# ANALYTICAL TECHNIQUES AND ANALYSIS OF COAL TARS, WATERS, AND GASES

by

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*Abstract*

*Analytical techniques applicable to coal gasification waste products (tars, waters, and gases) are described. Methodology for the qualitative analysis of these samples involves solvent partition, hplc, and gc-ms.*

## INTRODUCTION

One of the problems inherent in the investigation of a fuel conversion process such as coal gasification, is the development of analytical methodology that will permit an adequate assessment of the potential pollutants from such a process. In the case of laboratory scale gasifiers, this methodology can also be applied as a means of studying the effects of different coals and/or parametric variations on gasification. The need therefore is to develop a scheme which is reproducible, reasonably fast, and which can be applied to both volatile and nonvolatile pollutants (for gasification, those materials collected in tar and water traps located immediately after the reactor are considered nonvolatile, while those materials carried downstream with the gas are considered volatile).

Our appproach utilizes mass spectrometry as a basic means of identification. For volatile materials, components are collected directly from the gas stream onto polymer sorbents from which they are solvent extracted or thermally desorbed and transferred to a gas chromatograph-mass spectrometer-computer (gc-ms-comp). Nonvolatiles are subjected to a solvent partitioning process to separate the mixture into chemically similar groups. Each group is then either analyzed directly by mass spectrometry (ms) or is chromatographed using high performance liquid chromatographic (hplc) techniques and then subjected to ms analysis.

## VOLATILES-QUALITATIVE ANALYSIS

Methodology pertinent to the collection and analysis of organic volatiles has been developed in our laboratories in relation to air pollution studies, and has been described in detail elsewhere.[1] By this process, the volatile organics are collected from the gas stream directly by passage of a portion of the stream through a glass cartridge containing Tenax GC (poly-*p*-2,6-diphenyleneoxide). The adsorbed materials are then removed *in toto* from the Tenax by thermal desorption and helium purge to a cooled (liquid nitrogen) capillary trap (Figure 1). The vapors are then released from the trap by rapid heating to 175 °C, and transferred onto a high resolution capillary gc column. This column is interfaced to a double focusing mass spectrometer. Upon initiation of a run, the mass spectrometer continuously scans the column effluent from 28-400 amu approximately every 7 sec. The information from all scans is then accumulated by an on-line computer onto magnetic tapes. The data acquired includes peak intensities, total ion current (TIC) values and Hall probe signals (instrument calibration indicators). Up to approximately 1,000 spectra can be stored during a single analysis.

Processing the mass spectrometric data involves extraction of the TIC data and plotting TIC against the spectrum number. This yields a chromatogram which will generally indicate whether the run is suitable for further processing since it will give some idea of the number of unknowns in the sample and the resolution obtained using the particular gc column conditions. The computer is then directed to generate mass spectral plots of compound(s) represented by individual peaks in the TIC plot. Mass spectral plots consist of a plot of mass *vs* ion intensity and represent the characteristic mass spectra of the component(s).

Identification of resolved components can be

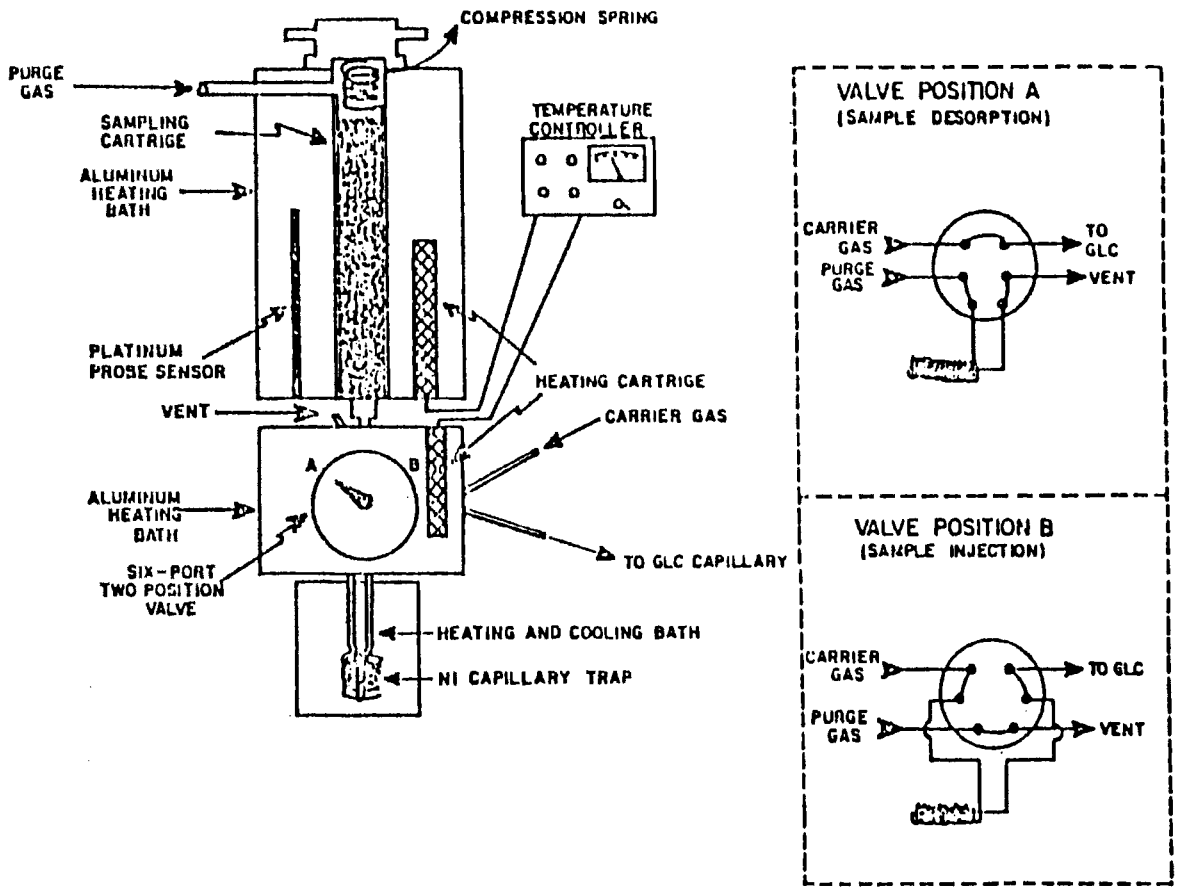


**Figure 1. Thermal desorption inlet-manifold.**

achieved by comparing the mass cracking patterns of the unknown mass spectra to an eight major peak index of mass spectra.[2] Individual difficult unknowns can be searched by use of various computerized systems such as Cornell University's PMB or STIRS systems, or the EPA MSSS. When feasible, the identification can be confirmed by comparing the unknown cracking pattern and elution temperature on two different gc columns with authentic compounds.

The treatment of volatile organics in the manner discussed has been applied not only to air samples, for which the process was developed, but to *in situ* coal gasification effluents. For the latter, some 200 neutral components have been identified. The method is reasonably sensitive; successful identification can be achieved with ~200 ng of individual component transferred onto the capillary column.

## NONVOLATILES-QUALITATIVE ANALYSIS

The nonvolatile organics comprise those materials associated with the condensed tars and waters as isolated by in-line traps. These substances are exceedingly complex[3] and require fractionation before direct analysis can be undertaken. Other investigators have utilized either of two procedures for this process, column chromatography or solvent partition. Chromatographic methods separate the crude material into fractions of like polarity and can function as a useful means of reducing a complex sample into one or more manageable proportions.[4] Solvent partition schemes have been devised, most notably by researchers from the tobacco industry[5], in which group separations are accomplished on the basis of similar chemical properties, e.g., acids, bases, etc.

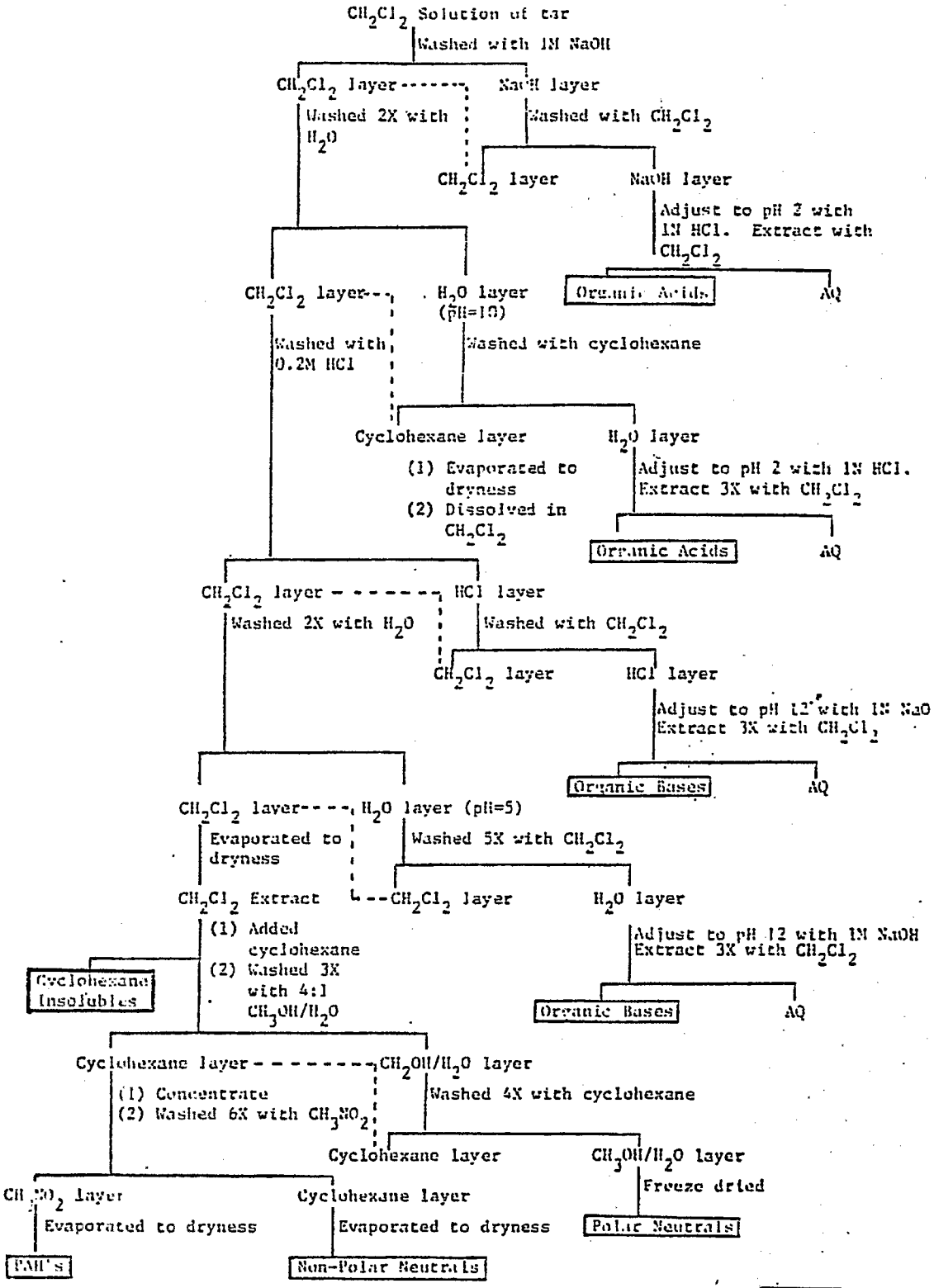




**Figure 2. Tar sample partition scheme.**

The latter approach seems more practical, particularly if fractions are to be derivatized or chromatographed further. The basic procedure adapted for use in our laboratories is depicted in Figure 2, and is a modification of a method utilized by Novotny[6] for air particulate extracts. Application of the scheme to three different gasifier coal tars produced the product distribution shown in Table 1. That the scheme provides generally good reproducibility was demonstrated by application of the process to identical aliquots from the same tar samples.

With the sample thus divided into chemically similar groups, derivatization and chromatographic techniques are applied as dictated by class properties or complexity of individual fractions. Thus the organic acid fraction is treated with diazomethane and dimethyl sulphate to convert carboxylic acids to esters and aromatic hydroxyls to methyl ethers. The compounds are then sufficiently volatile for gc analysis.

The remaining fractions are in most cases not amenable to direct gc analysis either because of the large number of components present or because of the presence of nonvolatile materials. Liquid chromatographic techniques are indicated here, especially hplc. This technique embraces virtually all forms of liquid chromatography, i.e., adsorption partition, ion-exchange and gel permeation, and is desirable chiefly because of the relatively high efficiencies obtainable with currently manufactured hplc columns. Although reverse-phase modes of chromatography have been shown to be very useful with regard to the separation of certain types of environmentally important compounds, the use of aqueous solvents is generally undesirable if the sample is to be recovered for further work. Consequently, we have explored primarily the use of adsorption and gel permeation modes as a means of further fractionating the partitioned samples.

**TABLE 1**

**CLASS DISTRIBUTION OF COAL TAR SAMPLES AFTER SOLVENT PARTITION (WGT. %)**

| Sample | H-1 | B-1 | B-2 |
|---|---|---|---|
| Acids | 14.2 | 3.4 | 2.7 |
| Bases | 1.3 | 41.9 | 1.5 |
| Cyclohexane Insolubles | 13.6 | 13.5 | 4.4 |
| Polar Neutrals | 12.1 | 5.6 | 8.6 |
| Non-Polar Neutrals | 3.2 | 7.5 | 20.1 |
| PNA Hydrocarbons | 18.2 | 22.8 | 38.9 |

Silica gel columns provide separation of the components of a given fraction based on the relative polarities of the individual compounds. Columns can be easily tailored for specific use by varying the column dimensions, the nature (and hence activity) of the silica packing, and the diameter of the particles used. Thus to effect a rapid clean-up of the PNA fraction (Figure 2), a large particle (37-75 micron) column of modest efficiency is sufficient for effecting the separation of PNA compounds, as a group, from more polar, non-PNA materials. This chromatographic step enriches the PNA fraction by removing approximately 1/3 of the total mass associated with the fraction. This greatly reduces problems relating to the analysis of the PNA's themselves. A sample of this enriched fraction was analyzed at this point by gc-ms. The ion plot is shown in Figure 3. Although many individual PNA compounds were identified from the mass spectra generated from this run, a better resolved chromatogram is desirable particularly from a standpoint of quantitation.

Further separations can be accomplished by injection of the enriched fraction onto a high efficiency (10,000-15,000 plates/meter), silica column, and collecting individual cuts for gc-ms analysis. The results of this hplc run are shown in Figure 4. Detection of eluting components was accomplished by monitoring uv absorbance (254 nm). The gc-ms analysis of the collected and concentrated cuts is not yet available. Although silica gel columns were used here and can in all probability be applied to other fractions, other materials such as alumina or bonded phase columns may also prove effective.

Another chromatographic procedure can be utilized to simplify the complex fractions as obtained from the partition scheme. Gel permeation has been used by many workers[6,7] and has in the past been characterized by low efficien-

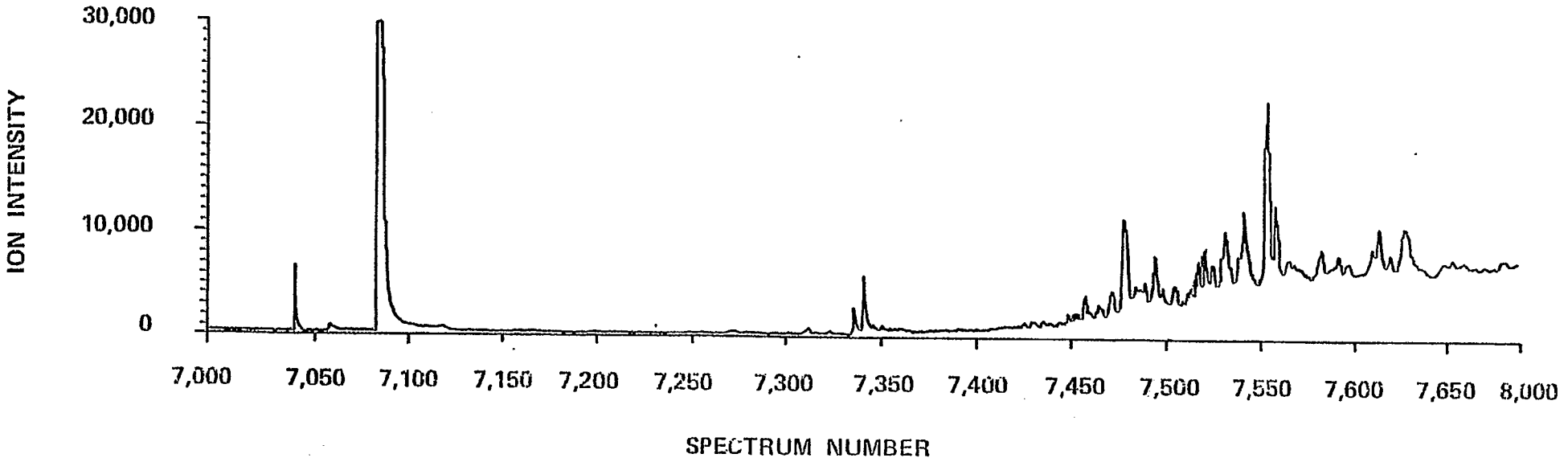


**Figure 3. Ion plot of PNA enriched fraction. OV-101 capillary.**

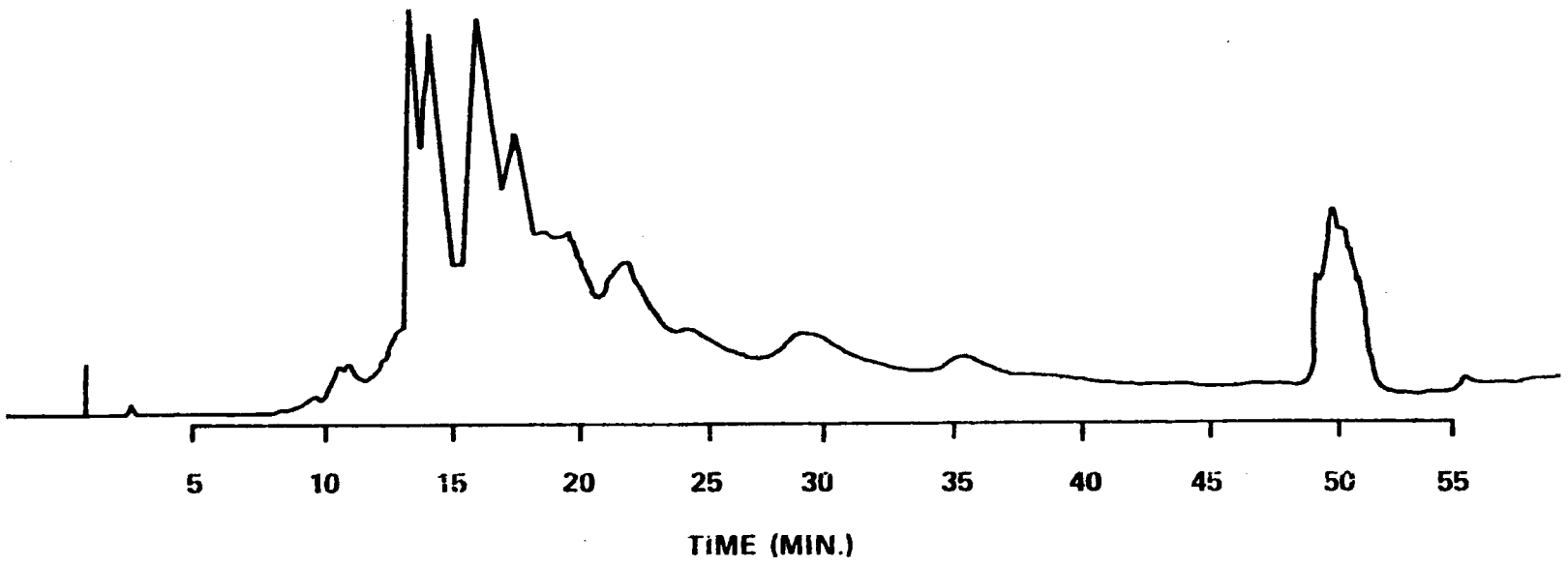


**Figure 4. Hplc (silica) of PNA fraction.**

cies and long run times. Recent developments in column technology now bring the advantages of hplc to this mode of chromatography. Thus fractions from the partition scheme can be subjected to gpc directly with compound separations made on the basis of molecular size. Since in a given chemical class molecular size correlates well with volatility, some information pertinent to subsequent gc-ms or ms analysis can be obtained from the chromatography. When the PNA fraction was chromatographed on a single gpc column, (μStyragel® - 100A pore size), the chromatogram depicted in Figure 5 was obtained. The large number of components and the continuum of molecular sizes combined to produce only a single undefined major peak, however arbitrary cuts of the column effluent will undoubtedly provide greatly simplified samples for subsequent analysis.

The coal gasification process produces by-product water in sizeable quantities and, since this water can be used as recycle cooling water, methods for its purification are being ex-

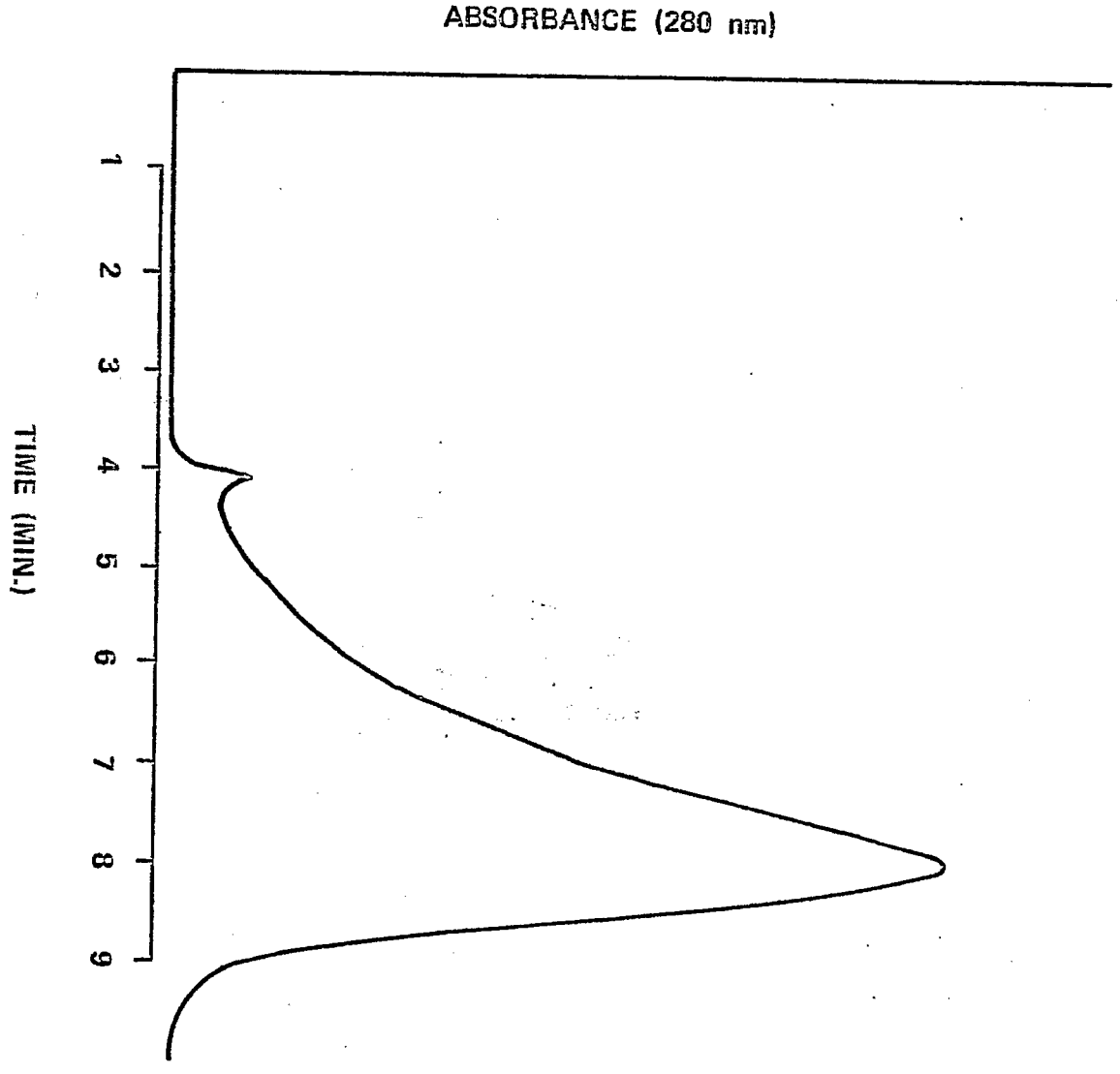


Figure 5. Gpc (μStyragel) of PNA enriched fraction.

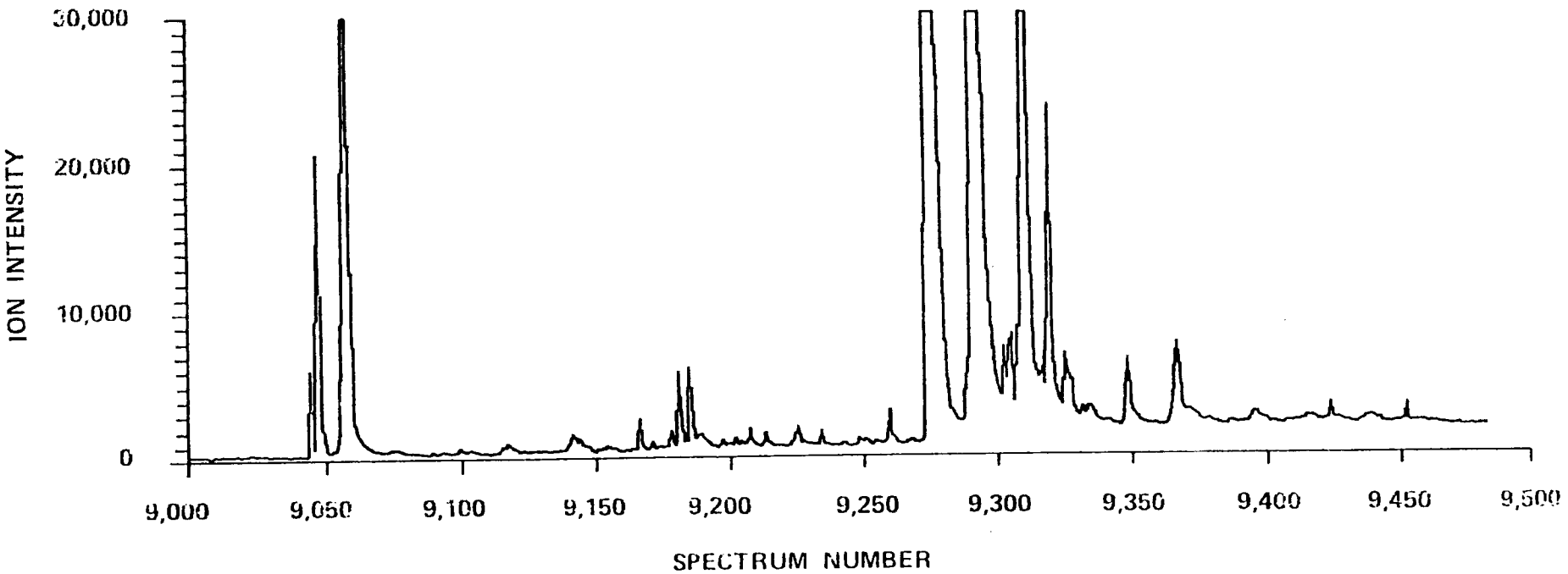


**Figure 6. Ion plot of condensed water extract following derivatization Carbowax capillary.**

plored. This involves a detailed knowledge of the contaminants which can comprise from 0.6-2.4 percent (by weight) of the condensate. This extractable material appears to be largely phenolic.[3] Thus after solvent extraction (methylene chloride) of a portion of the collected waters, the residue is subjected to treatment with diazomethane and dimethyl sulphate which converts the phenolic materials to aromatic methyl ethers. These compounds are amenable to high resolution gc-ms analysis, and can be thus analyzed without further processing. Treatment of a sample of condensate waters in our laboratories by the method described resulted in the TIC plot shown in Figure 6. Cursory examination of selected mass plots identified several aromatic alcohols including seven alkylated isomers of phenol. Other types of materials such as alkyl and aromatic ketones, carboxylic acids, and nitrogen-containing aromatics (1-2 ring) were also identified. Future runs will employ gc columns of increased resolution and selectivity. The methodology for the condensate waters appears adequate at this point for the tasks of identifying the contaminants of byproduct waters.

## CONCLUSIONS

Although optimization of the methodological schemes presented above has yet to be finalized, the basic procedures have been shown to be practical and can be summarized as follows.

*Volatiles:* Methodology consists of collection of volatile components on polymer sorbents, transfer to high resolution gc-ms-comp systems for identification, and quantitation.

*Nonvolatiles-Tars*: Methodology consists of separating tars into groups of chemically similar materials by solvent partition. Organic acids are derivatized then analyzed by gc-ms. Other groups are further fractionated by hplc using either gpc or partition chromatography. Collected subfractions are then analyzed by gc-ms or ms.

*Nonvolatiles-Waters*: Methodology consists of derivatization of extracted material followed by gc/ms analysis.

Much work remains before the approaches detailed here can be considered as complete and final. This is particularly true of the tar samples. Specific problems requiring additional fundamental research efforts include the study of materials that are too thermally labile or too nonvolatile for gc-ms analysis, and the problem of quantitation of individual components. Both of these topics will be the subject of future work relating to the analysis of environmentally important materials produced during coal gasification.

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