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GAS CHROMATOGRAPHY/ION MOBILITY SPECTROMETRY AS A HYPHENATED TECHNIQUE FOR IMPROVED EXPLOSIVES DETECTION AND ANALYSIS

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BACKGROUND - DEFINITION OF THE PROBLEM

Ion Mobility Spectrometry and Explosives

Ion Mobility Spectrometry is currently being successfully applied to the problem of on-line trace detection of plastic and other explosives in airports and other facilities. The methods of sample retrieval primarily consist of batch sampling for particulate residue on a filter card for introduction into the IMS The sample is desorbed into the IMS using air as the carrier and negative ions of the explosives are detected, some as an adduct with a reagent ion such as CL^- Based on studies and tests conducted by different airport authorities, this method seems to work well for low vapor pressure explosives such as RDX and PETN, as well as TNT that are highly adsorptive and can be found in nanogram quantities on contaminated surfaces. Recently, the changing terrorist threat and the adoption of new marking agents for plastic explosives has meant that the sample introduction and analysis capabilities of the IMS must be enhanced in order to keep up with other detector developments. The IMS has sufficient analytical resolution for a few threat compounds but the IMS Plasmogram becomes increasingly more difficult to interpret when the sample mixture gets more complex.

The current list of compounds that need to be targeted for detection in addition to the plastics explosives and TNT, now include the MNT isomers ortho and para MNT and DMNB. Most of theses compounds have been previously characterized in the IMS with different known conditions for detection as well separation of all the compounds [1]. Spangler et al found out in previous studies, while nitrotoluene compounds such as 2,4,6 TNT and 2,4 DNT can be separated according to their ion mobilities, the MNT isomers cannot [2]. In addition, EGDN which has been extensively studied as a vapor constituent in dynamite can only be detected as and EGDN-Cl^- or EGDN-NO_3^- ion cluster at IMS cell temperatures below 100°C as pointed out by Lawrence and Neudorl [3]. However, this is inconsistent with the optimum IMS operating conditions of 160 °C with hydrated NO_2 as the reagent gas when RDX, PETN , and TNT are directly introduced from air. The detection of DMNB by the IMS has been reported as the formation of ion clusters DMNB-H^-, DMNB- CL^-, and DMNB-NO_3^- that are separable according to their ion mobility spectra, but no additional fragmented species were found at cell temperatures above 100°C[4]. The idea of using dual IMS detectors with different front end separators and operating conditions to make up for the different species has been proposed, but there is the added complexity of effectively splitting the sample in a ratio that reflects the difference in available concentrations of the various compounds without taking multiple replicates.

There is also the added complication of knowing the actual ionization processes for all nitroester and nitroaromatic compounds in air at atmospheric pressure [5]. More ionized species have

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been reported with air as the carrier as opposed to nitrogen with differences in resolution as well as sensitivity for some the compounds. Lawrence and Neudorfl found more broader peaks coming from other chemical interferants in the atmosphere , which caused the EGDN-CL^- peak to vary enormously and disappear. While others have noted that the response to TNT is much lower by an order of magnitude in nitrogen as opposed to air, additional TNT isomers as well as DNT have been detected and they are available for sampling along with the primary TNT isomer in the explosive. The primary concern is the stability of the ions in air as opposed to nitrogen and the species' thermal stability and concentration prior to sample introduction. Non one has reported conditions in air for the detection of all the targeted taggants and explosives. It is possible to seed the remotely collected sample in a nitrogen carrier gas into the IMS, but that would not be efficient for the sample transfer. Direct air sampling onto an intermediate preconcentrator for trapping upstream of the IMS would be more effective in reducing ambient atmospheric effects, but that might also be selective as well to only one class of the targeted compounds.

One potential system design would be to interface a capillary GC to an IMS with a front end membrane separator to selectively introduce the sample without the oxygen. The benefits would be obvious in that the IMS resolution could be increased to selectively monitor the MNT isomers product ions in a drift time window after column separation. The GC column would be able to reduce any potential interference from halogenated compounds such as trichloroethane and tetrachloroethane that would be greatly accumulated in a preconcentrator along with the explosives. The GC limited sample introduction would also reduce the surface decomposition and adsorption effects on some of the compounds by allowing more rapid analyses in the IMS [6]. This design has been successfully employed in portable GC-ECD detection devices that are used for explosives detection as well as a handheld GC-IMS analyzer for chemical warfare agents. However in today's screening scenario, applying any of these designs poses additional problems for the IMS being used for explosives detection. The disadvantages arise from the additional front end components that reduce the current low level detection capabilities of the IMS itself which have made it a successful analytical technique used for trace plastic explosives detection.

Membrane Separators

In the past, the use of semi-permeable membranes to selectively introduce explosives sample into an ion mobility spectrometer has not had the effect of enriching the concentration of the explosive vapors over oxygen and other atmospheric constituents such as water which complicate the ionization process. The explosives molecules which are already present in low concentrations had to permeate through the membrane material primarily through its greater solubility in the polymethylsilicone substrate than the other lighter molecules Even with operation at elevated temperatures the adsorption desorption process governing the selectivity were not very efficient, so the sensitivity of the IMS tended to be diminished by as much as two orders of magnitude even though a high percentage of other non-organic molecules were rejected [7]. In addition , since the permeability of the explosives was not primarily dependent on the diffusion through the rubbery polymer membrane, a substantial pressure differential had to be applied over a thick membrane wall, usually in the form of a interstage pump to speed up the enrichment process for explosives sample in the membrane. In effect, the explosive molecules tended to have long residence times in the membrane separator which led to its retention in the membrane structure. In order to process large volumes of the air that contained the explosive sample, membrane separators with large surface area to volume ratios were built to permeate the explosives primarily through diffusion, with the use of compressors and vacuum pumps to establish the pressure differential over the membrane module [8]. When such a membrane preconcentrator was built and tested for coupling with an explosives detector its time constant for detection was

demonstrated to be several minutes to effectively enrich the level of TNT, which was woefully inadequate for real time explosives detection.

GC-IMS Integration

Even though a GC column has been successfully integrated to the IMS, one must consider that the IMS is a relatively large volume detector which makes it more suitable for larger sample screening of explosives in comparison to other detectors such as an ECD. This presents a pneumatic impedance mismatch due to the lower GC effluent flow rates and the larger IMS reaction volume of typically 7 cc. Baim and Hill found that in order to effectively integrate the GC column to the IMS without degrading the column resolution, the IMS ionization cell volume had to be reduced to match the GC effluent volume [9]. In another method that did not change the reaction region size, the GC effluent flow was increased with a makeup flow to fill most of the IMS reaction volume in real time and subsequently purged out with an even greater counter current drift flow to prevent lingering memory effects, as demonstrated by PCP in figure 1. However, this ultimately has the effect of reducing the concentration of explosives in the GC peaks to maintain the chromatographic separation between peaks. With the limited sample capacity of the capillary column most of the air sample containing the explosives would have to be split off in the first place before directly introducing it directly into the GC column for separation. The pneumatic impedance mismatch is even more severe between a high volume preconcentrator used at the front end and the capillary column.

Recent developments in GC column technology and membrane separators can be applied to the IMS to overcome any of the previous drawbacks to their use. The objective of this work was to come up with a preliminary design that would incorporate these components with an IMS for the purposes of enhanced explosives and taggant detection.

APPLICATION OF NOVEL EQUIPMENT TO THE IMS

Ultra Thin Hollow Fiber Membranes

Hollow fiber silicone tubing in membranes has been proposed in the past to selectively permeate large molecules, such as explosives, instead of air or an inert carrier gas into a mass spectrometer. However, Lucero et al determined that the permeation of the carrier gas (i.e. hydrogen) instead of the heavier organics was more efficient, by as much as 100% through a tubular palladium alloy electrolytic separator that was designed for a GC-MS interface [10] , as long as the pressure was substantially lower on the permeate side than the retentate side. The high diffusivity of carrier gases, such as hydrogen and helium, and the use of a membrane with greater selectivity over organic penetrants makes it possible to achieve a substantial enrichment of the sample over the carrier at lower time constants. This enrichment would be easy to achieve in a compact GC-MS membrane module since the MS inlet would be operating at pressures below a millitorr and the GC effluent would be fed in at low flow rates of 10 cc/min. However, this would not be the case for the high air sampling flow rates that are required of a membrane preconcentrator for an atmospheric pressure and large volume detector such as an IMS. The membrane sheet thickness would have to be much thinner to avoid the need to pressurize the sample on the feed side and the total surface area to volume ratio for the module would have to be reduced for a good pneumatic interface with the IMS.

Recently coiled membrane sheets made up of a thin membrane selective film on a porous support structure have been successfully manufactured and tested as membrane preconcentrators [11] These modules were tested by blowing different carrier gases including air into several types of membrane selective layers along with a dilute amount of toluene (which has a similar diffusion coefficient as some of the explosives). The results of selectivity, membrane area and enrichment are displayed in table 1 for a predetermined feed flow rate, residue flow rate and required enrichment. While the spiral wound membrane module surface area may be too large for the demonstrated enrichment of the toluene simulant the area can be reduced much further with the use of a hollow fiber membrane module.

The hollow fiber membrane module of figure 2 is composed of a polymer selective layer that is deposited from solution with water being forced through the inner core to form a fiber. The necessary surface area is obtained by stacking bundles of the fibers together in a heating mantle to provide the maximum surface area and minimum volume for the carrier gas and explosive vapor mixture that is being fed into the preconcentrator. The air, water, and ammonia permeate through the selective layer under the pressure differential being created by a vacuum pump while the retentate organics flow directly into the detector or other down stream separator. The membrane module design is dependent on the enrichment and flow rates necessary for the detector which continuously takes in the retentate flow that is separated from air as described in figure 2. The operating temperature can go up in excess of 100 °C and a coating with a low surface energy can be applied to cover adsorption sites and plug up defects. This structure is similar to some of the early designs for preconcentrators made up of bundles of capillary tubes for trapping the explosives. However, the inefficiency in purging out the sample during a desorption flow limited the use of those designs. With a hollow fiber membrane preconcentrator operating in continuous mode, there would be no additional inefficiencies arising from the adsorption/desorption processing of the sample flow. Ultimately a GC can be incorporated downstream of the preconcentrator before the detector to separate any background levels being produced by the polymer emissions from the membrane. However, such a GC column would have to be more pneumatically compatible with the retentate flow output of the preconcentrator than a standard capillary GC.

Multi-capillary Columns

The drawback of long retention times and limited sample capacity when using capillary GC columns with the IMS has limited its application to real time explosives detection. High speed chromatography for a field instrument generally requires reduced thermal mass, cold trapping, low injection bandwidths, and faster detector response, all of which are difficult to achieve with a gas sampling IMS. And shortening the column and ramping the temperature to reduce the analysis time does not produce an adequate resolution of some of the compounds that is worth the additional sample introduction problems for the IMS. Packed columns, which have a higher sample capacity and thus are more pneumatically compatible for integration than a narrow bore capillary, have been used in the past with the IMS, but there have been problems with the column bleed and the resolution. Ideally for an IMS, the sample capacity of the GC column would have to be increased to fill the reaction region of the IMS while retaining the high resolution of the narrow bore capillary under isothermal conditions.

The idea of bundling several capillaries within a larger tube to increase capacity is not new. The peaks are broader because of a difference in phase ratios in each capillary, but for an IMS which has a typical scan time of 20 msec depending on repetion rate, this would not be the limiting factor, since the scan time is well within a factor of 0.1 of the peak width. The problem has

been in effectively manufacturing and testing these columns. However, Ertl et al demonstrated that with a hexagonally shaped tube containing about 1200, narrow bore (50 to 200 micron) capillaries, they were able to get effective separations of compounds in less than a minute that took several minutes in a single capillary [12]. The conditions under which they established their separations included column lengths of 0.3 m, injection volumes up to 10 microliters, and carrier gas flow rates up to 300 ml/min. While the resolution is lower, Berkley noted that these polycapillary columns shown in figure 3, that were developed by the Limnological Institute in Irtutsk, Russia would be still be effective for separating high molecular weight compounds such as pesticides [13]. These bundled parallel capillary columns had specifications that were variable but included:

Efficiency: 8000 - 12000 TP/m (Theoretical Plates/meter)
Column Length: 150 mm - 1000 mm
Carrier Gas Flow Rate: 20 -120 ml/min depending on the detector
Gaseous Sample Volume: Up to 1 ml
Working Temperature Range: 20 - 200 °C

They were available in a selection of liquid phases and could be bundled and coated for the required sample capacity and desired analysis time.

These columns would be more ideal for the application of the real time detection of explosives as long as column specifications such as the maximum gaseous sample volume, the length, the operating temperature and the choice of phase can be traded off to achieve the desired separation. Separations of the high volatile and low volatile explosives EGDN, TNT, PETN, and RDX have been done within 22 seconds with an Ekho GC-ECD running isothermally at temperatures typically around 172 °C [14]. The specifications with the multi-capillary column that was run with the system included 1,000 parallel capillaries, 40 micron diameter, 25 cm length. The samples were collected from air onto a trap that injected the sample through a gas sampling valve connected to the multicapillary GC. A chromatograph obtained directly from headspace vapor sample of dynamite is shown in figure 4. It seems that of all the targeted compounds the higher volatile taggants or explosives such as EGDN o-MNT, and p-MNT would be the most difficult to separate with the multicapillary GC than the plastic explosives at isothermal temperatures over a short analysis time.

For operation with an IMS the retention times and widths of the sample peaks can be optimized for complete separation by the either the column itself or in conjunction with successive ion mobility separation by an IMS. The lower pressure drop over the length of the column because of the reduced impedance to the flow also means that this type of column would constitute a better pneumatic match with the IMS, with the carrier flow rate coming directly from the column. There would be no need for additional pumping in the IMS cell to make up for the pressure loss as long as the preconcentrator module supplies a continuous carrier flow rate into the column with a pulsed sample. The total analytical capability for a GC-IMS combination would still have to specified with the peak shape specifications of the IMS in question specially its efficiency or height equivalent theoretical plate. Assuming that this is adequate for the analysis of explosives, then the limiting factor would be the integration and time of response of the preconcentrator.

DESIGN SECTION

Ion Mobility Spectrometer Instrumentation

Any Minimum Detectable Limits (MDL) generated for low levels of explosives should be qualified. Factors such as the number of signal averages taken, the carrier flow rate, the integrator time constant, the gain setting, play a role in the S/N ratio observed for any IMS. Generally the IMS sensitivity will be the best the longer a sample concentration can be injected into the IMS and the longer the noise can be averaged out [15]. However, the sample will be injected for some explosives as a pulse and therefore have a shorter time constant. The concentration of the sample going into the IMS will have to be higher to make up for the shorter measurement times. This has resulted in the many different results reported as minimum detectable limits for the IMS to explosives. Some of the determinations have been made with the use of a continuous source which took long time constants to stabilize - which usually meant overcoming irreversible surface adsorption effects before the measured S/N ratio would stabilize. These minimum concentration levels reported for some of the low vapor pressure explosives over long time constants may never be available for direct sampling without some form of preconcentration.

For the purpose of on-line screening the analysis should take no more than 15 seconds for one replicate. The IMS will produce a different MDL for each explosive depending on the preferential adduct formation of the reagent ion with one particular explosive for enhancement of the signal. Various groups have reported that the use of methylene chloride in atmospheric pressure ionization will increase the signal response of nitroesters and cyclic nitramines such as RDX and PETN. Davidson et al conducted studies of chloride ion clustering in an API MS/MS system and identified the increases in sensitivity gained for several groups[16]. The ion clustering tended to suppress the response of the nitrotoluenes and the PETN nitroester peak tended to be diminished in comparison with the enhanced RDX nitramine peak with the chloride ion. Even though the IMS ionization process can be modified to detect most of the different taggants and explosives with high specificity, the differing concentrations can have an effect on the sensitivity of one explosive over the other. EGDN which would have the highest concentration in any sample matrix, can deplete the reactant ion to the point where the response to other less concentrated explosive species that have a short time constant such as PETN is suppressed. For this reason a GC column can act as a front end sample gate for the IMS to reduce any matrix effects on the response from the complexity of the sample.

Design Considerations

The IMS that will be specified for its potential integration with the other front end separators such the hollow fiber membranes and the multi-capillary GC is the PCP-110, because of the extensive information that exists on its performance for three explosives. The reported MDL of the PCP-110 IMS to all the explosives has been reported to be the best with hydrated NO_2 as the reagent gas. Its operating conditions for the optimal detection of three of the primary explosives, RDX, TNT, and PETN has been established as follows [17]:

Cell Temperature - 160^0C
Carrier Gas (Air) - 100 cc/min
Drift Gas (Air)- 500 cc/min
Reagent Gas- Hydrated NO_2
Scan Time for Plasmogram - 25 msec
Gate Pulse Width - 0.50 msec
Number of sweeps averaged - 150

The signal levels are shown in figure 6 for the three explosives. In this case the MDL for the explosive PETN , which is the least stable and at a lower concentration than TNT, should be taken as the limiting factor in the response of the IMS.

With a multicapillary GC column as a quantitative sample introduction system to the IMS the sample pulse profile of the specific peak can be matched to the concentration dependent response and the reaction volume of the IMS. This width is much more narrower than some thermal desorption profile which would be further broadened and attenuated by the interface to the IMS detector. For the IMS the average concentration of PETN that needs to be maintained in the reaction volume is 10.7 pg/cc before detection is possible with a short time constant. If the GC column is treated as a quantitative generator of explosives, the average concentration within the peak width at FWHM would have to be 10.7 pg/cc. The preconcentrator would have to produce the needed concentration level at this time interval as well as minimize the dead volume, outlet surface area and pressure drop to keep from diluting it before introducing it into an IMS. None of these limitations would necessarily be encountered in reproducing a similar quantitative concentration level with the GC.

The emphasis on meeting performance specifications for explosives detection with the overall design, would now shift to the front end membrane preconcentrator. If 1 ml of gaseous sample is pulsed into the multi-capillary GC column inlet from the membrane preconcentrator, then the sample concentration of PETN at the head of the column before dilution by the carrier gas and additional sample broadening by the GC column would have to be 75 pg/cc. This can be used to determine the enrichment factor necessary with a membrane preconcentrator for a predetermined sampling time and flow rates that is inclusive of all sample transfer inefficiencies. Given a maximum concentration that can be expected to be found in the sample flow of:

$$6.92 \times 10^{-12}\text{PPT}(314\ \text{g/mole})/(22{,}400\ \text{ml/mole}) = 97\ \text{fg/cc}$$

then the minimum enrichment required of the preconcentrator for PETN can be determine by the following ratio:

$$\text{Enrichment} = 75\ \text{pg/cc} / 97\ \text{fg/cc} = 773$$

This is a critical piece of information that can now be used to guide the design of a complete system that includes the membrane preconcentrator, the multicapillary GC, and the IMS.

We can now determine all relevant system operating conditions for these specifications that we have now set. From the flow rates and sampling time intervals other conditions, such as the preconcentrator structural and pneumatic requirements, can be determined for the required

enrichment and detection [18]. A nitrogen carrier flow rate of at least 100 cc/min through the multi-capillary GC would be required to provide the make-up carrier flow rate going into the IMS. The enriched sample flow rate or retentate flow rate coming out of the precocentrator would have to be matched to the current GC gaseous injection volume of 1 ml and the required pulse width for separation. Assuming that any pneumatic switching can be done in less than one second and the peak width of an explosive after real time separation is less than a maximum of 2 seconds, then the required retentate flow rate is 60 ml/min for one second pulsing. This 1 ml of gaseous sample volume would be made up of explosives and other organics as well as any residual air. These specifications are variable depending on the allowable capacity of the column and its efficiency. If a sampling time interval of 6 seconds is used for the preconcentrator then the feed flow rate of 7732 ml/min might seem apparent as the required sampling flow rate based on the following estimate:

7732 ml/min (6 sec) /60 ml/min (1 sec) = Enrichment.

However, this figure does not take into account transport inefficiencies through the outlet of the hollow fiber membrane module or the membrane material itself. A required inefficiency of 0.5 for vapor loss into the GC can be specified for the module depending on pressure, flows, surface area , temperature, and dead volumes involved. In this case the enrichment required would be 1546 to compensate for these losses. Depending on the mode of sampling the available concentration would be more dilute by an order of magnitude. This increase in the requirement necessary for enrichment to 1546, means that the sampling flow rate would have to be increased by an order of magnitude to 150 l/min. This is concurrent with the needs of high flow sampling portals and can be attained with a design presented.

Once again there will be a time constant in the response of the hollow fiber membrane preconcentrator and there will be a time constant associated with the pneumatic switching and sample injection into the GC. The main requirement is that it is established within real time. For a membrane preconcentrator that is operating continuously at elevated temperatures there would be no temperature cycles involved in trapping and desorbing the sample that change the condition of the equilibrated surfaces which in the end affect the time constants. The determining factor in the time constant would be the rate of the adsorption/desorption processes that govern the solubility in the membrane material, which would be low for organics like explosives in the membrane structure, since the polymer is not selective to permeating explosives. Once we have outlined the operating requirements and specifications we can sketch a preliminary design of key areas of the overall system such as the integration of all front end components.

RESULTS AND DISCUSSION

Preconcentrator/GC/IMS Interface Design

We have discussed how the multicapillary GC can be included as a low loss element in the system design. IMS instruments have been previously modified successfully to incorporate a GC. The PCP-110 can accept a capillary GC column axially with an effluent make-up flow and a purge gas to sweep it out, as seen in Figure 1. With a multi-capillary GC there would be no need for a make-up flow to be added to the effluent coming out of the column and into the transfer line to the ionization region. The mass transfer of the sample in the carrier coming out of the column can be matched to the reaction volume and drift flow of an IMS. Now the objective would be to come up with a design that does not trade off some of the current advantages of the IMS for explosives detection on the field, which include no carrier gases, large detector volumes, and low

time constants for response to explosives. This is largely dependent on the preconcentrator interface to the GC and operation which would be the limiting factor. The following design incorporates the requirements of the preconcentrator and the GC for operation, but it impacts the operation of the IMS in the least.

In the preliminary design proposed, the operation of the preconcentrator with the known requirements of the multi-capillary GC and IMS is shown in figure 6. The feed flow would come into the hollow fiber membrane preconcentrator enrich the organics over the air and dump the retentate flow directly to a drain behind the valve. The permeate mixture can flow through a secondary membrane module to further separate the residual nitrogen from the oxygen in the air permeate before introducing it into the column. The retentate flow from the secondary module would act as the carrier for the organic enriched retentate or residue flow that would be pulsed into the column. The nitrogen enriched residue stream can provide the necessary dynamic pressure for the carrier flow upstream of the multicapillary GC column. Downstream valves would provide a pneumatic switching of flows to pulse the sample from the organic enriched retentate flow out of the preconcentrator and into the carrier flow of the GC column. All the transfer lines from the outlet of the first hollow fiber membrane preconcentrator would be kept heated and have low dead volume. Under this scenario the next sample of the explosives enriched retentate flow would be taken once the column separation is completed (typically 10 sec.). But, the sample would be enriched to match the concentration MDL of the IMS.

The preconcentrator/GC sample introduction system would operate under two modes of operation; a purge cycle and a sampling cycle. In the purge condition the first valve would be open downstream to act as a drain for the retentate flow out of the membrane preconcentrator and the second valve would be closed. A portion of the N_2 enriched retentate flow from the secondary membrane would be diverted down the same drain. This would sweep out any organic remnants out of the line leading to the GC column before beginning the sample pulsing.

In the sampling condition, the first valve would be closed and the second valve open to divert the flow into the GC column. Through the action of some slight pumping the majority of the explosives enriched retentate flow would be diverted to the other drain created by opening up the second valve. The sample would then be swept into the GC column by the continuos nitrogen flow going into the column. Some of the nitrogen retentate flow may be diverted down the second drain but the residual flow going into the column can be set to prevent the diffusion of the explosives flow.

In another more simplified design as shown in figure 7, the explosives enriched retentate flow would go directly at the head of the column. And during the purge cycle the nitrogen sweep flow would be flowing past the hollow fiber membrane outlet to dump the sample to a drain when it is not being introduced to the inlet of the GC column. The nitrogen flow rate would have to be set at a much higher rate to prevent organics from diffusing through this flow barrier. At the same time a separate continuous nitrogen stream would have to be established to make up the continuous carrier flow going into the GC column. When the valve is closed during the sampling period all the sample and nitrogen retentate flow would be diverted directly into GC column and any residual nitrogen flow would be dumped to atmosphere or go to the IMS to be used in the drift gas. However, in this design the flows would be less steady and some of the sample from the last pulse might bleed into the column with a portion of the nitrogen flow sweeping through the line between the outlet of the preconcentrator and the inlet of the GC column during the purge condition.

Potential Problems and Improvements

Some additional calculations are required to further assess the feasibility of the design. The required dynamic pressures have to be determined to establish more exact flow rates. In addition the pneumatic impedances of key components in the system such as the multicapillary GC and any lines where the flow is split have to be determined. In order to make the valveless flow switching process more predictable, the pneumatic impedances across each transfer line would have to be fixed against these other specifications to maintain the proper flow rate [19]. For instance the impedance seen by the explosives flow would have to be much greater over the line to the drain than the impedance over the line representing the multicapillary GC. A representative pneumatic flow network would have to be determined to set all the flows and impedances for proper operation. In addition, most of the design assumes that the time for establishing these conditions would happen quickly, But in reality, even with fast switching solenoid valves (< 1 sec) and reduced dead volume, the flow switch would take at least one second. This would mean that a 2 sec sample pulsing of a 3 sec time constant for switching flows on and off must be taken into account. The concentration of the explosives stream must be great enough to overcome any time lag in response.

The estimates given for the makeup of the flow going into the GC and IMS needs to be better defined experimentally. It may not be possible to effectively enrich nitrogen over air in the secondary membrane module, so the carrier flow may not be that pure. In this case, a nitrogen generator would have to be used instead of the second module to provide the constant carrier flow. The width of the sample pulse and necessary separation time before the next pulse makes inefficient use of the explosive sample available in the enriched retentate flow that is being dumped to the drain . In this case, an actual adsorbing trap possibly made up of bundled glass capillary tubes can be used downstream at the outlet of the hollow fiber membrane preconcentrator to trap the low vapor pressure explosives such as RDX and PETN while the other organics that are more volatile flow directly through the intermediate trap down to the drain. When the sampling cycle is turned on the trap could be quickly ramped in temperature to desorb the plastic explosives without degrading taggants or other less stable explosives. However, the design would have to incorporate a low pressure drop collector so as not to impede the remainder of the flow during pulsing and switching. And it would have to be thermally isolated to be continuously cooled, while the sample is being accumulated and heated quickly to desorb during the switch of flows. The nitrogen enriched carrier flow into the GC would also have to be controlled with mass flow meters and a servo loop so as not to affect the stability of the chromatographic peaks. The long term degradation and hang-up of sample by the GC would also have to be included as a factor, since a system such as this is assumed to be operating on line for a long period of time.

In the designs proposed the method of sample introduction may be more complex because of the addition of the GC, but the end result would be a more efficient concentration of the sample to enhance the resolution and detection of the IMS.

Conclusions

The main objective was to present a preliminary design based on known operating conditions and a set of assumptions. The intention was to increase analytical and chemical resolution of the IMS based on a certain set of criteria and specifications. However, there is the possibility for tradeoffs in the design depending on changes in the sampling time interval, the GC sample capacity, and the required membrane selectivity. These tradeoffs can now be evaluated

against this preliminary design to meet the same requirements but additional modeling of the membrane preconcentrator design would have to be done as well as optimizing GC conditions for the best separation and shortest analysis time. The design has been shown to be feasible and as long as other components such as valves, pumps, flow lines, can be better defined and selected from the requirements set forth, then it will be possible to build such a system at low risk.

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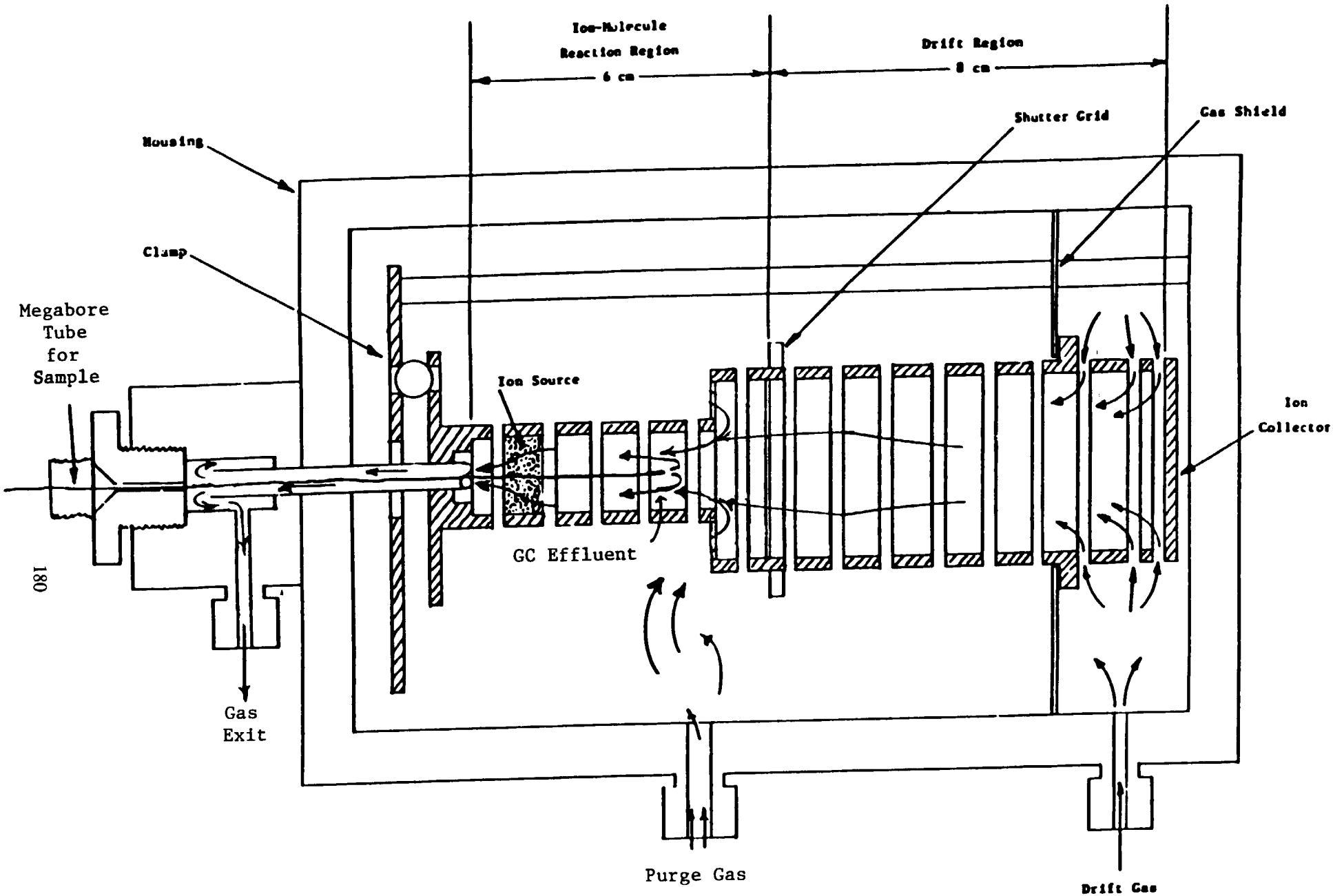


Figure 1. Ion Mobility Cell Modified for GC Inlet for Transfer Line

Carrier gas	Carrier gas pressure-normalized permeation flux ($10^{-6}cm^3/cm^2 \cdot s \cdot cmHg$)	Selectivity gas/toluene	Enrichment	Membrane area (m^2)
Nitrogen	2	14	700	108
Air	4	29	850	53
Carbon dioxide	50	360	987	4.3
Helium	140	1,000	995	1.5

Table 1. Table of vapor enrichment at feed flow rate of 10 L/min, residue flow rate of 10 ml/min, and Temperature of 22 °C.

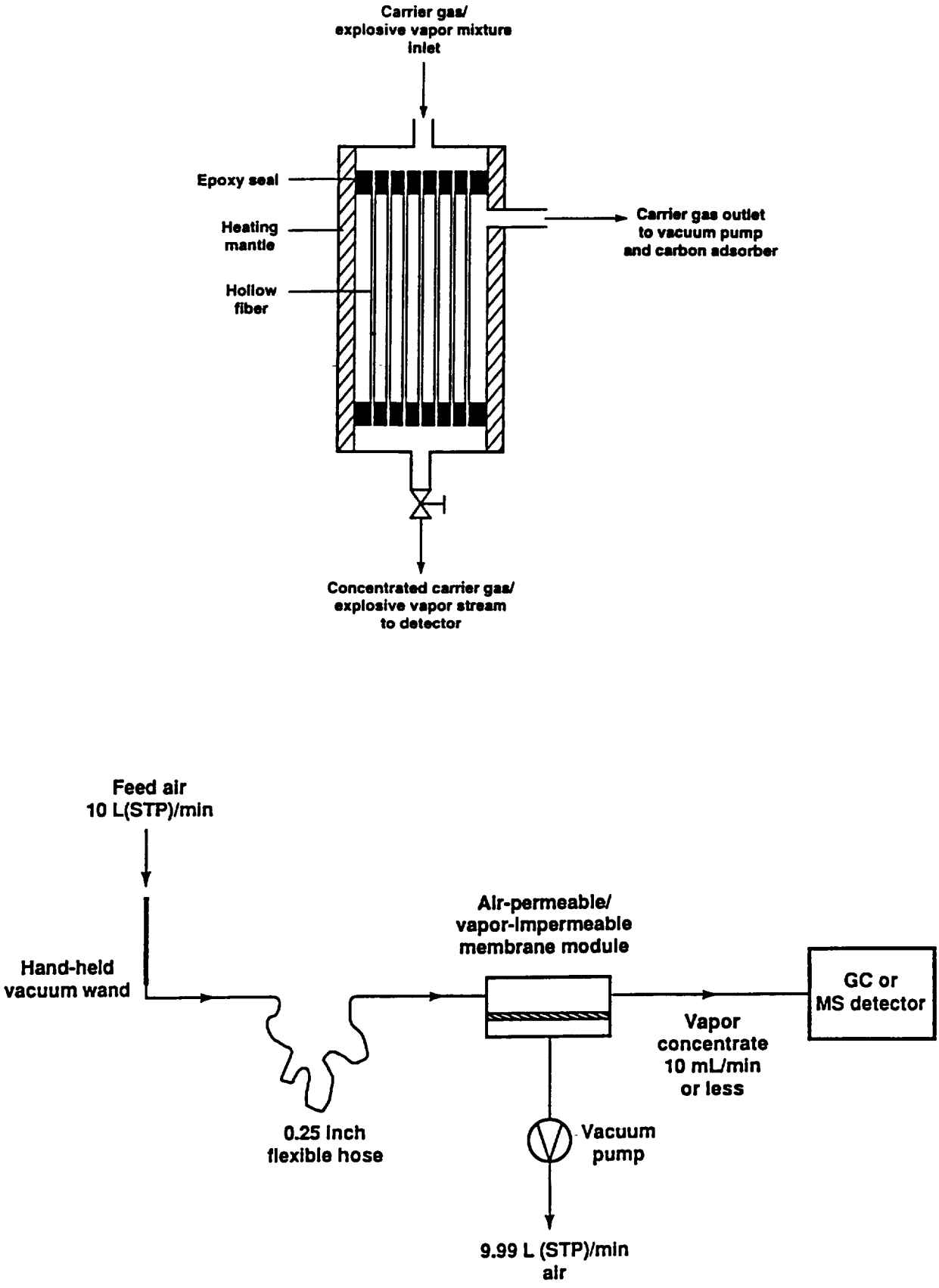


Figure 2. Schematic of a Hollow Fiber Membrane and its Use as a Preconcentrator

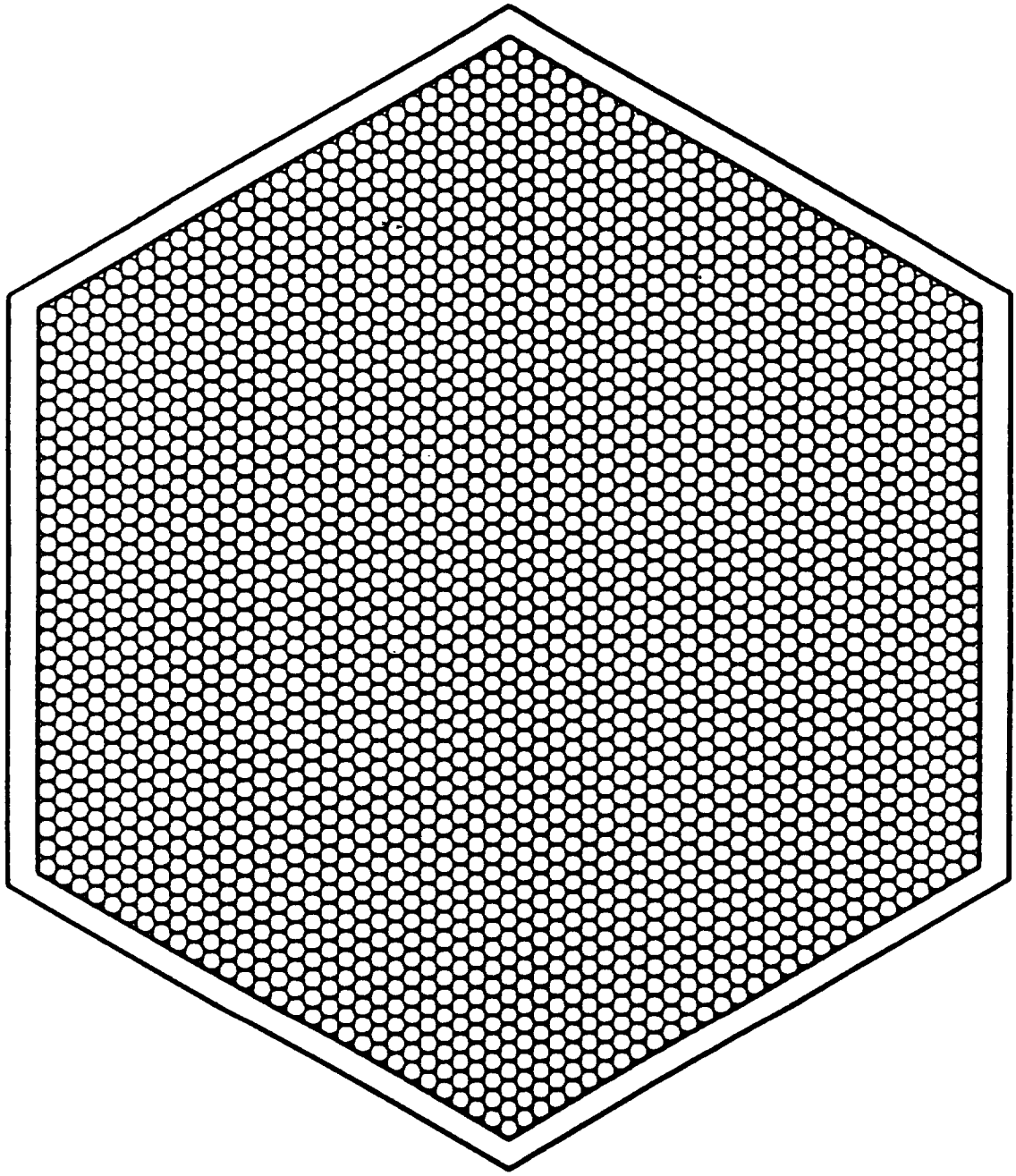


Figure 3. Cross section of a polycapillary column 6 mm width , 20 cm length

GC-Runs of Explosive Vapors (1mg in a 1l-Bottle) and Room-Air-Background

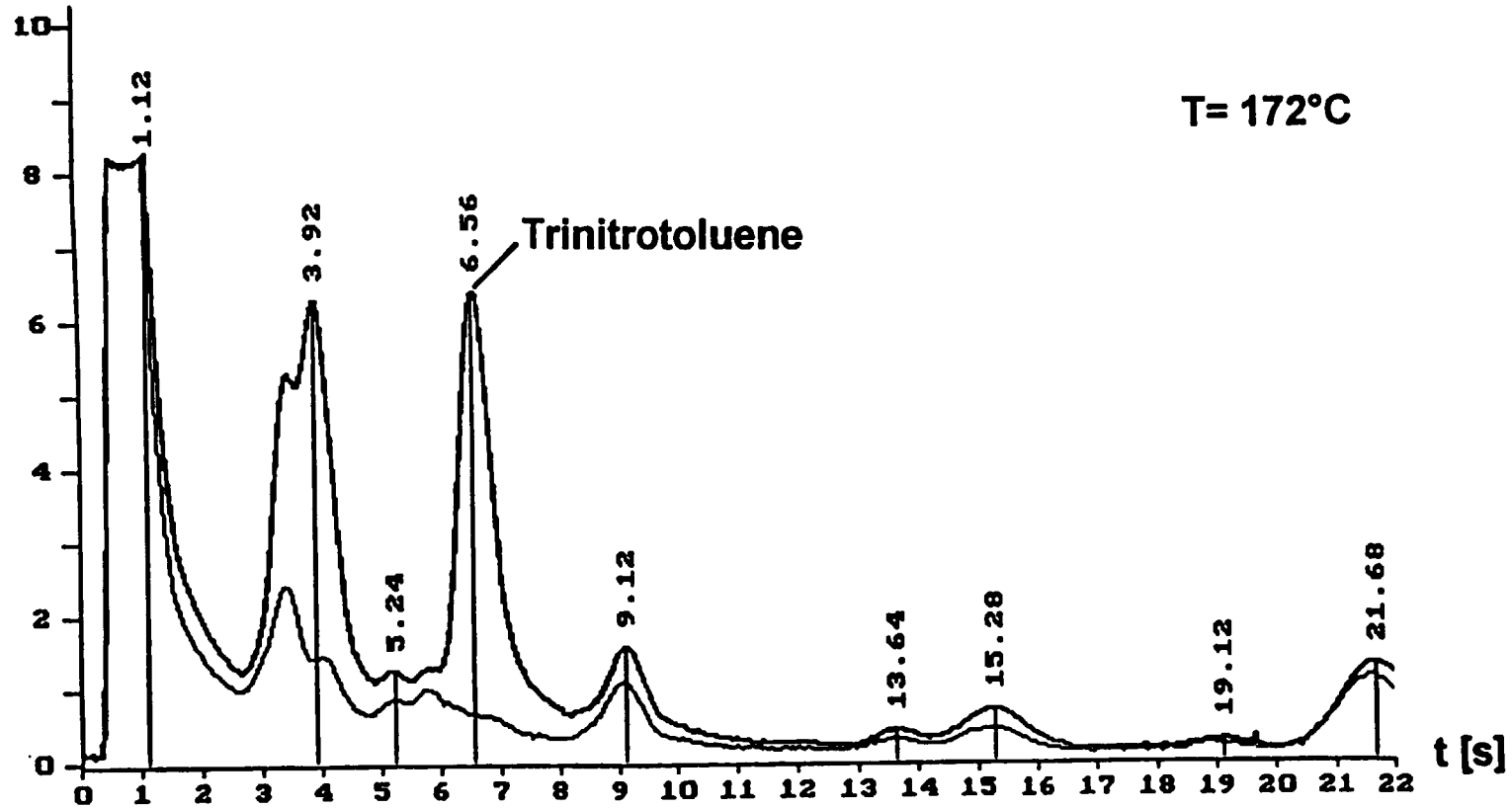


Figure 4. GC Chromatogram: Explosive Vapors sampled directly from room air

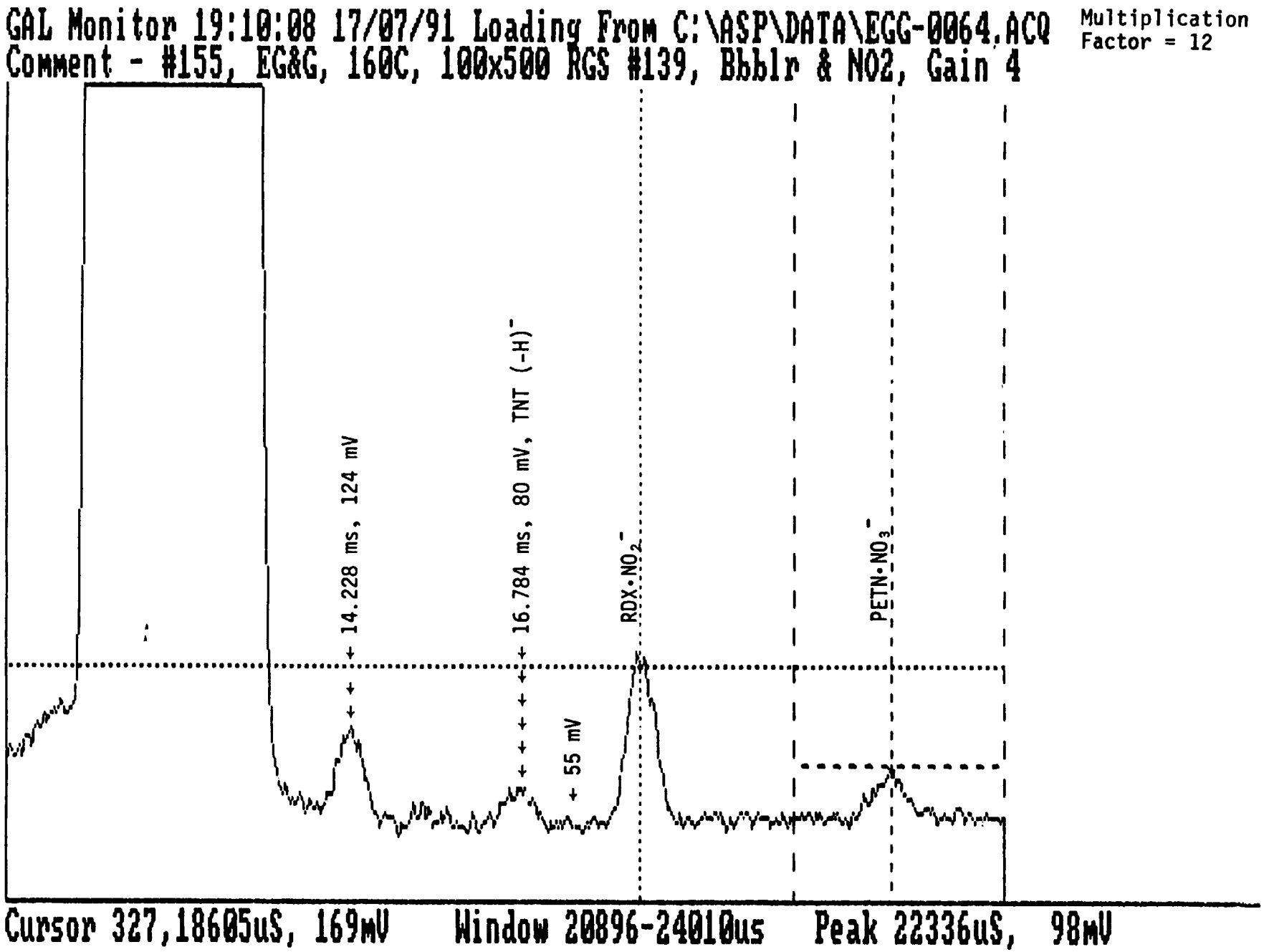


Figure 5. Injection of Solution Containing 50 pg TNT, 50 pg RDX, 75 pg PETN, @ 764 Torr

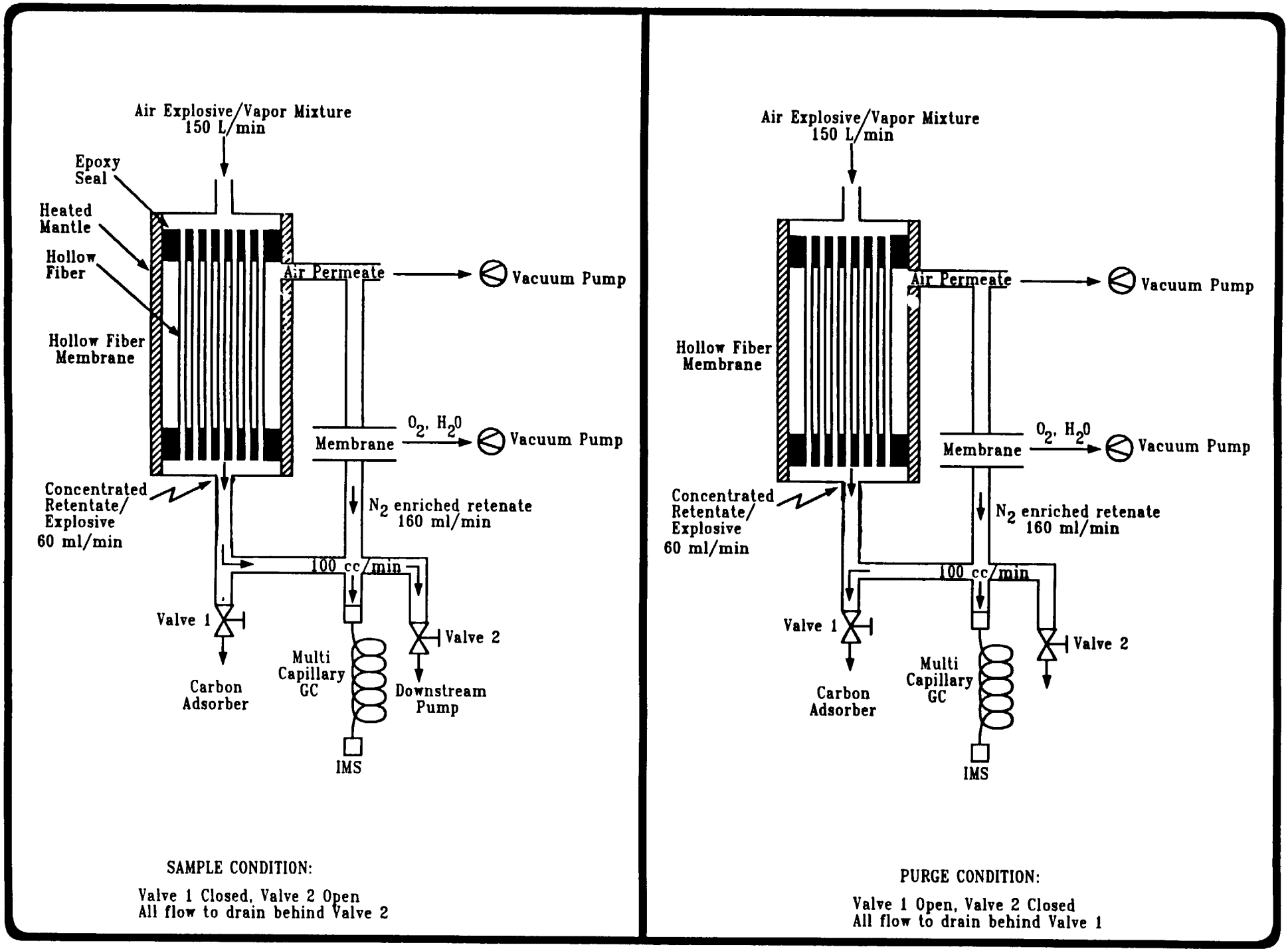
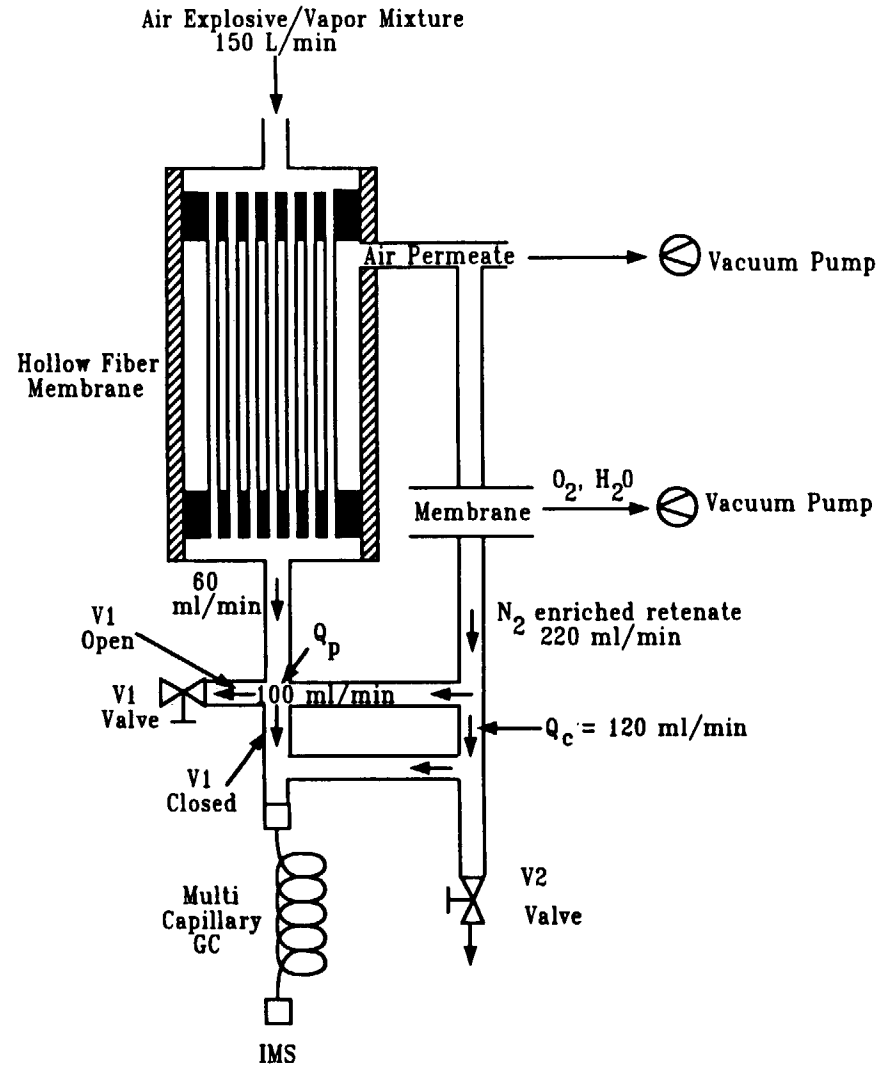


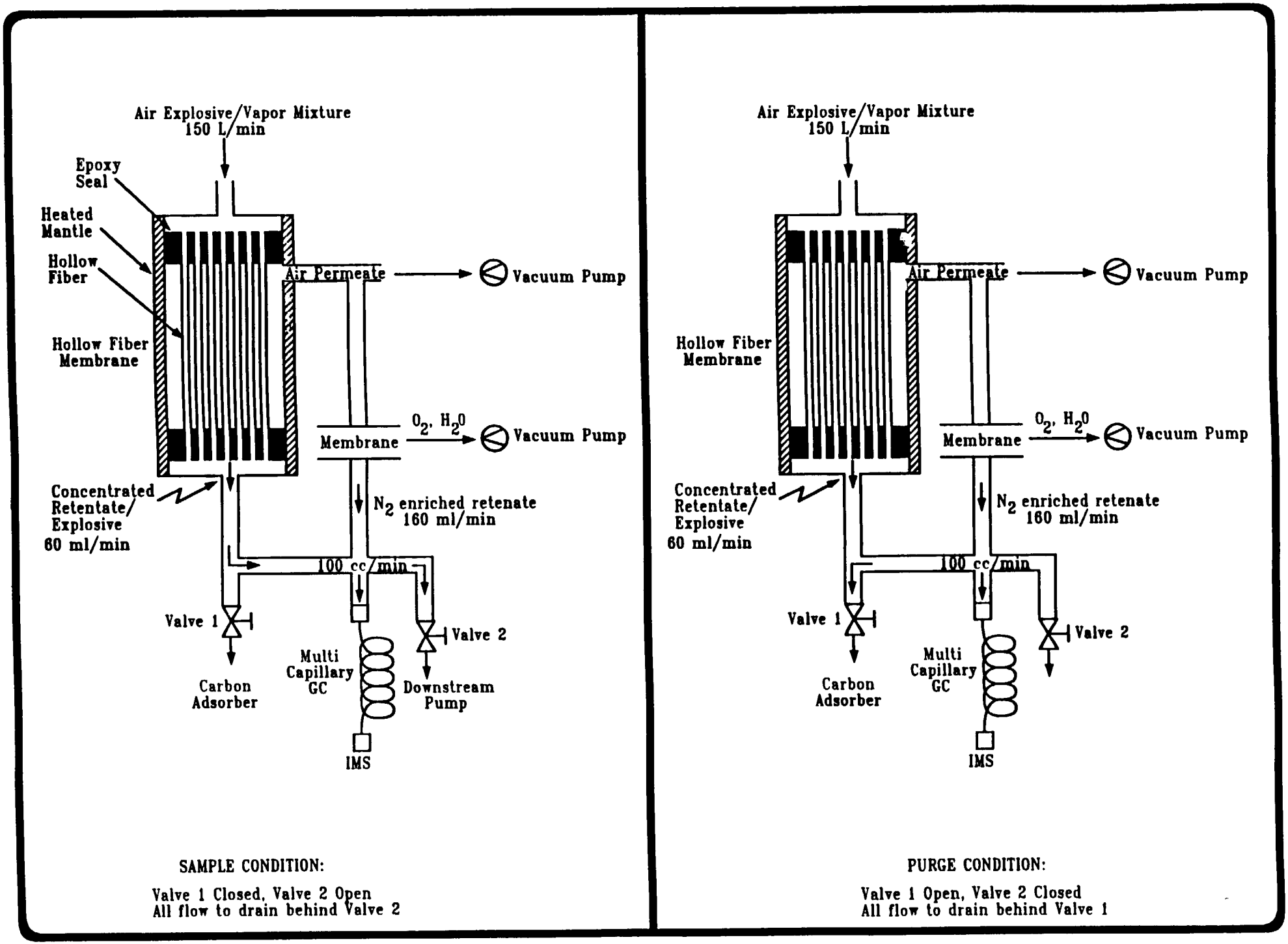
Figure 6. Preconcentrator/GC Interface Schematic



PURGE CONDITION: V1 Open, V2 Closed
Purge Flow Q_p to drain
Carrier Flow Q_c to GC Cloumn

SAMPLE CONDITION: V1 Closed, V2 Open Slightly
Purge Flow Q_p to GC Column
Carrier Flow Q_c to GC Column and Drain

Figure 7. Preconcentrator/GC Interface Schematic



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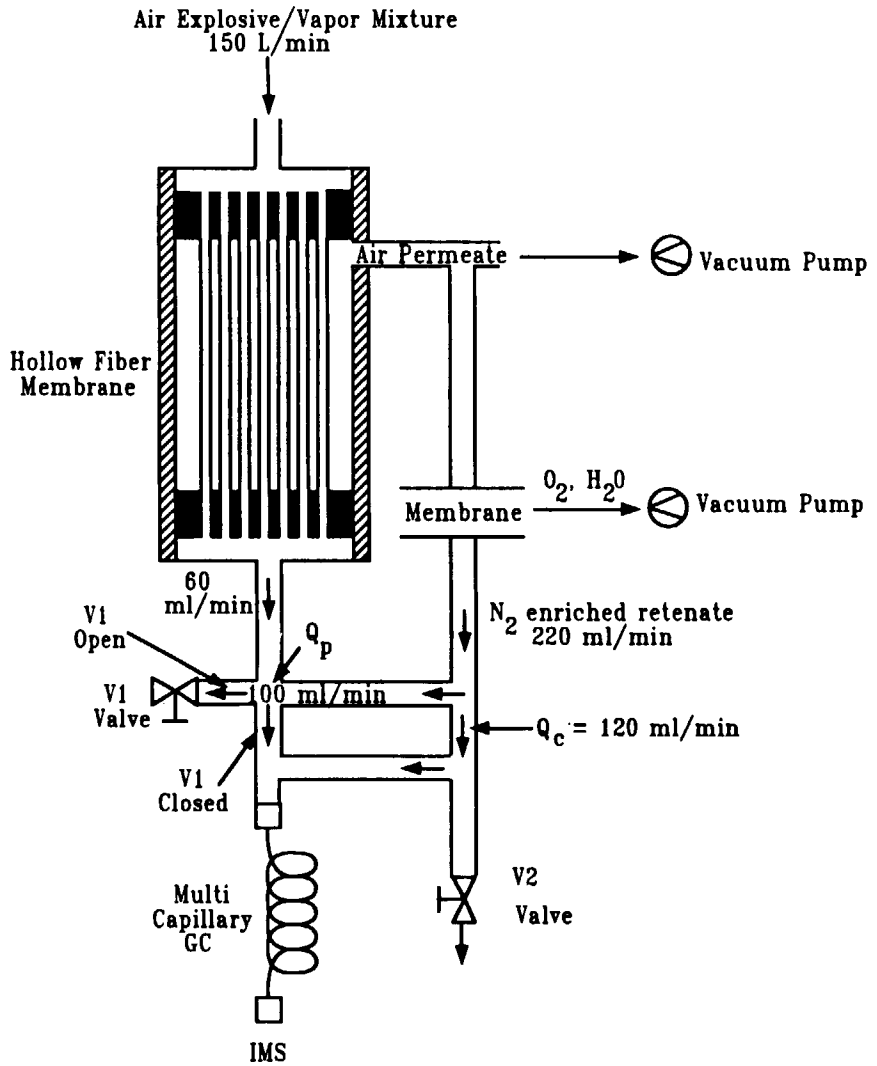

PURGE CONDITION: V1 Open, V2 Closed
Purge Flow Q_p to drain
Carrier Flow Q_c to GC Cloumn

SAMPLE CONDITION: V1 Closed, V2 Open Slightly
Purge Flow Q_p to GC Column
Carrier Flow Q_c to GC Column and Drain

Figure 7. Preconcentrator/GC Interface Schematic