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Journal of Chromatography A, 753 (1996) 101–108

JOURNAL OF CHROMATOGRAPHY A

Determination of polyacrylamide in polyvinyl alcohol by pyrolysis–gas chromatography with atomic emission detection

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Received 13 May 1996; accepted 30 May 1996

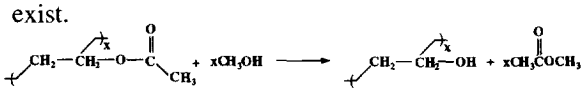
Abstract

Polyacrylamide as an additive incorporated into polyvinyl alcohol was qualitatively identified by pyrolysis–gas chromatography with atomic emission detection. The peak pattern used in this qualitative analysis has been further structurally identified through mass spectrometry. The degradation mechanisms to produce those peaks have been proposed. The atomic emission detection demonstrated its superior elemental selectivity advantage in this study. The comparison between atomic emission detection and mass spectrometry is also discussed based on these types of applications. This is a good example of how using a selective detector can greatly reduce sample preparation and enable a qualitative identification.

Keywords: Polyacrylamide; Poly(vinyl alcohol)

1. Introduction

Polyvinyl alcohol (PVOH), also known as poly(vinyl alcohol), is a water soluble synthetic resin. It is prepared by the alcoholysis of poly(vinyl acetate) [1]; the theoretical monomer, CH_2=CHOH, does not exist.



Polyvinyl alcohol is a dry solid and is available in granular or powdered form. The physical properties of polyvinyl alcohol vary according to the molecular mass of the parent poly(vinyl acetate) and the degree of alcoholysis [2].

The wide range of chemical and physical properties of polyvinyl alcohol has led to its broad industrial use. The main uses of polyvinyl alcohol is in textile fiber, although it must be chemically treated to become water insoluble [3]. In other areas of application, polyvinyl alcohol serves as a thickening agent for various emulsion and suspension polymerizations. Significant volumes are also used in such diverse applications as joint cements for building construction, packing film where water solubility is desired, emulsifiers in cosmetics, temporary protective films to prevent scratching of highly polished surfaces, and soil binding to control erosion. Among these types of applications, the polyvinyl alcohol forms tough, clear films that have high tensile strength and abrasion resistance. Its oxygen-barrier qualities are superior to those of any known polymers.

In various types of adhesives, low levels of polyacrylamide are added into the adhesive formula-

0021-9673/96/$15.00
PII S0021-9673(96)00530-4

tion [4]. The role of polyacrylamide in adhesion is not exactly known. However, there is a hypothesis that the polyacrylamide performs as an adhesion promoter to enhance the ability of the adhesive in wetting and penetration into the adherend. In order to understand the effect of polyacrylamide in the polyvinyl alcohol type adhesive, an analytical method was needed to determine the presence of polyacrylamide in the polyvinyl alcohol. There is no known way to separate such a mixture. At the low polyacrylamide levels in the formulation, most of the non-destructive spectroscopic methods suffer from lack of sensitivity or from interference.

Pyrolysis–gas chromatography (Py–GC) is one of the methods generally used in the qualitative and quantitative analysis of low level additives and polymer composition. Both polyvinyl alcohol and polyacrylamide have been intensively studied by Py–GC and Py–GC–mass spectrometry (MS) [5–12]. Major pyrolysis components have been identified, and their structures have been assigned [12].

Pyrolysis of polyvinyl alcohol produces a great number of fragments. Many of the pyrolysis products interfere with low level additives detection. It is very difficult to determine low level additives using Py–GC with flame ionization detection (FID). In order to exclusively detect low level additives, a more selective detection method is required, such as elemental-selective detection i.e. atomic emission detection (AED) or fragment-selective detection like mass-selective detection. AED is extremely useful when looking for specific element-containing components such as nitrogen, sulfur, phosphorous, metals and halogens.

In this study, low levels of polyacrylamide, as an additive in the polyvinyl alcohol, have been qualitatively detected by Py–GC with atomic emission detection. The group of nitrogen containing peaks which were matched with a standard of polyacrylamide has been further identified by MS. The degradation mechanism which produces those components has been proposed. The elemental selectivity of AED was demonstrated. A comparison between AED and MS is also discussed based on this kind of application. This study is a good example of how, using the appropriate detector, sample preparation can be greatly reduced while still obtaining a qualitative detection.

2. Experimental

2.1. Sample preparation

2.1.1. Polyvinyl alcohol and polyacrylamide standard

The polyvinyl alcohol (powder, 99+% hydrolyzed, catalog No. 34,158-4, Aldrich), was used without further purification. The polyacrylamide standard (50%, w/w, in solution in water, catalog No. 43,494-9, Aldrich), was used as its solid form by drying an aqueous solution at 80°C under vacuum overnight.

2.2. Test samples

Two samples were prepared for this study, sample A has 1.0% (w/w) of polyacrylamide added into polyvinyl alcohol resin and sample B is a pure polyvinyl alcohol resin.

2.3. Pyrolysis–gas chromatography–atomic emission detection

Samples of polyvinyl alcohols and polyacrylamide were weighed (approximately 4 g of polyvinyl alcohol samples and 0.04 g of the polyacrylamide standard) into quartz tubes and equilibrated for 10 min in a 200°C interface connected to the injection port of a Hewlett–Packard (HP) 5890 gas chromatograph equipped with an HP 5921A atomic emission detector. Samples were pyrolyzed (CDS 120 Pyroprobe Pt coil) at a set temperature of 700°C with a maximum heating ramp (approx. 20°C/ms) for a 20-s interval. The pyrolysis products were carried by the helium carrier gas through the injection port. The separation was performed on a fused-silica capillary column (J&W DB-5, 30×0.25 mm I.D., 0.5 μm film) using a linear temperature program (40°C for 4 min, then 10°C/min ramp to 250°C and 15-min hold), with 10 p.s.i. head pressure (1 p.s.i.=6894.76 Pa), and a 20:1 split ratio. The transfer line between the GC and the AED is a deactivated fused-silica capillary column. The temperature of the transfer line is set at 250°C. GC–AED used O_2 and H_2 as reagent gases with detection at 174 nm and 193.1 nm emission line for nitrogen and carbon respectively.

2.4. Pyrolysis–gas chromatography–mass spectrometry

For the Py–GC–MS study, the Py–GC conditions above were the same, except the separation was performed on a fused-silica capillary (J&W DB-5, 30 m×0.25 mm I.D., 1.0 μm film) using a linear temperature program (40°C for 4 min, then 10°C/min ramp to 280°C and a 12-min hold). The mass spectrometer is a Vacuum Generation (VG) TRIO-1 quadrupole system. Electron ionization mass spectrum was obtained every second over the range 29–350 u with the detector multiplier at 425 V, a ionization source current of 1500 μA, a source temperature 180°C, and the transfer line between GC and MS set at 280°C.

2.5. Direct insertion probe mass spectrometry

For the direct insertion probe mass spectrometry study, the polyacrylamide sample was dried and then placed in the quartz cup in a direct insertion probe. The insertion probe was operated under a linear temperature program (35°C with 10°C/min ramp to 350°C). The mass spectrometer was a Finnigan SSQ700 triple quadruple system. Electron ionization mass spectrum was obtained every second over the range 29–300 u.

3. Results and discussion

Figs. 1 and 2 show the carbon and nitrogen traces of the Py–GC–AED results of sample A. Figs. 3 and 4 show the same traces of sample B and Figs. 5 and 6 show the traces for polyacrylamide standard. When the carbon trace of sample A (Fig. 1) and sample B (Fig. 3) are compared, it can be seen that the pyrolysis of polyvinyl alcohol produces a large number of carbon containing species. The carbon trace from GC–AED is very similar to the chromatogram from a GC–flame ionization detection (FID). The carbon trace obtained in GC–AED could not detect 1.0% polyacrylamide in the polyvinyl alcohol.

The purpose of this study was to qualitatively determine the existence of low level (about 1.0%, w/w) polyacrylamide additive (which is a nitrogen containing polymer) in a polyvinyl alcohol matrix.

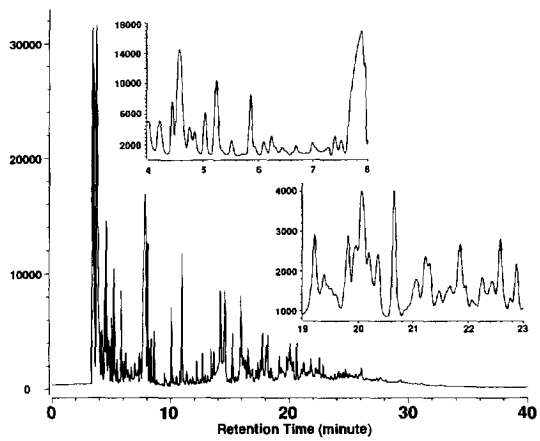


Fig. 1. AED carbon trace pyrogram of polyvinyl alcohol sample A.

The nitrogen trace of both samples (Fig. 2 of sample A and Fig. 4 of sample B) shows a very clear difference. The most significant difference is found in the retention time regions of 4–8 min and 19–23 min. At retention time 4–8 min, sample A consists of a pattern of four peaks (peaks 1, 2, 3 and 4), but sample B is clean in that retention time region. In the same way, at retention time 19–23 min, sample A consists of a pattern of five peaks (peaks 19, 20, 21, 22 and 23). Compare the retention time index and peak pattern of nitrogen trace between sample A (Fig. 2) and polyacrylamide standard (Fig. 6). The polyacrylamide can be qualitatively identified in sample A. AED allows the selective monitoring of

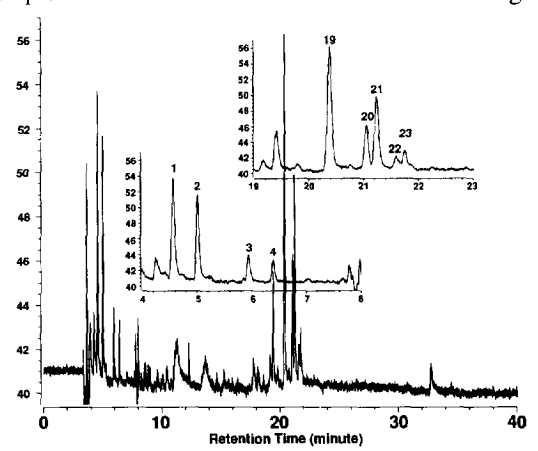


Fig. 2. AED nitrogen trace pyrogram of polyvinyl alcohol sample A.

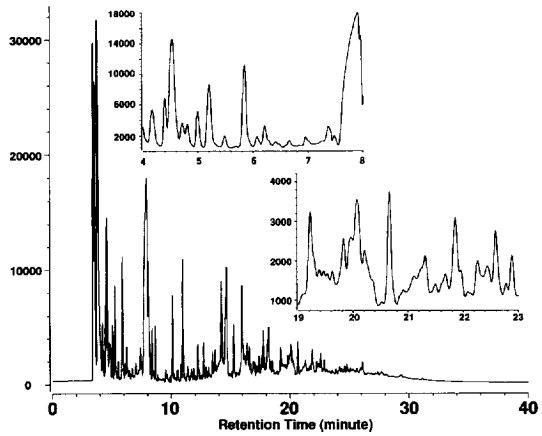


Fig. 3. AED carbon trace pyrogram of polyvinyl alcohol sample B.

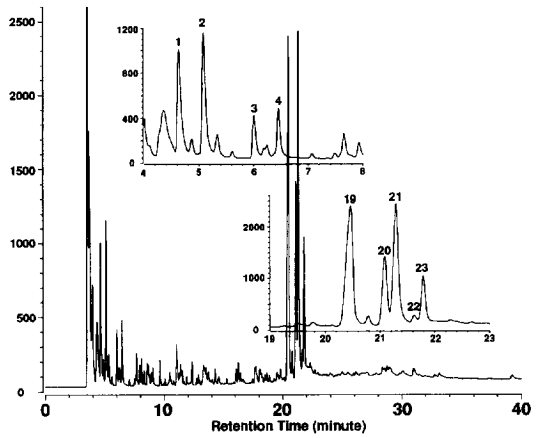


Fig. 5. AED carbon trace pyrogram of polyacrylamide standard.

nitrogen containing compounds to produce an enhancement of the sensitivity permitting the detection of very low concentrations of polyacrylamide additive.

The carbon trace of sample A (Fig. 1) does not show the pattern of polyacrylamide because of the interference from the pyrolysis products of polyvinyl alcohol that completely covers the signal. It has been reported [11] that the pyrolysis of polyacrylamide only produces some saturated and unsaturated low aliphatic nitriles such as acetonitrile, acrylonitrile, propionitrile, methacrylonitrile and isobutyronitrile. These peaks can be found both in the nitrogen traces of sample A (Fig. 2) and polyacrylamide (Fig. 6). The pyrolysis of polyacrylamide actually produces much more complex products as shown in Fig. 7 Table 1.

The nitrogen traces from all the samples showed several negative peaks. These negative peaks in the nitrogen traces of the samples is caused by a phenomena called "quench effect". This effect can be seen when large amount of substances (in this case, the non-nitrogen containing species) move through the detector and the plasma does not have enough energy to maintain the same level of nitrogen atomic excitation. This in turn causes low emission intensity and creates the negative peaks. In other words, these negative peaks indicate that there is a

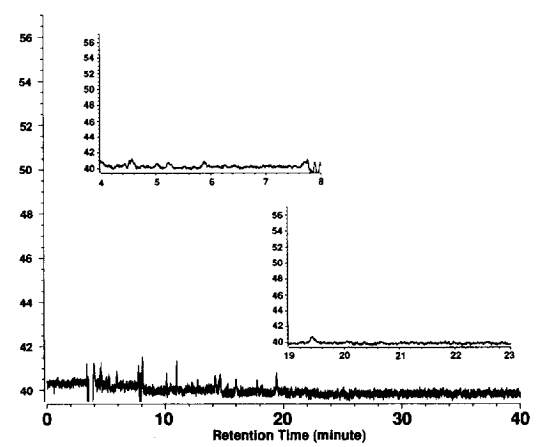


Fig. 4. AED nitrogen trace pyrogram of polyvinyl alcohol sample B.

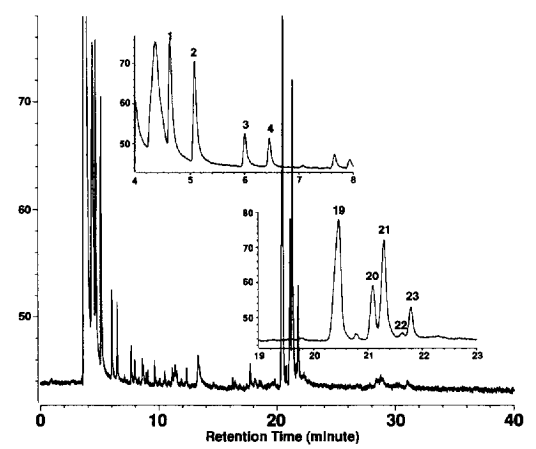


Fig. 6. AED nitrogen trace pyrogram of polyacrylamide standard.

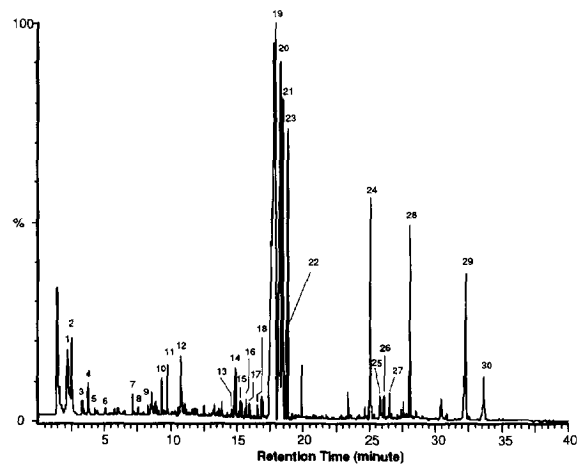
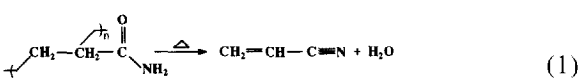


Fig. 7. The total ion current pyrogram from Py–GC–MS of polyacrylamide standard.

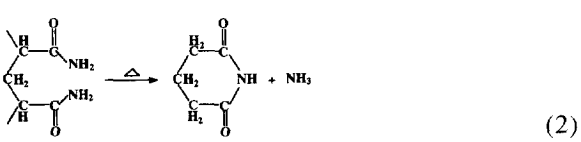
large amount of other elemental containing substances (mostly carbon) passing through the detector.

Fig. 7 shows the total ion current (TIC) pyrogram of the Py–GC–MS of polyacrylamide. The structure assignment for the most prominent peaks are listed in Table 1. The pyrolysis products of polyacrylamide can be roughly divided into monomers, dimers, trimers and tetramers. The monomers are the saturated and unsaturated low aliphatic nitriles generally resulting from the acrylamide functional group loss of water and chain scission, as shown in reaction



(1)

Most of the dimers are the end products of the polyacrylamide loss of an ammonia to form a six member ring of glutarimide and chain scission, as shown in reaction



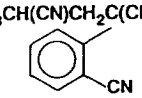
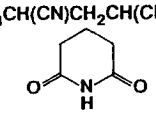
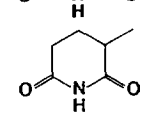
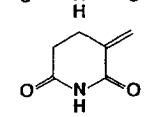
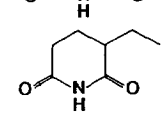
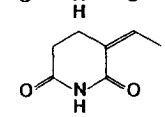
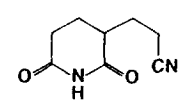
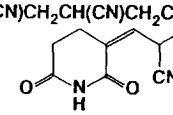
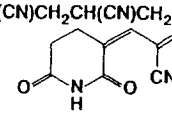
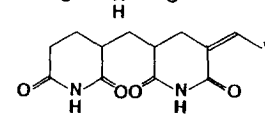
(2)

The trimer formation may involve degradation of pathway (1) or combination of pathways (1) and (2). There are trimers with three nitrile functional groups as well as one glutarimide and one nitrile functional group. The tetramers found in this study, were formed by degradation reactions similar to pathway (2) except the chain scission reaction was initiated with four monomer units. Because the transfer line between the GC and the AED can be heated to only 250°C, the AED nitrogen trace for polyacrylamide does not show any response above dimers.

Thermal degradation mechanisms of polyacrylamide may be studied through direct insertion probe mass spectrometry. In a thermal degradation process, the determination of which mechanisms happen first, (a) chain scission, (b) loss of water and ammonia, can be explored by the mass spectra collected during the temperature ramp up of the direct insertion probe. Fig. 8 shows the single ion monitoring and total ion current plot. The single ion monitoring of masses 17, 18, and 113 indicates the polymer will lose ammonia (m/z 17) and water (m/z 18) first to form nitrile functional groups and the cyclic ring structure of glutarimide, followed by polymer chain scission to form saturated and unsaturated low aliphatic acrylonitrile and glutarimide (m/z 113). Fig. 9a shows the mass spectrum of the early portion of the ramp (probe temperature 260°C) for polyacrylamide. Ammonia (m/z 17) and water (m/z 18) are the major components at that temperature. Fig. 9b shows the mass spectrum of the later portion (probe temperature 310°C) of acrylamide, glutarimide (m/z 113) and its family (m/z 125, 127, 139, 141) are the most prominent products which indicate that the polymer backbone chain scission is part of the mechanism by which monomers, dimers, and trimers are formed.

In terms of price, performance, and efficiency, there is always an interest in comparing atomic emission and mass spectrometry as detectors for gas chromatography. An understanding of all polyacrylamide Py–GC fragments is necessary in a study in order to decipher the peak patterns by MS. Even when the appropriate peaks can be located, the resulting spectra will still suffer from a large amount of interference which will make the spectra hard to interpret. Although the mass spectrometry detector has direct identification power, in a very complex matrix like the one in this study, the advantage of mass spectrometry detection cannot be fully utilized. This opens the opportunity to a more specific detection method like AED which selectively obtains data from nitrogen containing species. The chro-

Table 1
Py–GC–MS peak assignment of polyacrylamide

Peak label	Retention time (min)	Molecular mass	Structure
1	2.17	41	CH_3CN
2	2.48	53	$CH_2=CHCN$
3	3.30	55	CH_3CH_2CN
4, 5, 6	3.73, 5.02, 5.98	67	$CH_3CH=CHCN^*$
7, 8, 9	7.08, 8.25, 8.53	81	$CH_3CH_2CH=CHCN^*$
10, 11, 12	9.32, 9.76, 10.75	95	$CH_3CH_2CH_2CH=CHCN^*$
13	14.78	108	$CH_2(CN)CH_2CH(CN)CH_3$
14	14.88	106	$CH_2(CN)CH_2C(CN)=CH_2$
15	15.21	120	$CH_3CH(CN)CH_2C(CN)=CH_2$
16	15.70	117	
17, 18	15.93, 16.55	122	$CH_3CH(CN)CH_2CH(CN)CH_3^*$
19	17.93	113	
20	18.28	127	
21	18.47	125	
22	18.65	141	
23	18.85	139	
24	25.05	166	
25	25.84	159	$CH_2(CN)CH_2CH(CN)CH_2C(CN)=CH_2$
26	26.10	178	
27	26.52	173	$CH_3CH(CN)CH_2CH(CN)CH_2C(CN)=CH_2$
28	28.07	176	
29, 30	32.27, 33.62	264	

* Isomers of this structure.

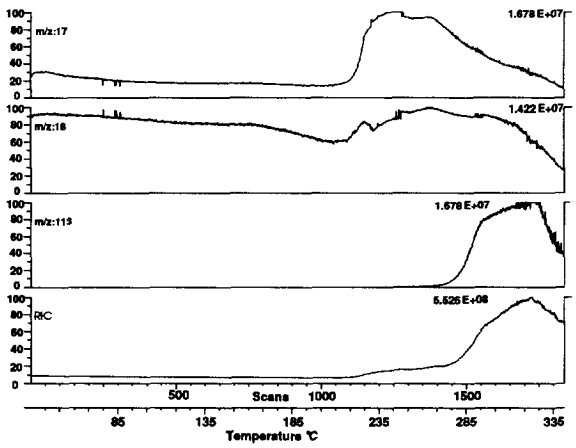


Fig. 8. The total ion current and single ion monitoring of polyacrylamide standard.

matogram is much cleaner, and the peak pattern required for identification is preserved. Qualitative identification is obtained by matching retention time index and peak pattern. In this application, AED was far more effective than MS or FID.

4. Conclusion

A 4-mg sample of polyvinyl alcohol with 1.0% (w/w) of polyacrylamide additive has been successfully identified by Py–GC–AED. The major components generated by the Py–GC of polyacrylamide and polyacrylamide containing polyvinyl alcohol have been identified by MS. The structures of these compounds have been assigned. Degradation mecha-

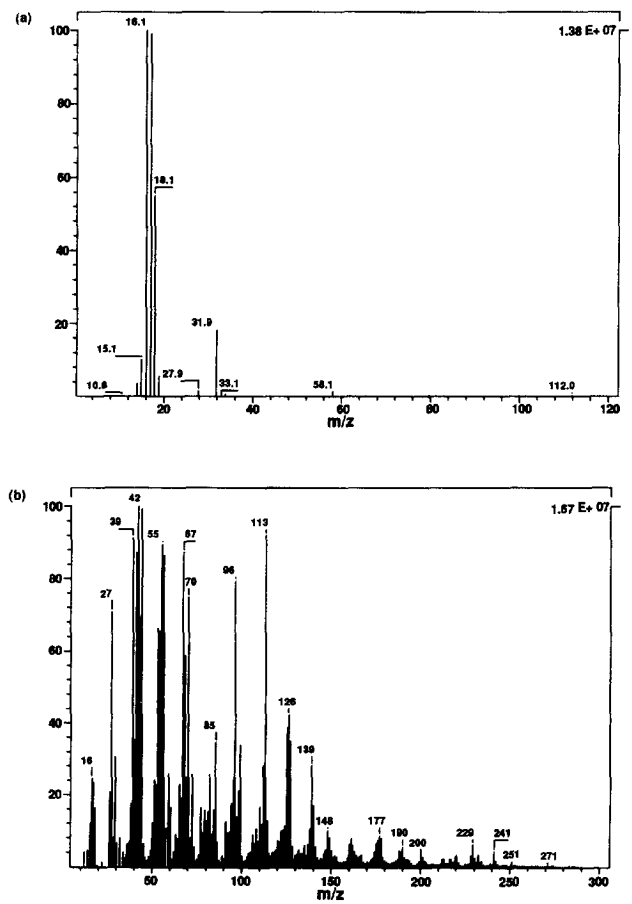


Fig. 9. (a) The mass spectrum at 260°C from Fig. 8. (b) The mass spectrum at 310°C from Fig. 8.

nisms which led to the production of these compounds have been proposed.

AED possesses unique elemental selectivity and can sometimes enable analysis of samples which exhibit severe matrix interference by other technology. The identification of low levels of a polyacrylamide additive in polyvinyl alcohol polymers by Py–GC–AED is a very good example. Other applications such as the environmental and the biological areas could also benefit from the minimal sample preparation requirement of this highly selective elemental detector.

Acknowledgments

The authors will like to express their thanks to Sergio Cutié, Kent Hodges, Chuck Smith, and Pat Smith for sharing their pervious experience in this topic. The help from John Green, Bruce Bell, and Bill Scott in the mass spectra interpretation and direct insertion probe mass spectrometry experiment is also greatly appreciated.

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