GAS CHROMATOGRAPHY/MASS SPECTROMETRY APPLIED TO PRINTING INK PROBLEM

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Abstract: The analytical technique of computerized gas chromatography/mass spectrometry (GC/MS) will be demonstrated to be an invaluable technique for solving a wide range of graphic arts related problems. Such instrumentation provides for the separation and unequivocal identification of complex chemical species. This paper will describe the utilization of a Hewlett Packard 5985 GC/MS in the following applications. (1) Its use for the identification and quantitation of specific polynuclear aromatic hydrocarbons in complex ink raw material ingredients. (2) The identification and quantitation of volatile compounds such as those retained on printed substrates or those found in the printing process environment. (3) The adaptability of GC/MS for the identification of monomers and oligomers used in radiation curing coatings and inks.

INTRODUCTION

The subject of this paper deals with the application of gas chromatography/mass spectrometry (GC/MS) as a technique for analyzing printing ink related problems. By way of background, there are a number of fundamental considerations that are basic to the presentation of this topic.

To begin with, printing inks themselves are highly formulated mixtures of various raw materials consisting of pigments, resins, solvents and performance additives of all kinds. In turn, these individual components are often complex chemical species in their own right. Furthermore, as an ink, the combination of these components may have one hundredfold differences in concentration ranges with respect to each other.

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Finally, the numerous processes and substrates utilized in printing can broaden the scope of the challenge for analyzing ink.

Over the years, a variety of conventional instrumental and wet techniques as well as some unique separation procedures have been used. The instrumental techniques include infrared spectroscopy, ultraviolet spectroscopy, nuclear magnetic resonance spectroscopy, gas chromatography, liquid chromatography and others. Unfortunately, even with all of these advanced techniques, many problems still go unanswered. This means that there is a constant need to develop new methodology for the solution of analytical problems related to printing ink.

GC/MS is an instrumental technique that has been used successfully by our laboratories over the past two years to broaden the scope of our work. It has allowed us to accomplish several specific goals. In its simplest application, it can improve upon existing methodologies. In this regard GC/MS has provided increased speed (i.e., greater sample throughput), definitive, qualitative results, a high degree of sensitivity, and a unique selectivity for components in complex sample matrices. In other circumstances GC/MS can provide unique solutions to problems that could not be solved prior to the introduction of this technique. Lastly, GC/MS may also function as a basic research and development tool to study, monitor and relate chemical structure to product performance both on and post-press.

DESCRIPTION OF GC/MS

The modern GC/MS (see Figure 1) represents a marriage of several diverse and powerful technologies. These are gas chromatography (GC), mass spectrometry (MS) and a computerized data handling system (DS). Gas chromatography, of course, is an instrumental technique which separates various components of a complex "volatile" mixture into its constituent parts. Mass spectrometry is an analytical technique that can reveal specific, structurally related information about a compound. The data system is used to acquire, manipulate and present the mass spectral data in an intelligible format.

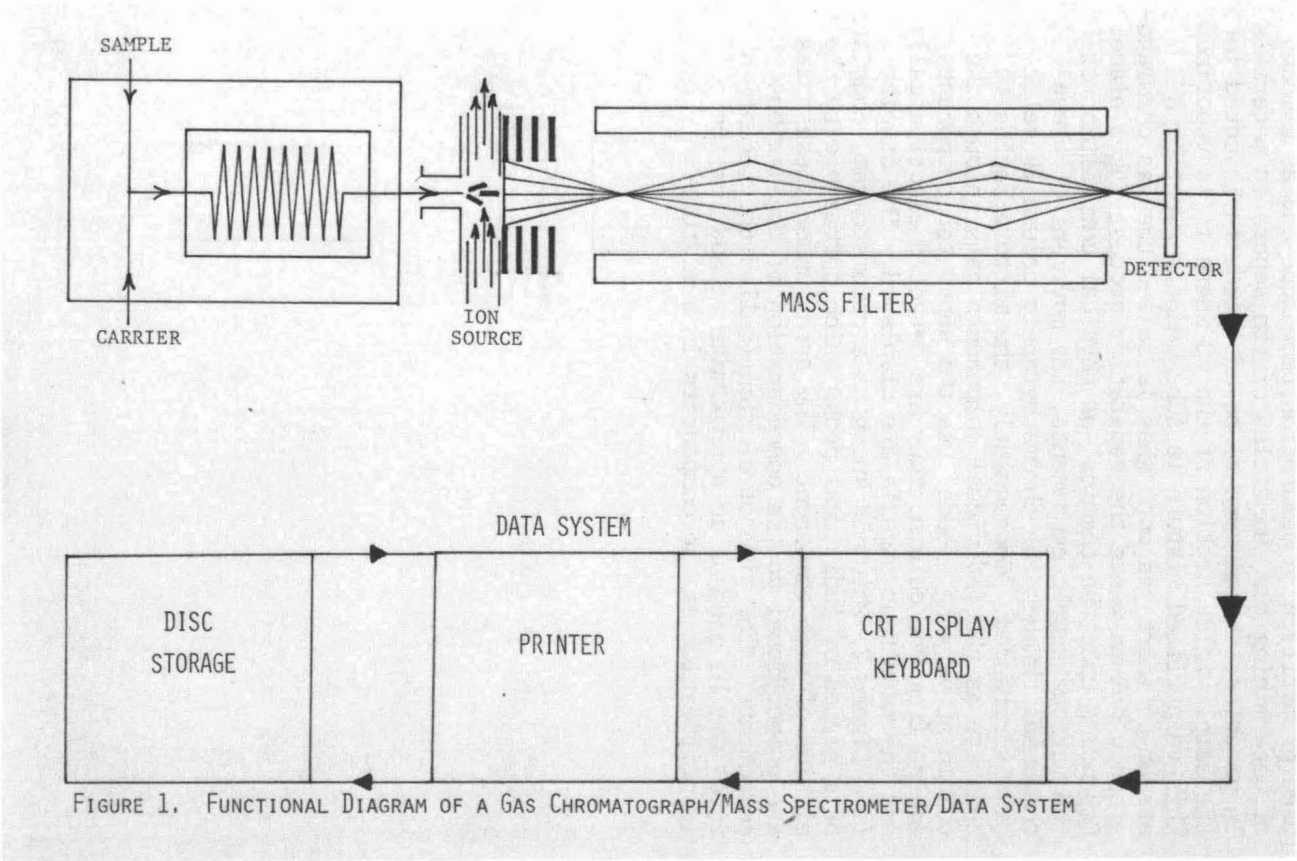

FIGURE 1. FUNCTIONAL DIAGRAM OF A GAS CHROMATOGRAPH/MASS SPECTROMETER/DATA SYSTEM

Gas chromatography, as a stand-alone instrument, is used primarily as a separation technique and as a means of determining the quantities of the separated materials. In practice, the mixture to be analyzed, is injected into the sample inlet section of the GC where it is vaporized. This volatilized mixture is subsequently swept by a stream of inert gas onto what is called the gas chromatographic column where the separation process takes place. Depending upon the chemical or physical composition of the various sample components, the movement of these compounds through the chromatographic column is selectively retarded. Consequently, the mixture begins to separate as the individual components pass through the column at varying speeds. As the separated components emerge from the column, they are detected electronically and the resultant signals are displayed. The display (see Figure 2) which is known as a chromatogram, consists of a series of individual peaks which correspond to the elution of each component. The areas under these peaks are proportional to the concentration of the various components. The time of elution (called the retention time) may be used as an approximate method for the identification of the components in a mixture.

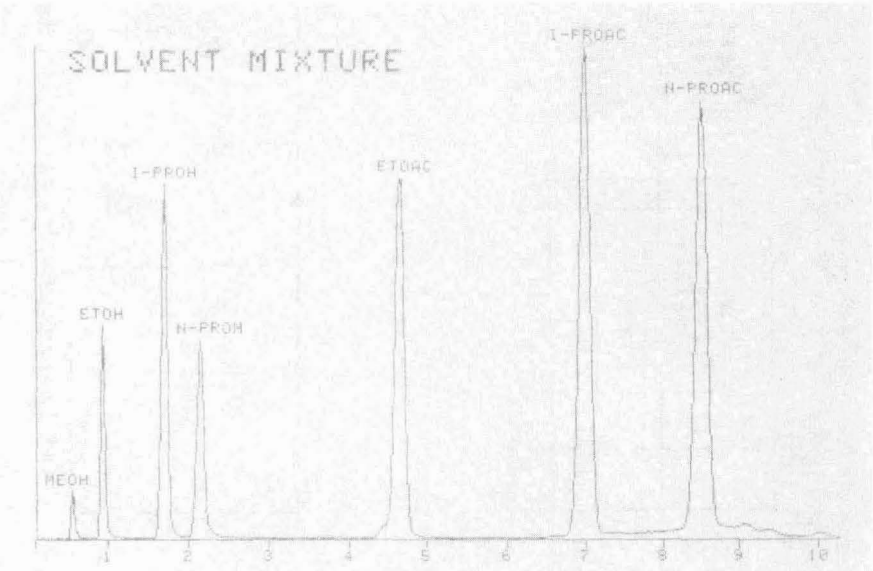

Figure 2. A Typical Gas Chromatogram of a Solvent Mixture.

Mass spectrometry is an analytical technique which is used to determine structural information about a given compound. The basic function of a mass spectrometer is to produce charged particles (ions) from a sample and then separate these ions according to their mass-to-charge ratio (m/e). Molecules from the sample to be analyzed are introduced into a section of the mass spectrometer called the ion source where they are bombarded by a high energy electron beam and broken apart into charged molecular fragments. In many instances, these fragments (or ions) can be related directly to functional groups or structural components of the original molecule. Furthermore, the array of fragment ions represents a unique and a distinctive pattern that is dependent upon the structure of the parent molecule.

The graphical representation of the masses and abundances of the various ions produced from a given molecule (i.e., the fragmentation pattern) is known as a mass spectrum. A typical mass spectrum (in this case Benzophenone) may be seen in Figure 3, where the abscissa represents the molecular weight of the ion fragments divided by the charge, and the ordinate represents the relative intensity of these ions. In this example we see that Benzophenone has three major peaks (ion fragments). The heaviest ion in the spectrum is at m/e 182 which is known as the molecular ion and represents the loss of

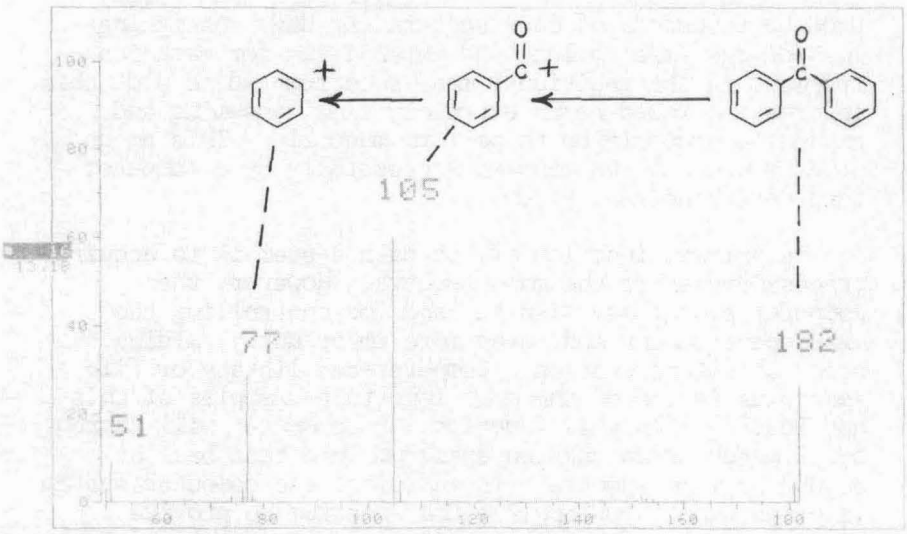

Figure 3. A Typical Mass Spectrum; e.g. Benzophenone

a single electron from the molecule. The other, lower molecular weight ions at m/e 105, and m/e 77, respectively, represent the various fragment ions formed by the cleavage of bonds in the molecular ion. It is important to remember that each molecule ruptures in a reproducible fashion common to its original structure. Therefore, one can either use this fragmentation pattern (mass spectrum) to derive the structure of the parent molecule or simply regard it as a unique finger-print of the original molecule.

Individually, both the gas chromatograph and the mass spectrometer have several severe limitations. The gas chromatograph has problems qualitatively analyzing complex mixtures of unknowns. The mass spectrometer requires samples to be relatively pure, otherwise ions from unrelated compounds will be detrimental to the interpretation of the spectrum. When the two disciplines described above are combined to form one system, the resultant instrument produced (i.e., the GC/MS), is now able to separate the components of a mixture from other potentially interfering components and unequivocally identify each separated component. In this respect, this single new instrument is more powerful than either of the two component parts.

The last element in this instrumental unit is the computerized data system. The modern GC/MS produces a tremendous amount of data. A single GC/MS can easily produce thousands of mass spectra per day. Assigning mass/charge (m/e) values and intensities for each ion fragment in the individual mass spectrum and to plot this information would be an extremely time consuming and expensive proposition to perform manually. This amount of data can only be managed successfully by a computerized data handling system.

The primary function of the data system is to acquire, process and store the mass spectra. However, the computer system may also be used for controlling the mass spectrometer and, even more importantly, aiding the spectral interpretation. Computerized library or file searching is one of the most important examples of this application. In this function, the computer will search for a match of an unknown spectrum in a data base of 30,000 or more spectra. In addition, the computer system is often used to manipulate the spectrum to provide greater clarity for interpretation or presentation of the

data. Several examples of this will be seen in the body of the paper. A typical computerized data system for a mass spectrometer will consist of:

A.) A dedicated mini-computer which is essentially the heart of the system.

B.) An interactive CRT video terminal which is used to both control the GC/MS and display the data.

C.) A printer to produce hard copies of the displayed data.

D.) A memory storage device (i.e., a disc drive) to store and file all the data acquired.

APPLICATIONS

Polynuclear Aromatics

The applications for which GC/MS/DS may be used have been quite extensive in our laboratories. An interesting example of an effort to improve an existing analytical methodology is the analysis of polynuclear aromatic compounds (PNA's). In general, when analyzing for these specific compounds in ink raw materials, we find ourselves in a situation where the PNA species to be determined are present in trace quantities within a complex sample matrix.

Published literature on this subject indicates that this type of analysis has been attempted with varying degrees of success by several different methods, principally, gas chromatography and/or liquid chromatography. Usually, these methods also require extensive sample preparation by either solvent extraction techniques or preparative liquid chromatography. Even with optimum sample preparation, however, somewhere in the order of up to 10% of the original sample matrix remains with the compounds of interest. This residual material will quite often interfere with any subsequent analysis by either preventing accurate quantitation or producing erroneous data.

In our work we were interested in determining the presence of specific PNA compounds in high boiling hydrocarbon oil distillation cuts. Several of the standard approaches were tried with marginal success. The main difficulty appeared to be in obtaining reliable quantitative data below 10 parts per million for selected polynuclear aromatic compounds. The ultimate aim of our work was to bypass the time consuming preparative steps and develop a method for the direct analysis of selected PNA compounds. In our efforts to accomplish this we chose Benzo(a)pyrene as a benchmark compound for the analysis.

Our approach was to rely upon a gas chromatographic column that would isolate polynuclear aromatic compounds from the sample matrix and then use the mass spectrometer/data system to detect and enhance the PNA's that were present. In practice a sample of oil is injected directly into the GC/MS/DS equipped with a unique chromatographic column. This column, which is coated with a liquid crystal phase, has the ability to separate saturated hydrocarbons from polynuclear aromatics. In Figure 4a you see an example of standard PNA's run on this column. You will note that Benzo(a)pyrene elutes at 12.7 minutes. In Figure 4b we have a chromatogram of an ink oil sample. You will note that this curve shows no evidence of a peak at the retention time characteristic for Benzo(a)pyrene. The reason for this is that the baseline noise of the gas chromatograph far exceeds the contribution to the detector signal from the very trace amounts of BAP in our sample. However, there are ways to resolve this signal from the background noise.

A unique feature of this instrument is that we can adjust the selectivity of the mass spectrometer to achieve high sensitivity for a specific compound. This is accomplished by tuning the analyzer section of the mass spectrometer to respond to a specific ion or series of ions characteristic of the compound of interest. In this particular case, the analyzer was tuned to 252 mass units which is the largest mass fragment for the compound Benzo(a)pyrene. You will note Figure 5 where the ink oil sample has been rerun looking only for mass 252. This curve now clearly indicates a peak at 12.7 minutes retention time which is characteristic of B(a)P. This technique is known as selected ion monitoring (SIM). In the same chromatogram one also observes that we have now

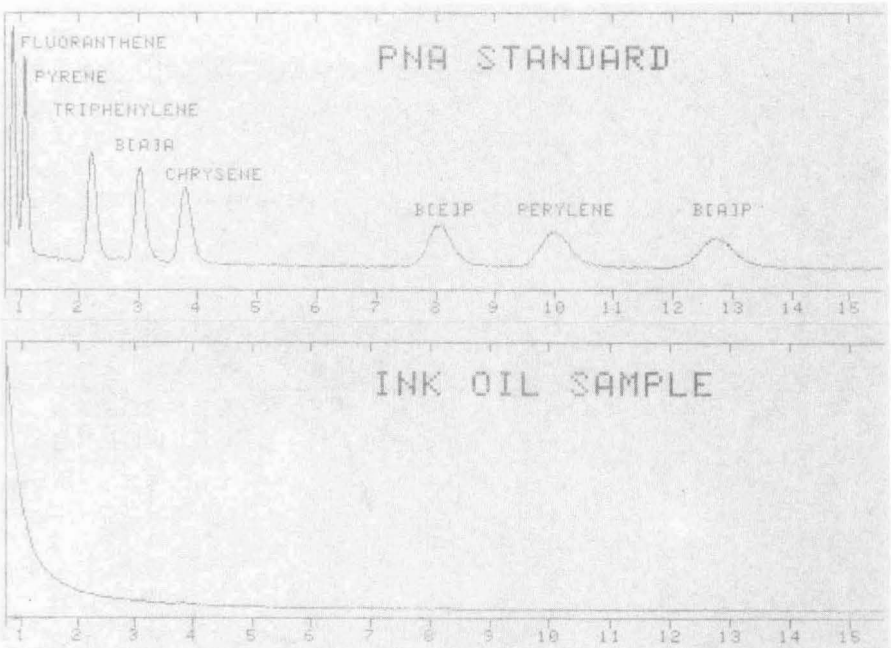

Figure 4. Samples Run on Liquid Crystal Column
a) Standard PNA Mixture (Top)
b) Ink Oil Sample (Bottom)

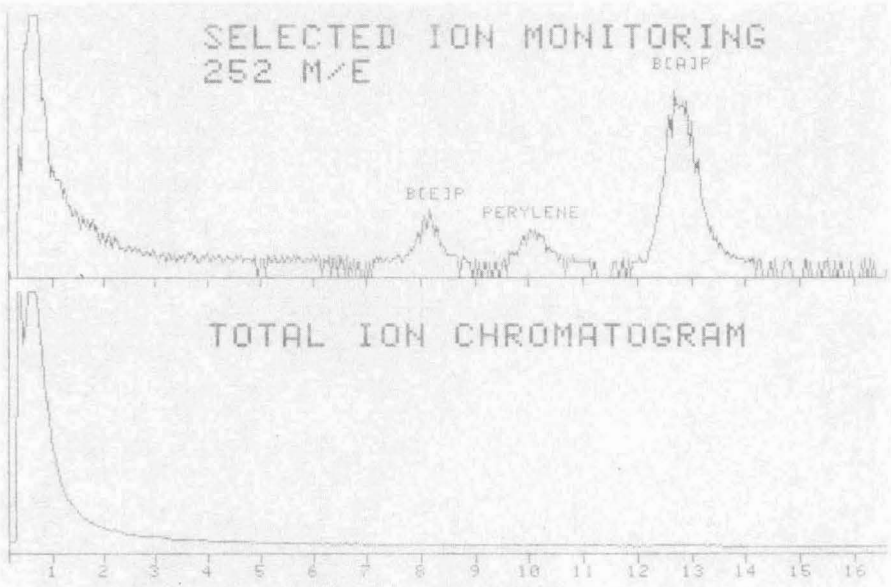

Figure 5. Ink Oil Run on Liquid Crystal Column
a) Selective Ion Monitoring Mode (Top)
b) Normal Mode (Bottom)

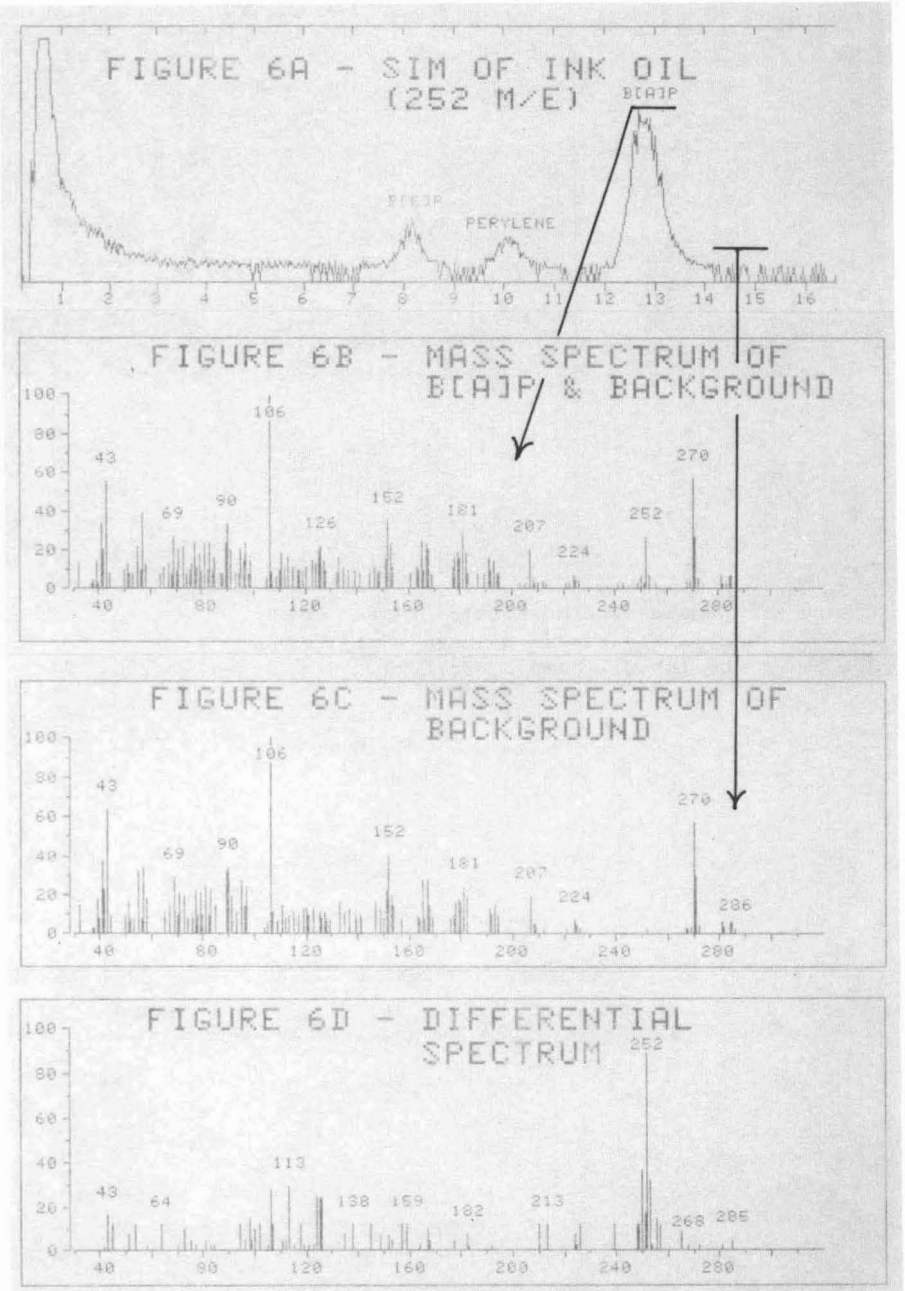

Figure 6. Example of Subtraction of Mass Spectra

detected several other PNA compounds with the same major mass fragment (Benzo(e)pyrene and Perylene). This method could be extended to determine virtually any other PNA in a given sample by simply selecting the proper ion or ion series to monitor.

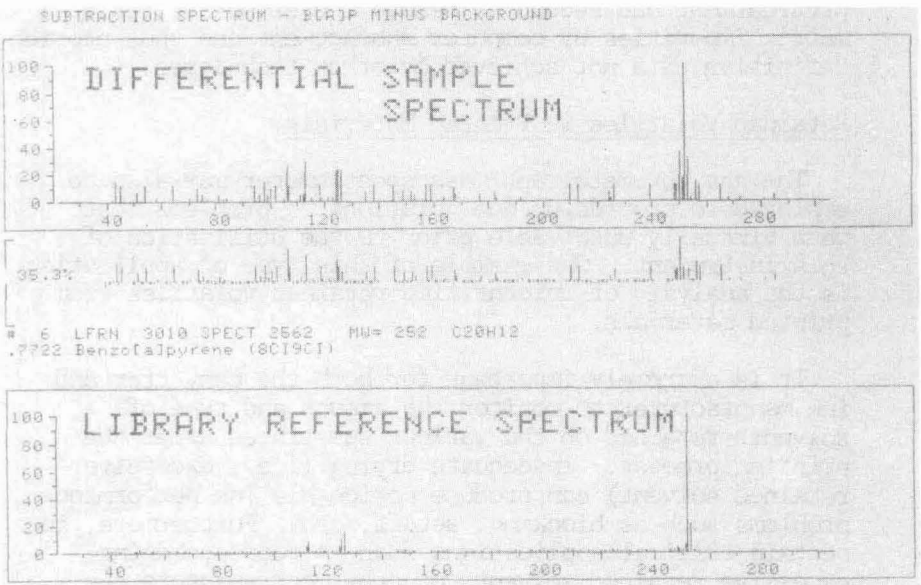

Figure 7. Library Reference Spectrum vs Differential Spectrum

Once the compound of interest has been tentatively identified by the SIM technique, we can verify its presence by computerized manipulation of the mass spectral data. Figure 6b shows the mass spectrum taken at the retention time which corresponds to the apex of the Benzo(a)pyrene chromatographic peak at 12.7 minutes. You will note that the mass spectra is unusually complicated and represents a combination of ion fragments from B(a)P (252 amu) and background interferences from the sample matrix and column bleed. Figure 6C shows the mass spectrum taken at the retention time 15.0 minutes which corresponds to the end of the B(a)P peak. In this case,

the mass spectrum represents only the background interferences. By performing a computerized spectral subtraction, one is able to remove these interferences and obtain the computer generated spectra depicted in Figure 6d. When this mass spectrum is compared to the mass spectrum of an authentic sample of B(a)P, Figure 7, you will note that the match is quite good. In summary, the contribution made by GC/MS/DS to the solution of this problem is, first the ability to directly analyze the sample without pretreatment and second to remove the effect of residual matrix impurities by computer enhancement and thus provide definitive data not achieved by other techniques.

Retained Volatiles In Printed Materials

The gas chromatograph/mass spectrometer may also be employed to provide unique solutions to problems that were virtually unsolvable prior to the utilization of this instrument. One example of this type of application is the analysis of unidentified retained volatiles from printed materials.

It is extremely important for both the converter and ink manufacturer to monitor the amount and type of solvents retained on the various substrates after the printing process. Inadequate drying (i.e., excessive retained solvent) can produce noticeable ink performance problems such as blocking, setoff, etc. Furthermore, in certain critical applications such as food packaging, excessive retained solvents or other contaminants can adversely affect the odor or flavor of the foodstuffs.

Traditionally, printed materials have been analyzed for retained volatiles by some type of gas chromatographic procedure such as ASTM F-151 or a variant. Basically, this method consists of placing a specimen in a closed container, heating the sampling vessel to volatilize the retained solvents into the container headspace, removing a portion of the headspace vapors with a gastight syringe and injecting the sample into a gas chromatograph for analysis.

A typical example of a gas chromatogram from the headspace vapors of a printed film may be seen in Figure 8. Each of the peaks represents one or more volatile components in this headspace. The area of each peak corresponds to the quantity of materials present in the vapor headspace which in turn is related to the

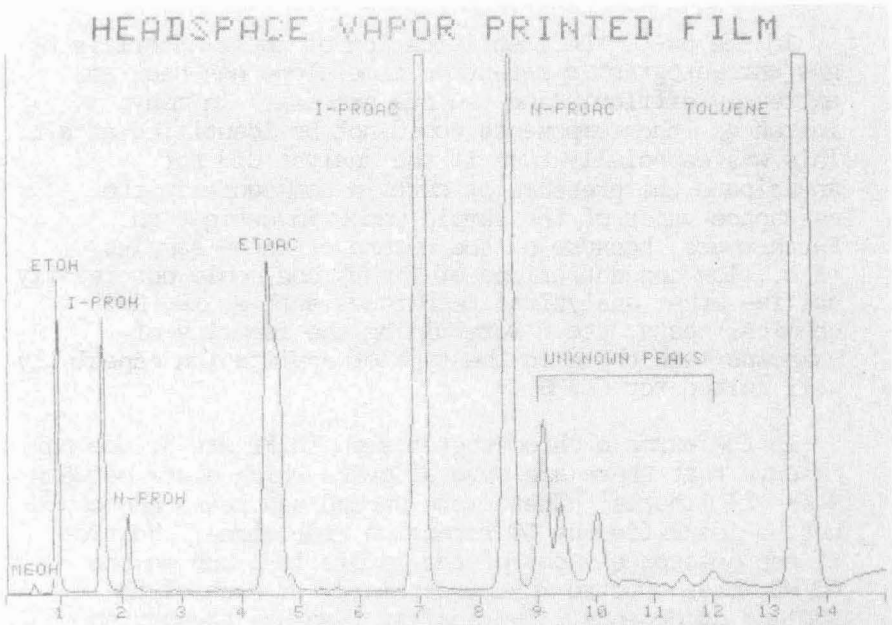

Figure 8. Gas Chromatogram of Headspace Vapor from Printed Film

amount of solvent retained in the printed film. The location or retention time of a given peak provides information regarding this component's probable identity. The unknown GC peaks are normally identified by comparing the retention time and area of these peaks to those from a standard reference mixture.

One major problem with this identification approach is that there are usually a few peaks whose retention times (i.e., identities) do not correspond to the solvents known to be in the ink formulation. The explanation for this is that the headspace vapor being analyzed originates from several sources. These compounds may arise from ink solvents, retained volatiles from the substrate, letdown solvents, laminating adhesives, decomposition products or other unknown contaminants. Even if these extraneous moieties in the total headspace vapor are relatively small compared to the retained solvents, it is possible that they can significantly affect odor. Therefore, it is extremely important to know their identity particularly in instances where there is an odor or flavor problem.

In the past, the identification of these materials by gas chromatographic retention time alone has been an extremely difficult and tedious process. In many instances, the components could not be identified at all. This was especially true if the analyst did not anticipate the presence of certain compounds in the headspace vapor of the sample under investigation. Furthermore, because of the nature of these samples (i.e., low concentrations of vapor) one could not readily utilize other analytical techniques such as IR, NMR, chemical tests, etc. Determining the identity of unknowns like these is the type of application especially well suited for GC/MS.

In the example chromatogram seen in Figure 8, one may observe that there are several peaks which elute between 9 and 13 minutes. These were unexpected peaks and could not be identified by GC retention time alone. However, if the headspace vapor of the sample is rerun on the GC/MS, mass spectra may be obtained for each of the subject components. The analyst then has the option of trying to identify the compound either by interpreting the mass spectra fragmentation pattern or by performing a computerized library search in which the mass spectrum of the unknown chromatographic peak is compared to a data base of over 35,000 other spectra. Figures 9a and 9b show examples of the library search and mass spectrum with cleavage pattern for one of the previously unidentified GC peaks in the headspace sample. This was identified as Cyclohexanone which probably originated from the manufacture or decomposition of one of the resins in the ink vehicle. This material has a fairly strong and pronounced odor and has been known to be the cause of various odor complaints in finished products. The remainder of the unidentified peaks in Figure 8 were various species of hydrocarbons which probably originated from a low boiling hydrocarbon solvent such as Lactol spirits or Heptane.

Another concern with the GC analysis of retained volatiles is the fairly common occurrence where two or more peaks may elute at the same time. In Figure 8, if one re-examines the gas chromatographic peak attributed to ethyl acetate at RT 4.5 min., one can observe that this peak is somewhat misshapen (i.e., not gaussian). This implies that possibly two materials are eluting at the same retention time. From past experience it is known that 2-Nitropropane elutes at approximately the

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REF. SPECT #=    1  LSN=     1. MW=   0  FRN=10422  RET. TIME=   9.1
        69 PEAKS,    26 SIGNIFICANT       MAX K   55.5

LIBRARY  3000    138 SPECTRA SEARCHED,    2 HIT(S)

.9694 + Cyclohexanone (8CI9CI)
        SPEC=  936  LSN=   936. MW=  98  C6H10O
        FRN = 3001 [NBS    936.]  CAS #  0000108941   EPA #  0000000961
        MATCHING PEAKS   CONTAMINATED   MISSING PEAKS  QUAL INDEX=  728
         43.8  20  94%    .0   0   0%     .0   0   0%  MULTIPLIER=  .56

.9141 + Cyclopentanone, 2-methyl- (8CI9CI)
        SPEC=  955  LSN=   955. MW=  98  C6H10O
        FRN = 3001 [NBS    955.]  CAS #  0001120725   EPA #  0000019707
        MATCHING PEAKS   CONTAMINATED   MISSING PEAKS  QUAL INDEX=  728
         45.0  21  67%   2.8   1  23%     .0   0   0%  MULTIPLIER=  .50
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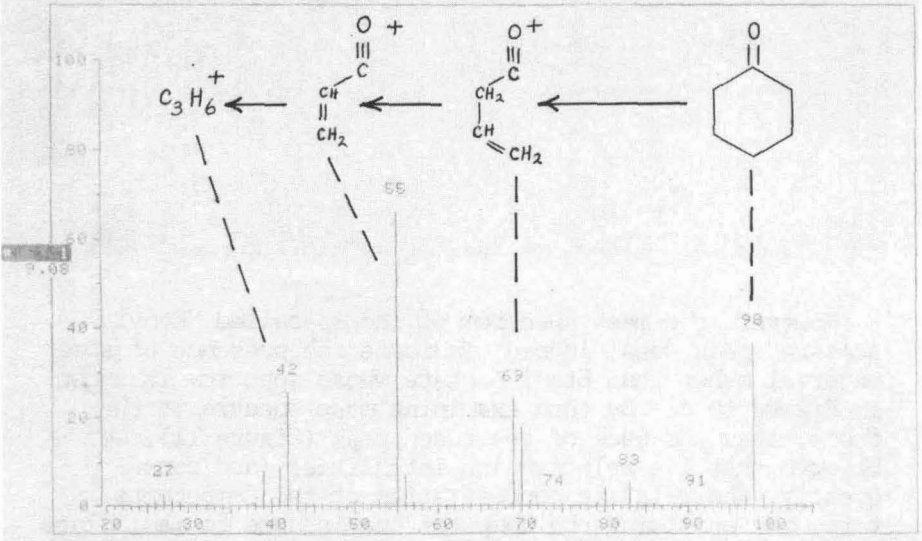


Figure 9. a) Computerized Library Search of Unknown
b) Mass Spectrum of Unknown Identified as Cyclohexanone

same retention time as Ethyl Acetate. Using traditional GC techniques, it would be difficult to determine whether 2-Nitropropane was present with Ethyl Acetate. However, this type of determination is a relatively simple matter using GC/Ms. The mass spectrum of 2-Nitropropane (Figure 10 a) has three major ion fragments at 27, 41, and 43 m/e. An examination of the mass spectrum (Figure 10 b) from the "Ethyl Acetate" GC peak shows no significant ion fragments at 27 or 41 m/e characteristic of 2-Nitropropane.

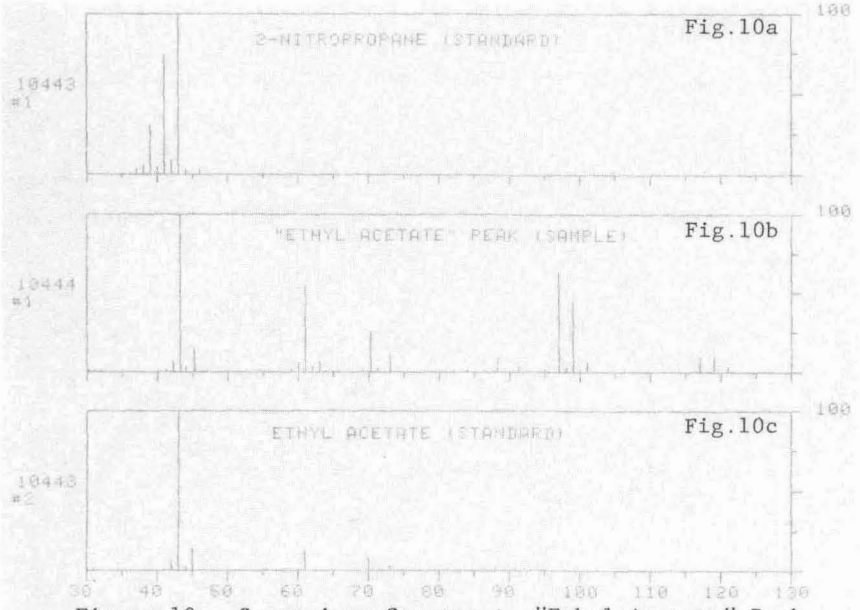


Figure 10. Comparison Spectra to "Ethyl Acetate" Peak

However, the mass spectrum of the so-called "Ethyl Acetate" peak does, indeed, indicate the presence of some material other than Ethyl Acetate whose spectrum is shown in Figure 10 c. By then examining mass spectra at the front, apex and back of the fused peak (Figure 11), we observe that the relative ion intensities (and consequently, the relative concentration of the components) vary. By utilizing the computer one is able to manipulate and isolate spectra characteristic of the two components under the fused peak. These spectra were then identified in a conventional manner. In our specific example we can see that one of the compounds under the peak is, indeed, Ethyl Acetate (Figure 12 a) while the other compound is identified as 1,1,1-Trichloroethane (Figure 12 b). It is clear that GC/MS allowed one to perform an analysis that could not have previously been accomplished without this type of instrumentation.

Radiation Curable Systems

As mentioned above, the GC/MS/DS is an excellent tool for elucidating the chemical structure of a compound. Knowledge of chemical structure can be related to an understanding of the performance characteristics of a product. The following is an example of such an

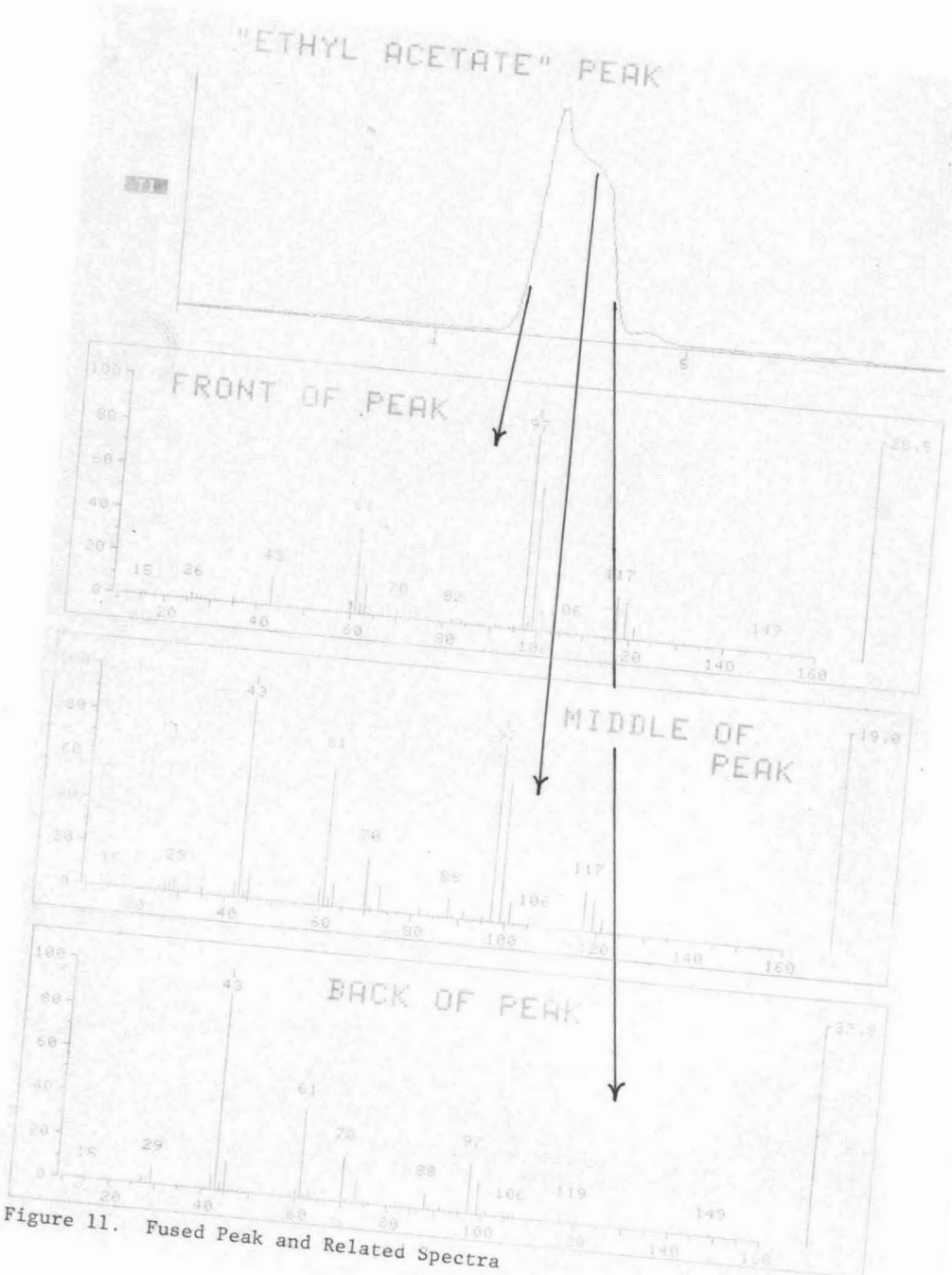


Figure 11. Fused Peak and Related Spectra

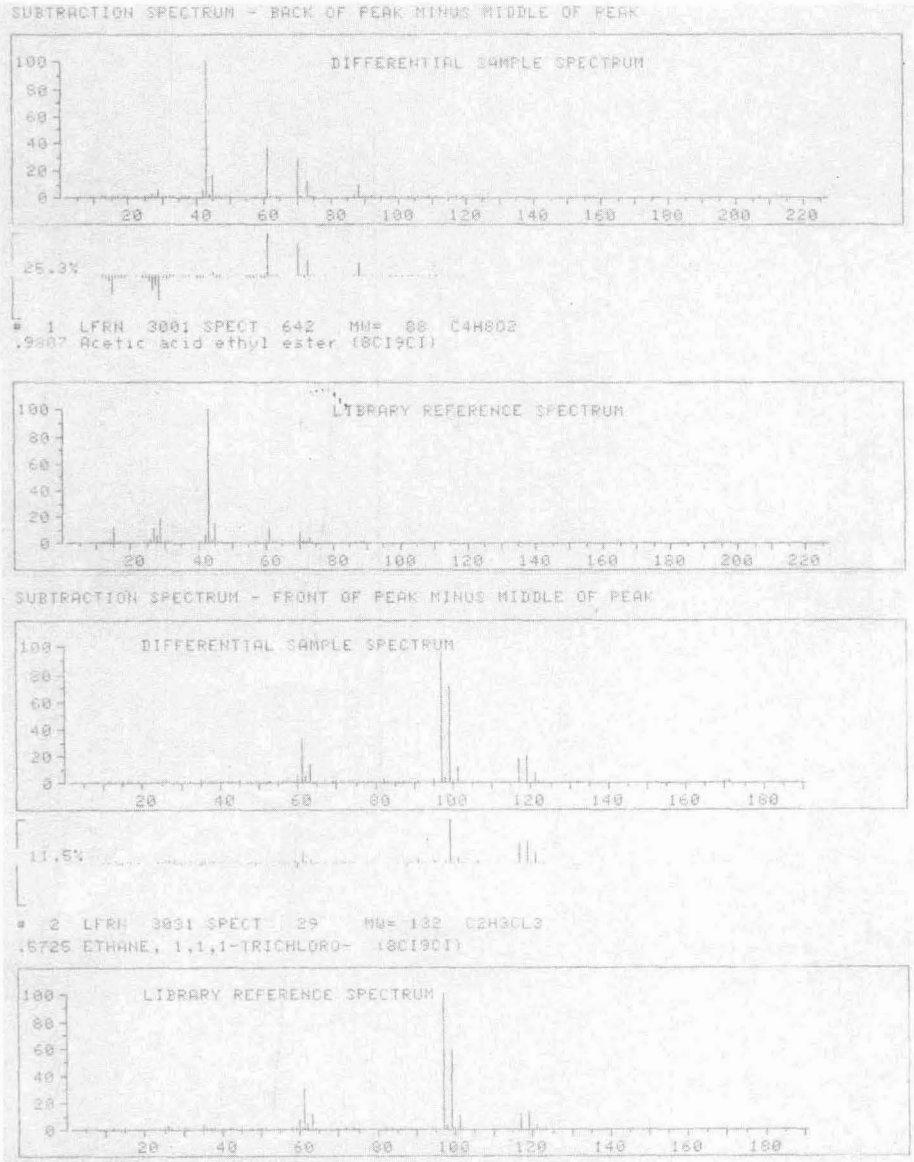


Figure 12. a) Ethyl Acetate (Top Two Spectra)
b) 1,1,1-Trichloro Ethane (Bottom Two Spectra)

application of this technique as a basic research tool applied to radiation curable systems.

It is well known that inks or coatings based on multifunctional acrylates can present an increased risk of causing adverse skin reactions in the uncured state compared to many conventional polymer chemistries. This is due in general to the low molecular weight of radiation curable prepolymers, but is particularly characteristic of specific acrylate moieties. In general, the presence of free Hydroxyl functionality on an acrylate prepolymer intensifies the potential for skin irritation.

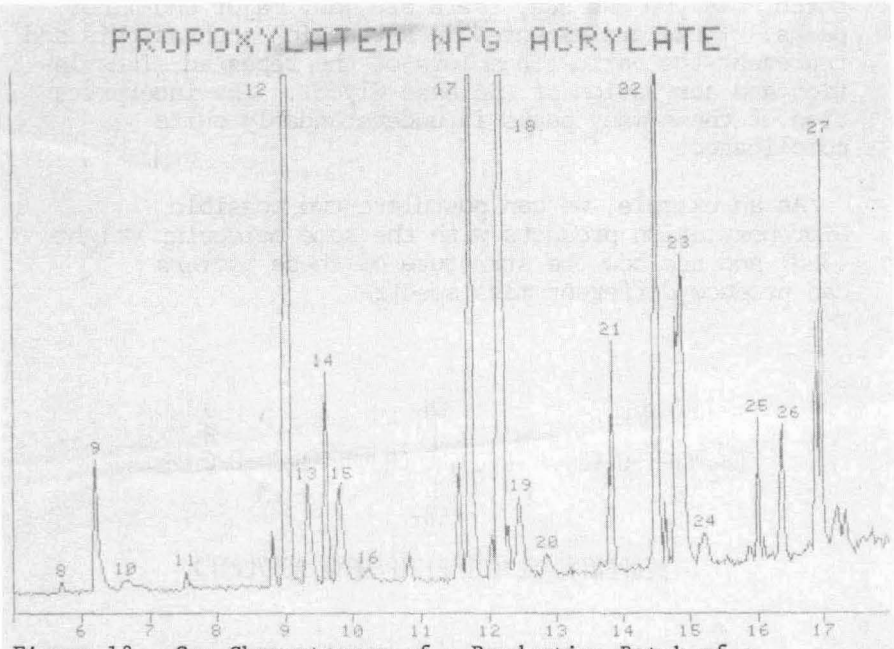
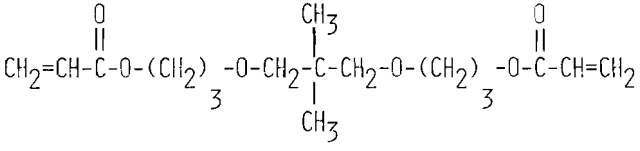


Figure 13. Gas Chromatogram of a Production Batch of a Propoxylated Neopentyl Glycol Acrylate

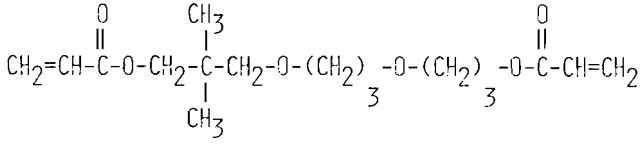
The compound Neopentyl Glycol Diacrylate (NPGDA) has excellent reaction rates in radiation curing systems. However, its use in inks and coatings is restricted because of its adverse skin reactions. A cooperative development project was initiated with a supplier to product propoxylated versions of this acrylate in an

effort to reduce its potential for skin irritation while preserving its reactivity. The synthesis route was a two stage reaction involving first the alkoxylation of Neopentyl Glycol followed by an acrylation reaction. Samples from initial batches of Propoxylated NPGDA were found to have a good order of photochemical activity, but retained a higher order of skin irritation potential than expected. In an effort to understand why this was true, an analysis was sought to determine the identities of the major components in the production batch. First a GC method was developed that resolved the components in the sample. Each component was then structurally identified by the use of GC/MS based on the theoretical interpretation of mass spectral fragmentation patterns. Figure 13 is the actual gas chromatogram of a typical production batch. As you can see, there are many major and minor peaks. These are expected in a reaction such as this and represent the various homologs of the repeated alkoxylation and acrylation of the base Glycol. The interpretation of these many peaks is understandably quite complicated.

As an example, we can postulate two possible Dipropoxylation products with the same molecular weight (328) and see how the structure of these isomers can produce different mass spectra.



NEOPENTYL GLYCOL BIS(PROPYL ACRYLATE)

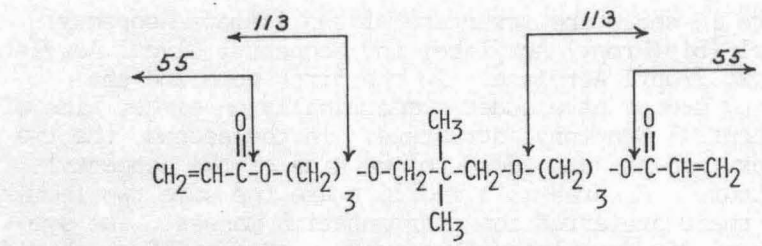


NEOPENTYL GLYCOL ACRYLATE, PROPOXY PROPYL ACRYLATE

Figure 14. Structures of Two Isomers

Figure 14 shows the structure of the isomers Neopentyl Glycol (Bis(Propyl Acrylate) and Neopentyl Glycol Acrylate, Propoxy Propyl Acrylate. In the first compound the propoxy groups have added symmetrically on either side of the central Neopentyl structure. In the second, the two Propoxy groups have added to one side of the Neopentyl structure. Figures 15 a and 16 a are the same two isomers with their preferred ion fragmentation masses. The symmetrical Bis Propyl Acrylate product (Figure 15 a) should yield mostly 55 and 113 m/e fragments. The asymmetrical Propoxy Propylacrylate product (Figure 16 a) also should yield 55 and 113 m/e fragments. However, it also should produce some 141 m/e fragment characteristic of the non-propoxylated side of the molecule as well as 171 m/e fragments characteristic of the propoxylated side of the molecule. Figures 15 b and 16 b show the mass spectra for these two peaks from the gas chromatogram of the batch product. The first shows only 2 main fragments at 55 and 113 m/e units and is attributed to the Bis Propoxy Acrylate. The second spectrum (Figure 16 b) shows the expected fragment at 141 and 171 m/e typical of the unsymmetrical adduct. As is seen, each geometric form should produce a different mass fragment pattern and the predicted values do occur in the spectra. It is worth mentioning that spectra can deviate from the predicted values due to rearrangements which some fragments undergo to achieve resonance stability. This can complicate the interpretation process.

Looking again at the actual chromatogram from the total batch product (shown in Figure 13), one can see 27 resolved components. In general, the order of elution represents mono, di, tri and higher orders of propoxylated compounds in the product. At the apex of each component peak a spectrum was recorded and analyzed in a fashion similar to that explained above for the 328 molecular weight isomeric components. Table 1 lists the compounds identified and accounts for 99.8% of this early commercial batch. Table 2 shows the seven major components present in amounts over 2% and their relative abundances. This accounts for approximately 90% of the product. It is instructive to note that while there is virtually no Neopentyl Glycol Diacrylate formed in the product, two of the seven major components are hydroxy acrylates. These plus other hydroxy species account for nearly 10% of the batch product. It is these compounds which were felt to be responsible for the unexpectedly high skin irritation potential observed with this early



NEOPENTYL GLYCOL BIS(PROPYL ACRYLATE)

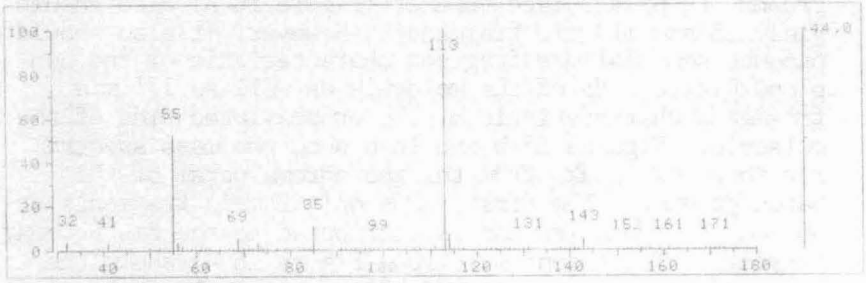
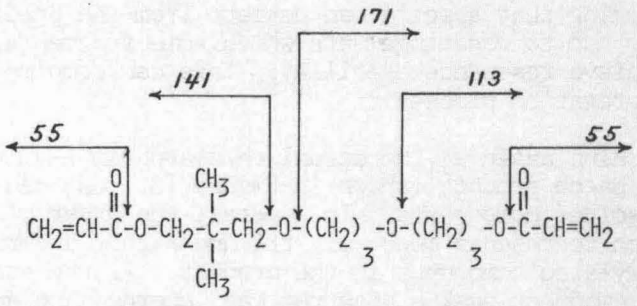


Figure 15. a) Fragmentation Pattern (Top)
b) Mass Spectrum (Bottom)



NEOPENTYL GLYCOL ACRYLATE, PROPOXY PROPYL ACRYLATE

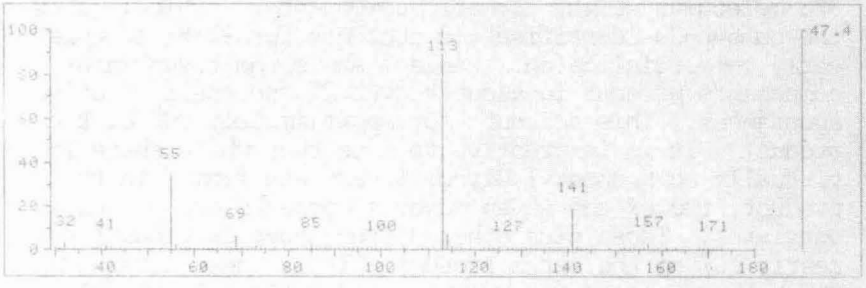


Figure 16. a) Fragmentation Pattern (Top)
b) Mass Spectrum (Bottom)

TABLE I

GC AND GC/MS ANALYSIS OF PROPOXYLATED NEOPENTYL GLYCOL DIACRYLATE

PEAK #	AREA %	MOL.WGT.	IDENTIFICATION
1	.005%	Unknown	UNKNOWN ACRYLATE
2	.05%	123	NITROBENZENE
3		94	PHENOL
4	.005%	Unknown	UNKNOWN PROPOXY ACRYLATE
5	.05%	184	PROPYLENE GLYCOL DIACRYLATE
6	.08%	Unknown	UNKNOWN
7	.1%	188	HYDROXY PROPOXY PROPYL ACRYLATE
8	.18%	212	NEOPENTYL GLYCOL DIACRYLATE
9	4.7%	216	HYDROXY PROPOXY NEOPENTYL GLYCOL ACRYLATE
10	.7%	216	NEOPENTYL GLYCOL PROPYL ACRYLATE
11	.5%	242	DIPROPYLENE GLYCOL DIACRYLATE
12	37.14%	270	NEOPENTYL GLYCOL ACRYLATE, PROPYL ACRYLATE
13	3.5%	274	HYDROXY PROPOXY NEOPENTYL GLYCOL PROPYL ACRYLATE
14	.74%	274	HYDROXY PROPOXY PROPOXY NEOPENTYL GLYCOL ACRYLATE
15	.14%	274	NEOPENTYL GLYCOL PROPOXY PROPYL ACRYLATE
16	1.1%	300	TRIPROPYLENE GLYCOL DIACRYLATE
17	10.8%	328	NEOPENTYL GLYCOL BIS-(PROPYL ACRYLATE)
18	25.47%	328	NEOPENTYL GLYCOL ACRYLATE, PROPOXY PROPYL ACRYLATE
19	.5%	332	HYDROXY PROPOXY PROPOXY NEOPENTYL GLYCOL PROPYL ACRYLATE
20	.83%	332	HYDROXY PROPOXY PROPOXY PROPOXY NEOPENTYL GLYCOL ACRYLATE
21	5.05%	342	NEOPENTYL GLYCOL ACRYLATE, PROPOXY BUTYL ACRYLATE
22	2.93%	386	NEOPENTYL GLYCOL PROPYL ACRYLATE, PROPOXY PROPYL ACRYLATE
23	1.4%	386	NEOPENTYL GLYCOL ACRYLATE, PROPOXY PROPOXY PROPYL ACRYLATE
24	.5%	390	HYDROXY PROPOXY PROPOXY PROPOXY NEOPENTYL GLYCOL PROPYL ACRYLATE
25	1.0%	328	ISOMER OF #17
26	1.4%	328	ISOMER OF #18
27	1.0%	444	NEOPENTYL GLYCOL BIS-(PROPOXY PROPYL ACRYLATE)
TOTAL AREA	99.82%		

batch. Reaction conditions were then modified to reduce the occurrence of these hydroxy compounds in later batches producing a very low level of irritation potential coupled with good cure speed. The GC/MS data was the key to relating this performance parameter to structure, thereby suggesting means of correcting and monitoring future batches.

TABLE II

GC AND GC/MS ANALYSIS OF PROPOXYLATED NEOPENTYL GLYCOL DIACRYLATE

PEAK #	AREA %	MOL. WGT.	IDENTIFICATION
9	4.7%	216	HYDROXY PROPOXY NEOPENTYL GLYCOL ACRYLATE
12	37.14%	270	NEOPENTYL GLYCOL ACRYLATE, PROPYL ACRYLATE
13	3.5%	274	HYDROXY PROPOXY NEOPENTYL GLYCOL PROPYL ACRYLATE
17	10.8%	328	NEOPENTYL GLYCOL BIS-(PROPYL ACRYLATE)
18	25.47%	328	NEOPENTYL GLYCOL ACRYLATE, PROPOXY PROPYL ACRYLATE
21	5.05%	342	NEOPENTYL GLYCOL ACRYLATE, PROPOXY BUTYL ACRYLATE
22	2.93%	386	NEOPENTYL GLYCOL PROPYL ACRYLATE, PROPOXY PROPYL ACRYLATE

CONCLUSION

As can be seen from the above example, the GC/MS/DS has become a most versatile tool for understanding and solving all types of ink related problems. The scope of this paper only allows one to touch upon examples of this versatility. In practice it has been applied to hundreds of problems with a high percentage of success. Implicit in these successes is a well maintained and professionally operated instrument.

The costs related to the operation and maintenance of this type of equipment must be considered in the acquisition process. As is most often the case with capital equipment, one must try to justify the costs prior to purchase. In the case of GC/MS/DS the range of applications exceed any expectations. The more one works with it, the more one seems to be able to accomplish. In the first year, the instrument more than returned its very high initial cost as well as the cost of a professional operator and maintenance. This instrument, which was once only found in more esoteric laboratories, has found its place in the practically oriented printing ink industry.