spectrometry. After the software was installed by the Varian technician, we could no longer investigate MS/MS. A molecular beam interface was employed to permit direct sampling of atmospheric species. The interface did not adequately reduce the pressure admitted to the ion trap. The result was spectra with peaks too broad to be interpreted.

5.0 Work Performed

Work during the first quarter was limited to the training of unpaid undergraduates in the use of the ion trap mass spectrometer. Plans were made to hire these students to work on the project during the summer. This approach makes best use of the time spent training them in the use of the system. Two graduate students have also been hired to work through the summer on this project to design and build the atmospheric sampling interface. A small amount of BTEX standard was obtained throught the WVU NRCCE.

During the second quarter development of methods for the determination of benzene, toluene, ethylbenzene and xylenes continued. Mr. Bledsoe and Mr. Sams worked to determine ionization parameters for chemical ionization of benzene using atmospheric water vapor. See attached spectrum. Initial evaluation of MS/MS of benzene indicated that the fragmentation pattern was concentration dependent. We believe that this is due in part to self CI, reaction of the analyte with itself, at higher benzene concentrations. At this point it was felt thatImproved software recently acquired from Varian should permit cleaner isolation of parent ions and reduce self CI effects.

Standards of the BTEX compounds in methanol and methylene chloride were prepared by Ms. Boyers to provide vapor concentrations of 1, 10, 100, and 1000 ppm for the BTEX components. The solvents methanol and methlyene chloride were found to create spectral interference and chemical noise. The problems with methylene chloride were so severe that it was ruled out as a solvent for future standards.

MS Toolkit Software was installed on the ion trap in July by a Varian service engineer. This software allowed the system to monitor selected ions, up to five at a time, but precluded the use of tandem mass spectrometry. In initial tests with this software, the detector of the ion trap mass spectrometer was repeatedly damaged by high ion currents. Discussions with Varian revealed that the source of this damage was the abundance of water in the trap employed for Water CI. When we first designed the experiments, we believed that the detector was not powered until a mass scan was initiated. A shortcoming of this software is that the detector is not monitored until the mass scan but is powered at all times. A result of this is that during the ionization period, the detector "sees" all ions generated, a very strong signal, and is effectively "blinded"(burnt out by excessive signal). The nature of this problem was discovered in late August. Using funds from the project and from the NRCCE, two detectors were replaced over the course of the quarter. Varian's support staff suggested that we might avoid this problem by employing a different approach to sample ionization. Investigations into alternatives began.

The molecular beam sampling interface designed and contructed by Mr. Steiner and Mr. Lewis, Figure 1, was installed on the system and tested for performance in early August. From the beginning problems were encountered with the gas load generated on the ion trap by the new interface. Initially, pumping of the interface was achieved with the backing pump of the turbo molecular pump on the ion trap. This approach failed to reduce pressure sufficiently to operate the ion trap. The original backing pump was replaced by a larger backing pump in an effort to alleviate the problem. At this point the trap was operational but yielded poor quality spectra. The spectra exhibited line broadening that we attributed to high working pressure within the ion trap. The system has no pressure monitoring device so exact internal pressures are not known. The next effort was to use two pumping systems, one for the interface and one for the ion trap. After acquiring the second pump, this was attempted. Again the spectra were too poor to provide useful information. At this point, in late August, we decided to reinstall the GC interface and redesign the atmospheric interface. We also suggested to Varian that future traps allow for a larger turbo molecular pump to be added to the system for atmospheric sampling work. We spent most of September returning the system to its original configuration and calibrating its performance to permit further investigations into the use of MS/MS to differentiate xylenes from ethylbenzene.

During October progress was made and the attached water chemical ionization spectra were obtained. It is clear from the spectra, Figures 2-4, that the water CI approach successfully produces molecular ions of the analytes of interest with no fragmentation. These spectra were the result of a series of investigations into the influence of ion reaction time on sensitivity and spectral purity. At the end of these investigations the next step was going to be resumed examination of the MS/MS speciation of the various xylene isomers. At the end of October the turbomolecular pump on the ion trap failed.

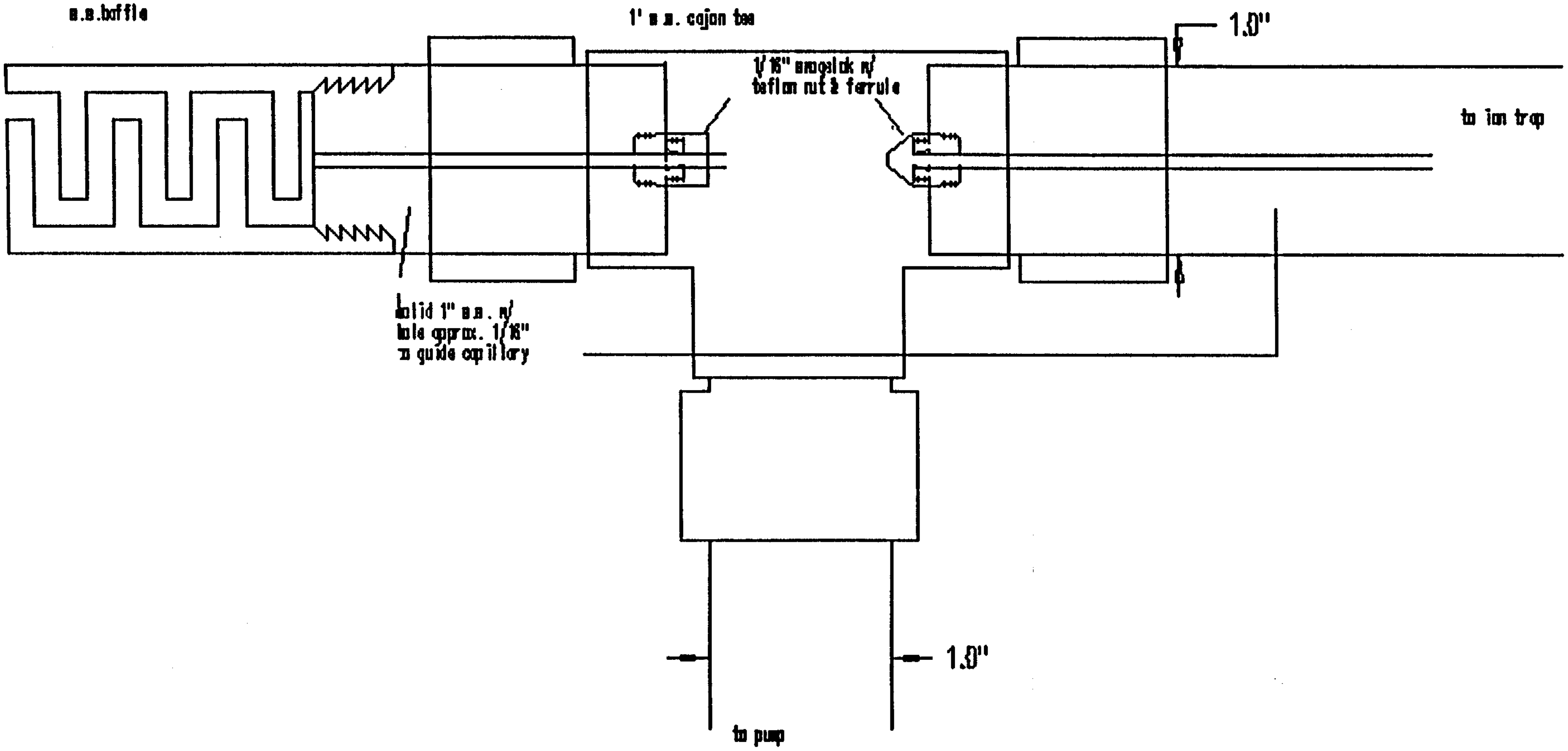
November was spent attempting to replace the failed pump with a larger version available at the NRCCE. The installation of the larger pump would not only allow continued investigation of the MS/MS method but would have also allowed reexamination of the molecular beam interface because the replacement pump would effectively quadrupled the pumping capacity. An adaptor for the pump was designed and after several modifications the November the replacement pump was mechanically in place by the end of November. At that point a problem was encountered with the system software. The system monitors the pump performance to provide a gauge of ion trap operating pressure. Unfortunately the replacement pump does not interface directly with the ion trap system- as a result the software does not get a pressure reading and the system protection software does not permit ion trap operation. Our initial contact with Varian yielded no solution to this problem. We unsuccessfully attempted to identify the protection circuit and its signal read by the software. The funding for the project reverted to the program and we were unable to replace the turbomolecular pump. A request by phone to utilize a portion of the $12200 unspent project funds to replace the pump was denied. We continued to try different approaches to bring the ion trap system back into operation, none of these were successful.

6.0 Conclusions

Water chemical ionization was demonstrated to effectively generate molecular ions for the analytes benzene, toluene, and xylene. Continued software difficulties are hampering modification of the ion trap system to permit reexamination of the molecular beam interface. Planned development of MS/MS methodology and field trial in the absence of funding was not possible because of failure of the ion trap vacuum system.

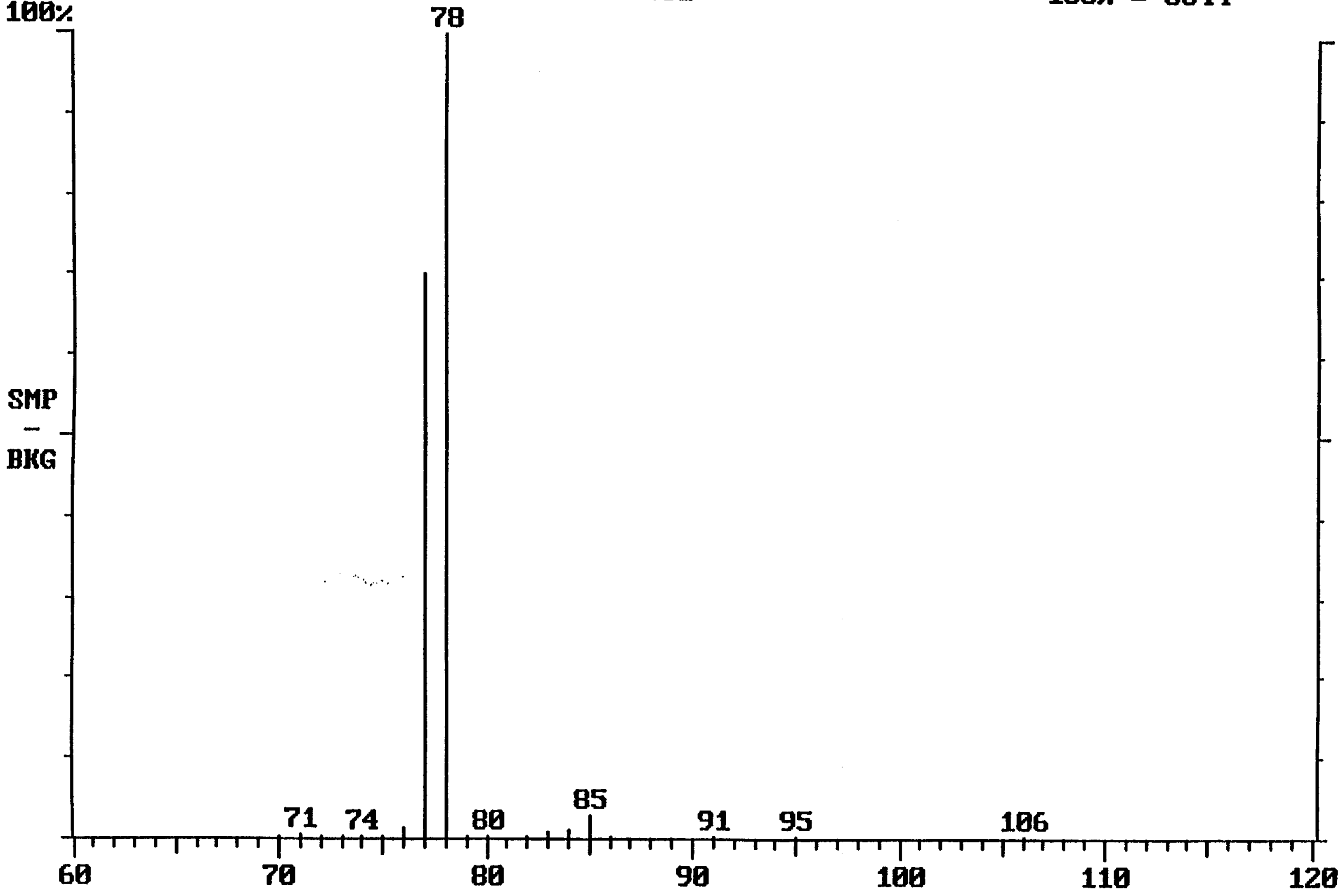
Schedule

Task #	% Complete
1	100
2	100
3	75
4	100
5	10
6	0
7	50
8	70
9	50
10	0
11	90

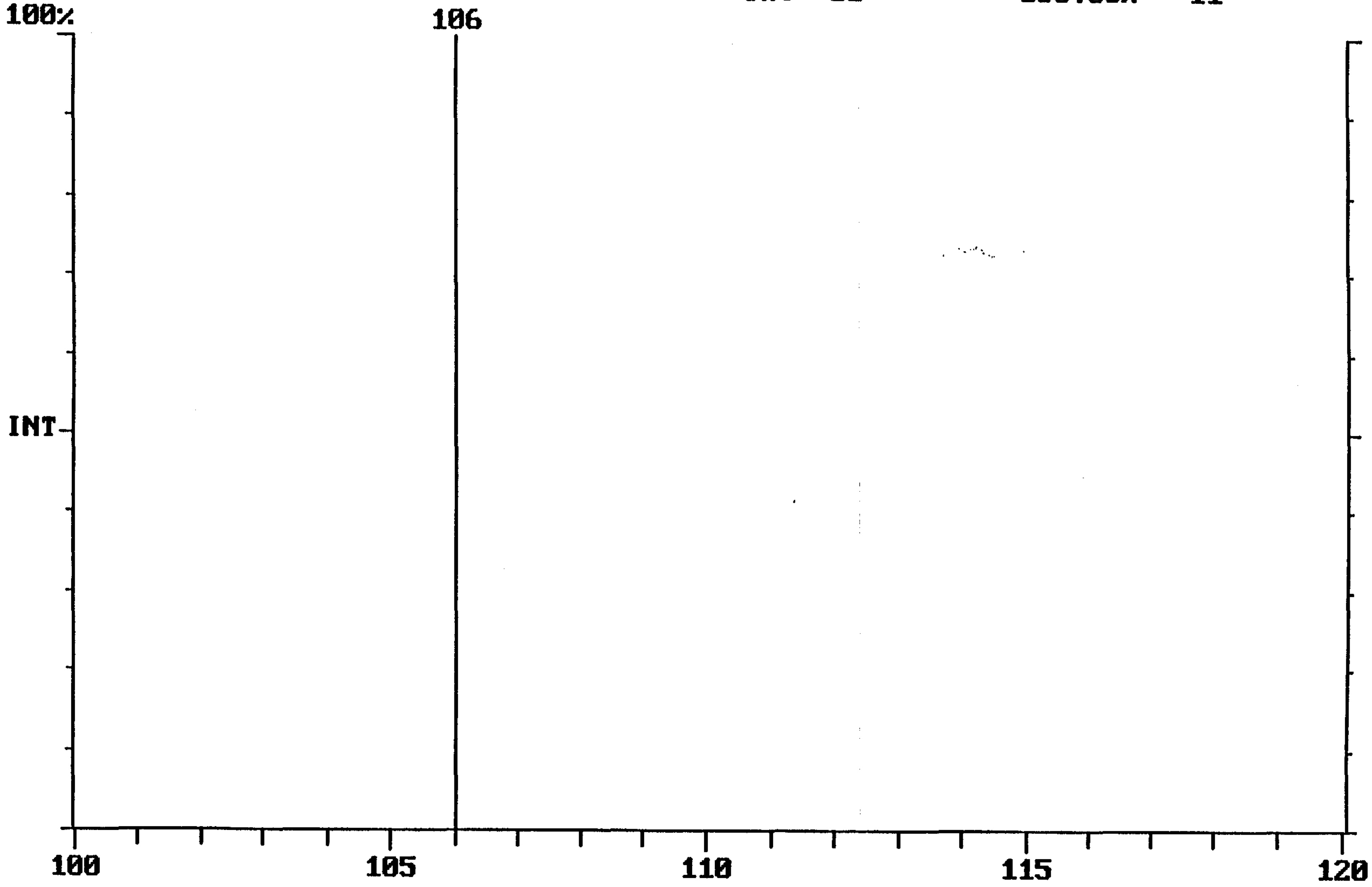

s.s.baffle
1" s.s. cajon tee
1.0"
1/16" swagelok w/
teflon nut & ferrule
to ion trap
solid 1" s.s. w/
hole approx. 1/16"
to guide capillary
1.0"
to pump

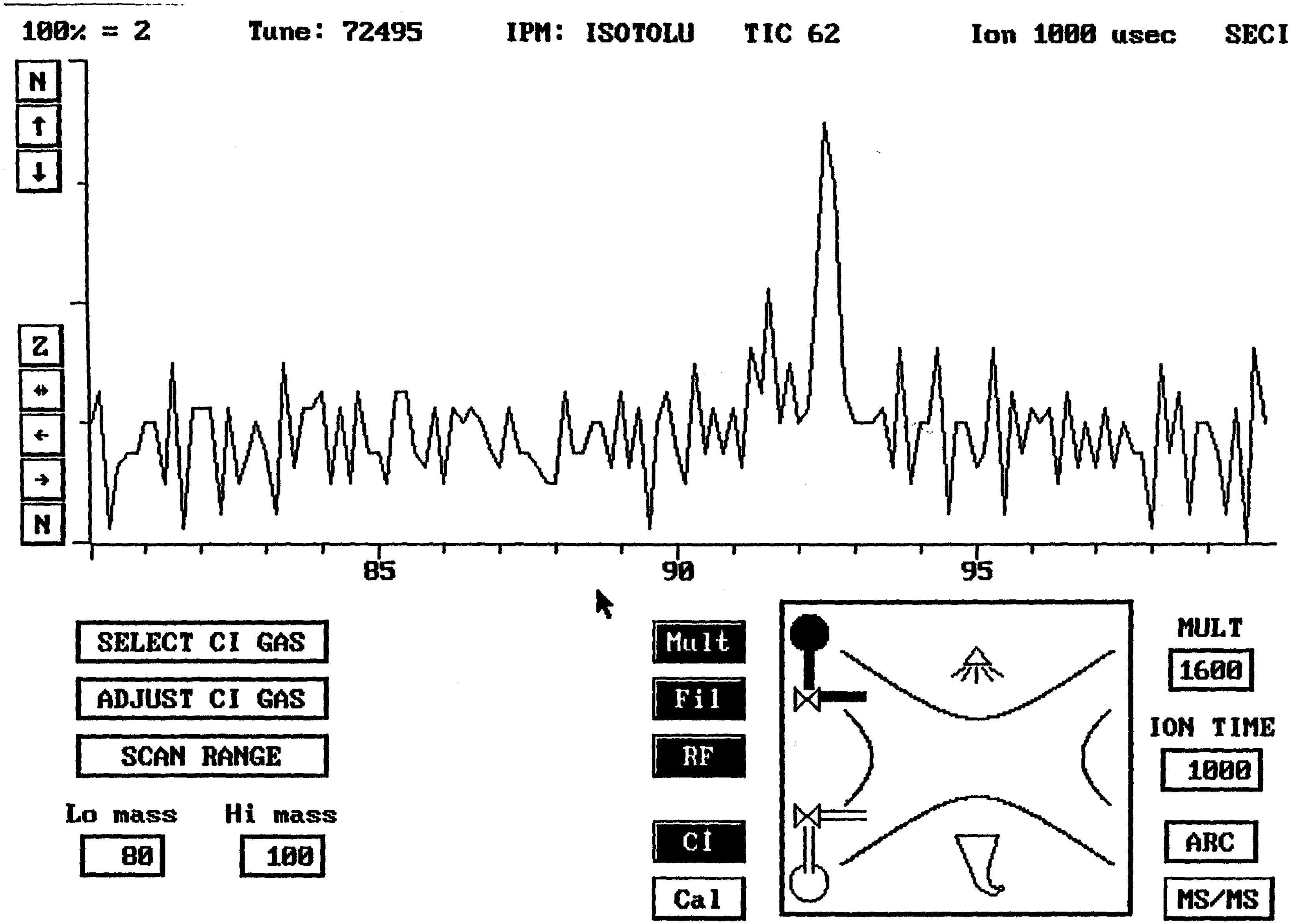
Average of: 605 to 609 Minus: 577 to 581

100% = 6644



Pks: 1 Base Pk: 106 Int: 11 100.00% = 11





100% = 2 Tune: 72495 IPM: ISOTOLU TIC 62 Ion 1000 usec SECI

Lo mass 80

Hi mass 100

MULT 1600

ION TIME 1000