

TEMPORARY
DATASHEET
&
INSTRUCTION MANUAL
FOR
MODEL 31800
LC/MS INTERFACE PROBE

Features:

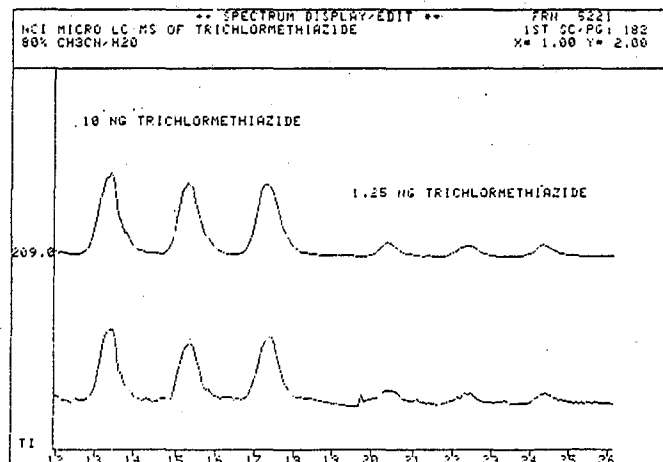
1. Can be used as a micro LC/MS probe or conventional LC/MS probe interface.
2. Provides mild, chemical ionization of labile compounds.
3. Transfers 100% of micro HPLC effluent to the mass spectrometer ion source.
4. Can be used with either reversed phase or normal phase HPLC effluents.
5. Can provide low nanogram LC/MS detection limits.
6. Chemical ionization usually provides molecular weight information of analytes.
7. The LC/MS probe exhibits minimal extra column band broadening.
8. Probes can be installed in HP 5985 B, Finnigan/MAT 3000 and 4000 series, Extranuclear and Nermag quadrupoles.
9. Utilizes existing vacuum lock (1/2" vacuum lock for Finnigan/MAT 3000 and Extranuclear shown on page eight of our catalog).

WARNING

Do not point probe tip at face. Keep mouth, nose and eyes away from "jetting" probe. Do not inhale vapors.

WARRANTY EXCLUSION

A plugged probe capillary is not covered by warranty. Work only in clean, lint-free environment. This probe is carefully cleaned and tested before shipment. Use recommended filters.



Courtesy of J.D. Henlon, Dale Skrabalak and C. Eckers, Diagnostic Laboratory, New York State College of Veterinary Medicine, Cornell University, Ithaca, NY 14853.

2/84

vacumetrics

2261 Palma Drive, Ventura, CA 93003-5789
(800) 235-3333; In CA: (805) 644-7461; Telex: 4991689 VACUX





PINHOLE APERTURES — SERIES 100

Series 100 Pinhole Apertures are available from 1 thru 1000 micron diameters. Each aperture is centered ($\pm .005$ inch) within a $\frac{1}{8}$ inch diameter stainless steel 300 series disc of varying thickness depending on pinhole aperture required.. Dustproof re-usable packages are supplied with each order.

FOR IMMEDIATE RESPONSE

603/898-1154

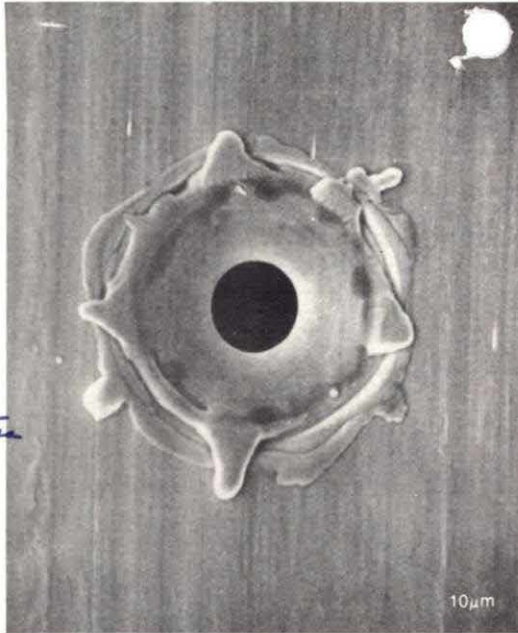
HPLC-5 42 μ m HPLC-2 84 μ m

PINHOLE SET PRICES — SERIES 100

\$124 Popular Set #0100-0 5,10,25,35,50,100 μ m

\$246 Standard Set #0100-2 2 $\frac{1}{2}$,5,10,15,25,35,50,100,200,400,800,1000 μ m

\$394 Deluxe Set #0100-3 2 $\frac{1}{2}$,5,7 $\frac{1}{2}$,10,12 $\frac{1}{2}$,15,17 $\frac{1}{2}$,25,35,50,60,70,80,90,100,200,400,600,800,1000 μ m



SEM PHOTO OF SERIES 100 PINHOLE

**FACTORY DIRECT
PINHOLE APERTURES**

Cat. No.	Pinholes	Substrate Thickness	Price
101	1 micron \pm $\frac{1}{2}$ micron	.0005	\$60.
102.5	2 $\frac{1}{2}$ micron \pm $\frac{1}{4}$ micron	.0005	36.
105	5 micron \pm 1 micron	.0005	32.
107.5	7 $\frac{1}{2}$ micron \pm 1 micron	.0005	24.
1010	10 micron \pm 1 micron	.0005	24.
1012.5	12.5 micron \pm 1 micron	.0005	22.
1015	15 micron \pm 2 micron	.0005	20.
1017.5	17.5 micron \pm 2 micron	.0005	20.
1025	25 micron \pm 3 micron	.001	20.
1035	35 micron \pm 4 micron	.001	20.
1050	50 micron \pm 5 micron	.001	20.
1060	60 micron \pm 10%	.002	20.
1070	70 micron \pm 10%	.002	20.
1080	80 micron \pm 10%	.002	20.
1090	90 micron \pm 10%	.002	20.
10100	100 micron \pm 10%	.002	20.
10200	200 micron \pm 10%	.002	20.
10300	300 micron \pm 10%	.002	20.
10400	400 micron \pm 10%	.002	20.
10500	500 micron \pm 10%	.002	20.
10600	600 micron \pm 10%	.002	20.
10700	700 micron \pm 10%	.002	20.
10800	800 micron \pm 10%	.002	20.
10900	900 micron \pm 10%	.002	20.
101000	1000 micron \pm 10%	.002	20.

For UPS Deliveries - Laboratory facilities located at: 289 Main Street, Suite 4, Salem, N.H. 03079

OPTIMATON
LASER APPLICATIONS SERVING INDUSTRY

P.O. BOX 310
WINDHAM, NEW HAMPSHIRE 03087

PLACE
STAMP
HERE

OPC6/82

Preparation for installation

Materials to be supplied by customer

1. Cooling water for probe. Flow should be 0.2 L/min, Tmax = 30°C. A closed circuit circulator with deionized water is recommended (eg. VWR #13270-290) from VWR Scientific Inc., P.O. Box 3200, San Francisco, CA 94119 or house cooling water and an appropriate drain may be utilized.
2. Ultrasonic cleaning apparatus (Vacumetrics No. 80005 or equivalent.)
3. Water, HPLC grade.
4. Methanol and acetonitrile, distilled in glass (UV) from Burdick and Jackson, Inc. 1983 South Harvey Street, Muskegon, MI 49442.
5. Micro cleaning solution, International Products Co., P.O. Box 118, Trenton, NY 08601.
6. Pressurized gas supply for cleaning such as Vacumetrics Duster-Chiller, catalog no. 31200.

CHOOSE ONE INSTALLATION KITCatalog no. 31801 Micro LC/MS Installation Kit contains:

3	ea.	One-shot pinhole diaphragm	(catalog no. 31810)
2	ea.	Kalrez O-rings	(catalog no. 31811)
2	ea.	Low dead volume filter unions	(catalog no. 33450)
5	ea.	LC Pigtails (5cm x 1/16" x 004")	(catalog no. 33310)
1	ea.	Flat tip Tweezers	

\$330.00

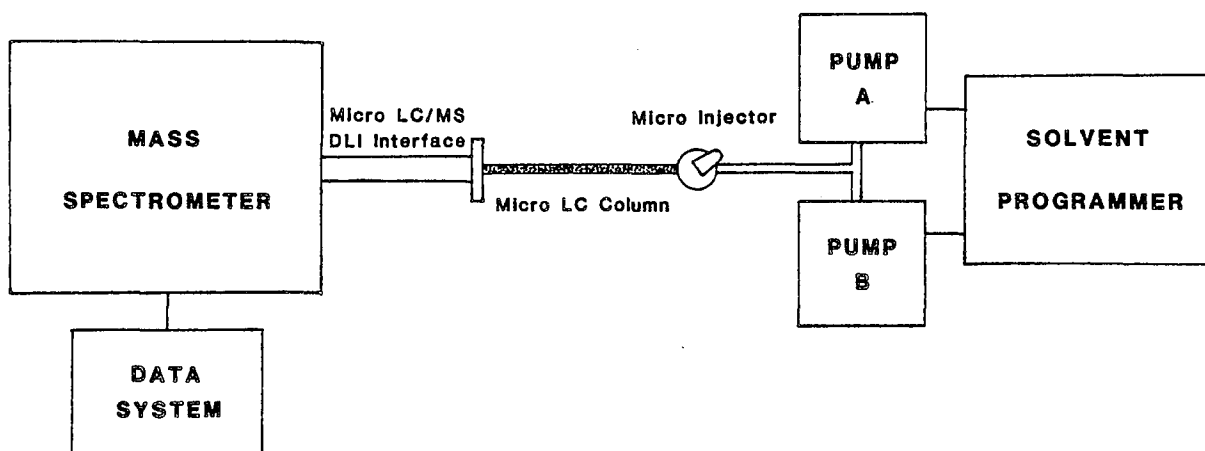
Catalog no. 31802 Conventional LC/MS Installation Kit contains:

① 3	ea.	One-shot pinhole diaphragm	(catalog no. 31810)
① 2	ea.	Kalrez O-rings	(catalog no. 31811)
2	ea.	Low dead volume filter unions	(catalog no. 33450)
① 5	ea.	LC Pitails (5cm x 1/16" x 004")	(catalog no. 33310)
✓ 1	ea.	Flat tip Tweezers	
1	ea.	Metering Valve	(catalog no. X31642-26)
1	ea.	Valco 1/16" Tee	(catalog no. 33675)

\$490.00

Micro LC/MS Operation

This micro LC/MS interface operates on the principle of Direct Liquid Introduction (DLI) first demonstrated by Baldwin and McLafferty (1) and later by Arpino (2) Henion (3) and Melera (4). Rather than the less sensitive split of 1-3% of the LC effluent to the mass spectrometer (MS), this micro LC/MS probe allows introduction of 100% of the micro LC effluent at flow rates ranging from 10-20 $\mu\text{L}/\text{min}$. The addition of a cryopump (2) to the MS vacuum system increases the acceptable micro LC flow rate to about 50 $\mu\text{L}/\text{min}$. This DLI method of micro LC/MS allows the solvent vapors to act as the ionizing (reactant) gas in the CI mode of operation.



The removable stainless steel diaphragm at the micro LC/MS probe tip has a 5 micron, laser generated pinhole in its center through which the liquid is jetted (5) into a desolvation region between the probe tip and the ionization chamber. The liquid jet (usually about one inch long at atmospheric pressure) breaks up into small droplets which undergo a desolvation under the vacuum and temperature conditions present in the ionization chamber. The mixture of gas and sample enters the ion source where chemical ionization takes place. In practice, the liquid jet is established with the probe outside the MS by establishing an appropriate micro LC flow (10-20 $\mu\text{L}/\text{min}$). The desired MS operating conditions are optimized by a combination of ion source pressure and tuning adjustments.

Description of micro LC/MS probe

Figure 2 shows the LC/MS probe interface schematically. The total LC effluent enters inlet line (A) which is a 1/16" OD, 0.004" ID stainless steel tube (E). This tube is terminated by a thin stainless steel diaphragm (H). This diaphragm has a precisely centered "one-shot" laser generated pinhole of 5 micron diameter, and is held firmly against the exit end of the capillary at the probe tip. The threaded end cap (I) accomplishes this by pressing the diaphragm against Kalrez O-ring (G) and the probe tip pedestal (D). The metal to metal diaphragm seal affords zero dead volume at the probe tip while permitting total transfer of the LC effluent through the pinhole into the CI ion Source. Water enters through inlet tube (B) to cooling chamber (F). The rounded end cap butts against the ion source inlet or desolvation chamber for the necessary "tightness" for CI.

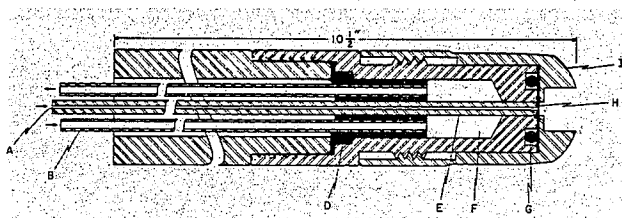


Figure 2

The UV detector is eliminated from the system to exclude its large extra column effects. An example micro LC column is a 1.0 mm id x 1.58 mm od x 25 cm seven micron partial ODS-3 (Whatman, Inc.) These columns have a plate count of about 40,000 plates/meter and are attached directly to the injector. The injector is connected by 0.004 in: id tubing (catalog no. 33310) through a 0.5 micron in-line filter (catalog no. 33450.)

When micro LC flow conditions have been established, the LC/MS probe produces a steady, one-inch long "jet" of total micro LC effluent necessary for optimum performance. When the "jetting" LC/MS probe is inserted into the standard solid probe inlet of a Hewlett-Packard 5985B MS, for example, a stable ion current baseline from m/z 100-500 is maintained over four hour time periods. The ion source temperature is elevated to 200-300°C, and the liquid nitrogen cryopump, if available, is operated in the normal manner.

The MS can be operated in either the NCI and PCI mode using the LC effluent as the CI reactant gas (1).

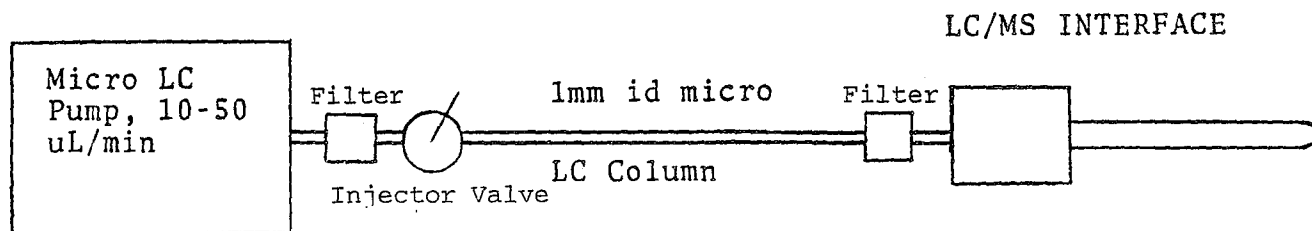
Set up of micro LC/MS probe

Figure 3 shows the connection of the probe to a micro LC. Connect the exit of the micro LC column directly to the micro LC probe inlet via the Valco in-line filter union (Vacumetrics part no. 33450, included.) An optional in-line filter is recommended between the LC pump and the sample injector ahead of the micro LC column to protect the precision parts of the micro loop injector if used.

Water cooling of the micro LC/MS probe tip is helpful because the probe tip may be heated by its proximity to the heated source block. Inadequate cooling of the probe tip can result in the formation of gas pockets at the SS - diaphragm interface. Such instability causes unstable operation of the jet and gives "jumpy" pressures and ion current baselines.

Before each working session it is highly recommended to carefully clean the SS - diaphragm by means of the following procedure if it does not "jet" properly on the first trial:

1. Remove the diaphragm from the probe by means of tweezers. Quite often when lifting the diaphragm from the tip, it will also extract the Kalrez O-ring with it. Do not attempt to separate them at this moment or damage might occur to the diaphragm.

Clean the diaphragm (or diaphragm and Kalrez O-ring combination) by heating it in a 100 ml beaker half filled with 1% MICRO cleaning solution prepared by adding 35 mL of MICRO solution to one gallon of distilled water and filtering this solution through an all glass apparatus containing 0.4 micron Millipore FHUP fluoropore filter. Put the hot solution in an ultrasonic bath for several minutes, then rinse with water (Baker HPLC grade #4218-3) and methanol (Burdick and Jackson's distilled in glass.) The ultrasonic treatment will inevitably separate the diaphragm from the Kalrez O-ring. Occasional plugging of the diaphragm can be eliminated by ultrasonic treatment for a few minutes in clean methanol. After prolonged operation at a surface temperature of 300-350 degrees C, a yellow deposit from the O-ring might develop at the contact surface with a diaphragm. This deposit can be eliminated by heating the diaphragm in a mixture of 1 part 30% H₂O₂ and 1 part formic acid to 60 degrees C. Rinsing with deionized water and filtered methanol in the ultrasonic bath restores the diaphragm to its pristine status.

2. Reassemble the O-ring in the seat by means of the tweezers. Spray the tip with some filtered methanol and make sure no particles are sticking to the O-ring (check with magnifying glass.) Cover the tip with a clean glass vial (a 3 dram vial works well.)

It is very important for this operation to be done in a clean atmosphere to avoid any particulates landing on the 5 micron orifice of the diaphragm.

WARNING

Neither the O-ring nor the diaphragm should be touched with fingers after the cleaning procedures. Use only tweezers to handle both of them.

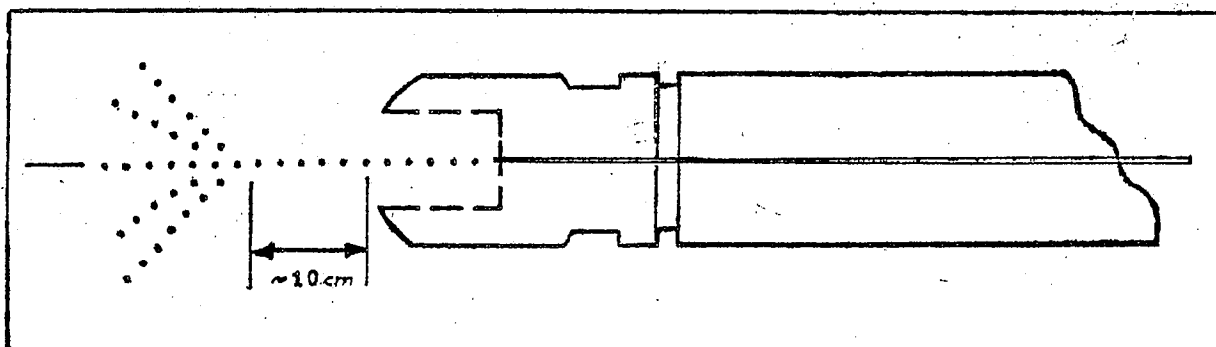
Start the micro LC flow through the LC/MS probe. With the liquid flowing, insert the end cap-diaphragm assembly on the probe's tip and tighten finger-tight. Add another $\frac{1}{4}$ turn by means of a wrench. Do not over-tighten, otherwise damage might occur to the diaphragm. Clean the outer mantle of the probe by means of a lint-free cloth impregnated with methanol.

3. Set the source temperature to 250 degrees C and allow it to equilibrate.

After the temperature has equilibrated, adjust micro LC flow to about 10 $\mu\text{L}/\text{min}$ without Cryopump, 40 μL with Cryopump.

At the beginning of this procedure the micro LC effluent should start dribbling out slowly from the 5 micron hole of the diaphragm into the cap. Wipe away the drop of solvent by inserting a Q-tip into the orifice, or blowing into the probe cap exit hole with a freon-charged bottle (Duster-Chiller, Vacumetrics no. 31200.)

As the pressure behind the diaphragm increases, a jet will suddenly develop. This can be seen by means of the loupe or by placing a metallic surface about 2-3 cm in front of the cap's orifice. Vary the micro LC flow until the jet's tip breaks into small droplets about one inch away from the cap's tip (see Figure 4.)



The jet must be straight. A "crooked" jet indicates partial clogging of the orifice or warping of the diaphragm and requires cleaning. Quite often one side of the diaphragm will give a better, straighter jet than the other side. This can be found out empirically by the operator. Also, unplugging can be obtained by simply reversing the diaphragm. Never increase the pressure difference to an excess of 300 psi over the HPLC system operating pressure or damage to the orifice might occur.

4. After filling the liquid nitrogen Cryopump, insert the jetting probe through the DIP port to the rough out position and open the small shutoff valve to the differentially pumped chamber. After 5 seconds insert the probe through the high vacuum valve to the MS manifold. A small initial increase in pressure may occur, but should subside to the normal operating pressure within 15 seconds.
5. Fully insert the probe into the manifold until positive contact is made with the source body or desolvation chamber. The manifold may read about 4×10^{-5} Torr depending upon what MS is used. The pressure reading on the ionization gauge must be very stable with small variations of $\pm 0.1 \times 10^{-5}$ Torr being allowed.

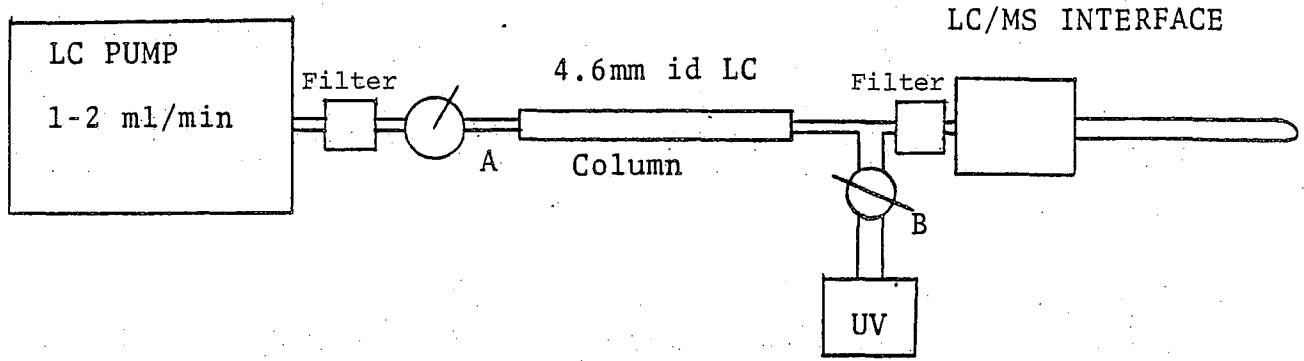
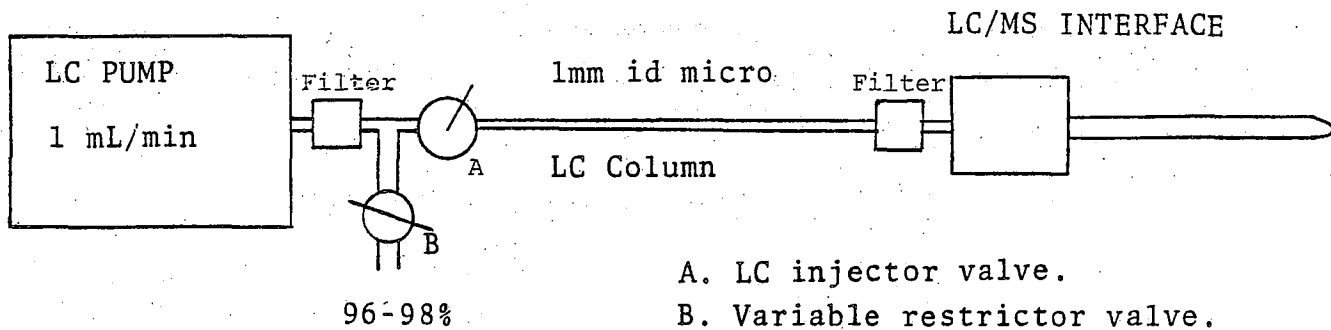
This stable condition has to develop within one or two minute, as air bubbles in the transfer line might initially cause larger deviations. Should large instabilities in the pressure readings persist for a longer period of time, cleaning of the orifice or additional degassing of the solution will be required.

An alternative micro LC system

Micro LC columns can be used with most commercial HPLC systems using a split-flow technique, and a Valco or Rheodyne micro injector. A Valco zero volume tee, Vacumetrics no. 33675 is installed between the pump and the injector. The instrument pump is set at the lowest possible flow rate (usually 0.1 mL/min or 100 μ L/min.)

One leg of the tee leads to the injection valve, the other to a capillary restriction valve or fine metering valve. To obtain the desired flow rate through the column, the total pump flow rate is apportioned between the injection valve and the restrictor valve by adjusting the restrictor valve. For example, by splitting the total pump flow 50/50, a total flow of 100 microliter/minute is split 50 microliter/minute to the column, 50 microliter/minute to the restrictor valve. That portion which flows through the capillary restrictor is fed into another Valco zero volume tee and detector. This flow provides additional make-up flow through the detector, making the cell volume insignificant to column performance. (Figure 5.)

Although this system will allow the use of microbore columns with standard equipment, more mobile phase is used than with modified, reduced volume equipment.

CONVENTIONAL LC/MS WITH MICRO LC/MS PROBEMICRO LC/MS WITH CONVENTIONAL LC PUMP

References

1. M.A. Baldwin and F.W. McLafferty, Org. Mass Spectrom., (1973) 7, 1355-57.
2. P. Arpino, M.A. Baldwin and F.W. McLafferty, Biomed. Mass Spectrom., (1974) 1, 1.
3. J.D. Henion, Anal. Chem. (1978) 50, 1687-1693.
4. A. Melera, Paper No. 085, 30th Pittsburg Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, OH, March 5-9, 1979.
5. N.R. Linblad and J. Schneider, Jour. Sci., Instr., (1965), 42, 635.
6. C. Eckers, D.S. Skrabalak and J.D. Henion, Clin. Chem., (1982) 28 1882-1886.
7. J. Henion, D.S. Skrabalak, E.A. Dewey and G. Maylin, Drug Met. Rev., (1983) 14, 961-1003
8. C Eckers, K.K Cuddy and J.D. Henion, J. Liq. Chromatogr., (1983) 6, 2383-2409.
9. T. Covey and J.D. Henion Anal. Chem., (1983), 55 2275-2280
10. F.R. Sugnaux, D.S. Skrabalak and J.D. Henion J. Chromatogr., (1983) 264, 357-376.

RIC+MASS CHROMATOGRAMS

DATA: 18021 #1

SCANS 100 TO 400

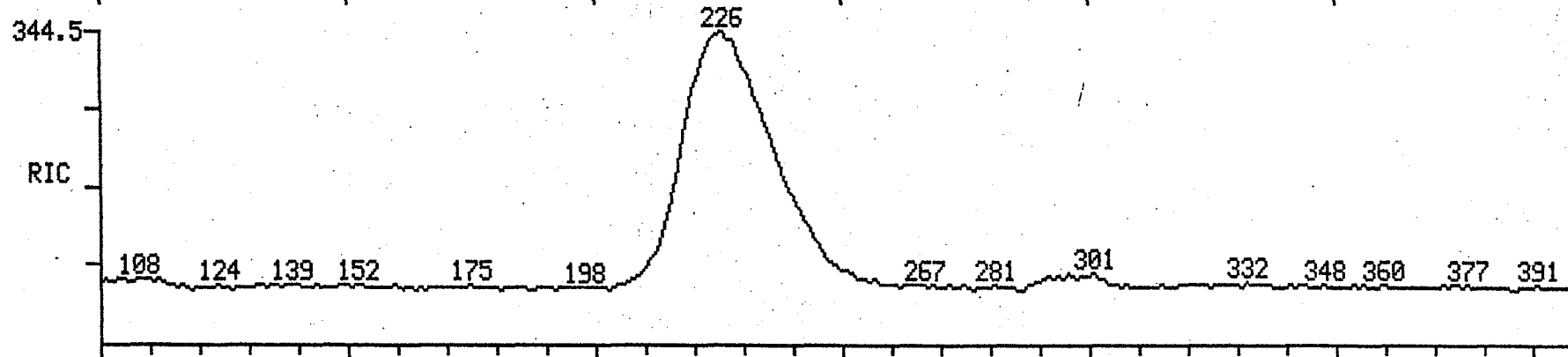
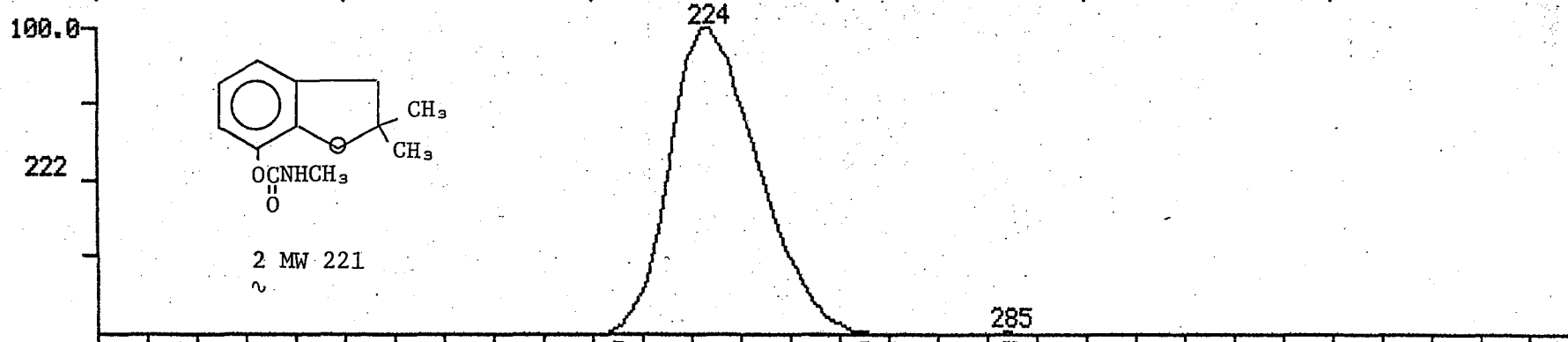
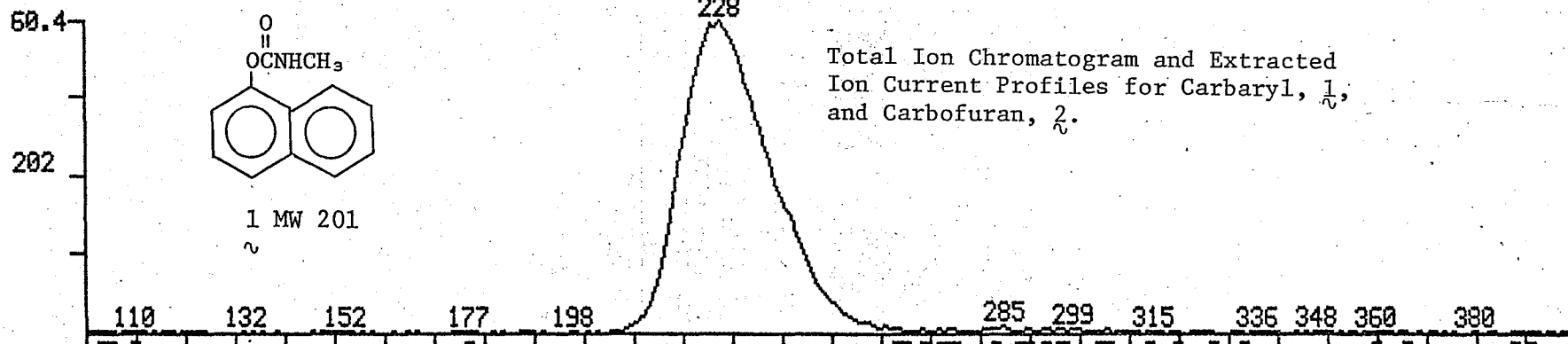
11/29/84 11:48:00

CALI: 1129 #4

SAMPLE: CARBARYL AND CARBOFURAN, 122 NG,

CONDS.: 40 UL/MIN, 100% CH3CN, 170, .14 TORR, 8.0 X 10-6

RANGE: G 1, 441 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3



100 150 200 250 300 350 400 SCAN
3:25 5:07 6:50 8:32 10:15 11:57 13:40 TIME

RIC+MASS CHROMATOGRAMS

DATA: 18021 #1

SCANS 100 TO 400

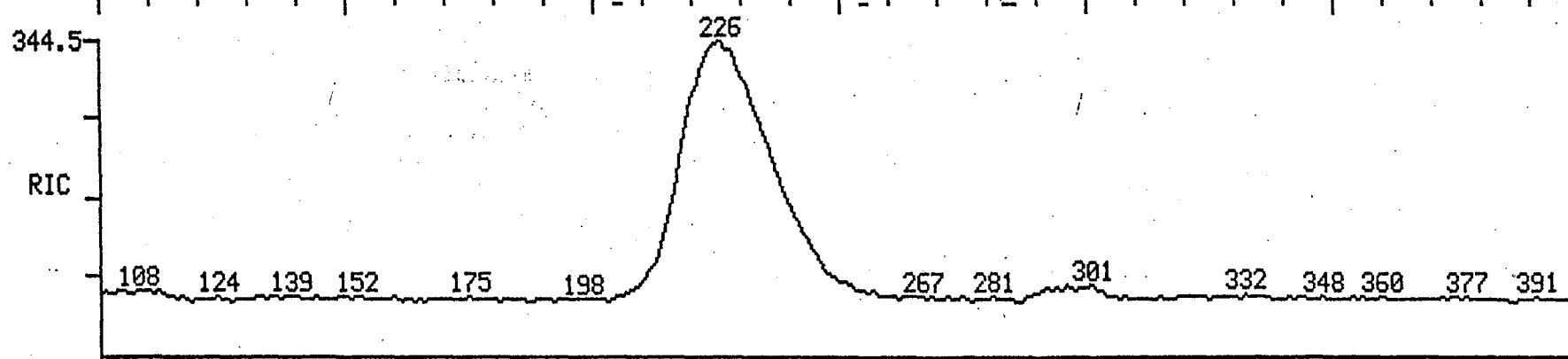
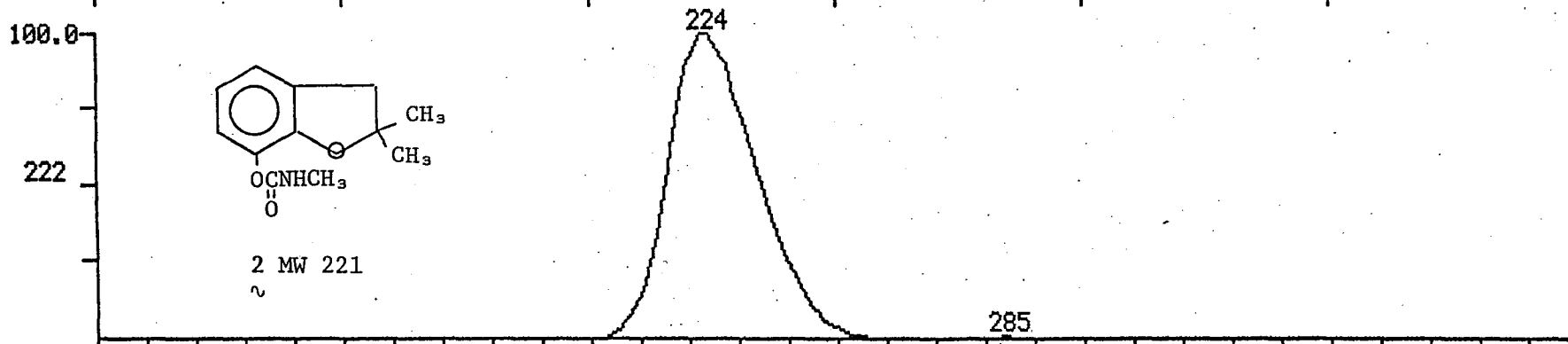
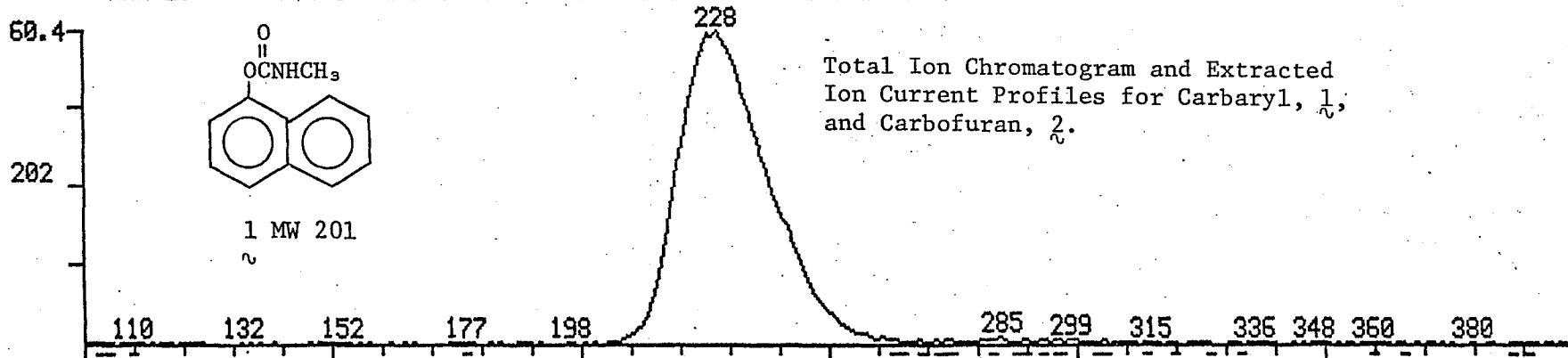
11/29/84 11:48:00

CALI: 1129 #4

SAMPLE: CARBARYL AND CARBOFURAN, 122 NG,

CONDS.: 40 UL/MIN, 100% CH3CN, 170, .14 TORR, 8.0 X 10-5

RANGE: G 1, 441 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3



100 150 200 250 300 350 400 SCAN
 3:25 5:07 6:50 8:32 10:15 11:57 13:40 TIME

