Journal of Chromatography, 160 (1978) 133–140

CHROM. 11,096

GAS CHROMATOGRAPHIC HEAD-SPACE DETERMINATION OF RESIDUAL ACRYLONITRILE IN ACRYLONITRILE–BUTADIENE–STYRENE RESINS AND MIGRATION INTO A SIMULATED FATTY FOODSTUFFS LIQUID

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(Received April 10th, 1978)

SUMMARY

Head-space methods are described for the determination of residual acrylonitrile in acrylonitrile–butadiene–styrene resins and in olive oil, which simulates fatty foodstuffs. Dimethylformamide was used as solvent for the resin, with flame ionization detection. The injection of water into the resin dispersion prior to head-space analysis greatly enhances the detection capabilities. The use of a nitrogen-selective detector required dimethyl sulphoxide as the solvent. The determination of acrylonitrile in olive oil was carried out employing both types of detector. The detection sensitivity was much greater with the nitrogen-selective detector.

INTRODUCTION

During 1974 public opinion[1] was aroused about the carcinogenity of vinyl chloride monomer, and consequently other monomers also became suspect. More and more plastic materials are being used in food and cosmetic packaging and in toys. For this reason the health authorities of many countries[2] decided to control the content and the toxicity of the residual monomers in such polymers.

Our laboratories have been investigating improved analytical methods for measuring the residual acrylonitrile content in acrylonitrile–butadiene–styrene (ABS) resins and its migration into the simulated liquid foods.

For this purpose the head-space gas chromatographic (HSGC) technique[3] is preferred to direct injection, because it permits the analysis of traces of volatile components of samples containing other high-boiling fractions without their influencing the gas chromatographic analysis. The direct injection of high-boiling fractions into the injection port would reduce the efficiency and life of the column owing to the formation of degradation products that would interfere with the chromatogram.

For example, if we analyse for residual acrylonitrile monomer in ABS resin solution, the resin degrades and wrong results are obtained.

We encountered problems in the analysis of acrylonitrile in olive oil (used as a carrier to simulate fatty foodstuffs)[4] in contact with plastic packaging. First, the high viscosity of the olive oil makes it difficult to employ a microsyringe for the injection into the column; second, the high temperatures involved in the injector would degrade the olive oil, giving numerous products which interfere in the chromatogram of acrylonitrile.

Head-space analysis is an indirect method for the determination of volatile constituents in liquids or solids by gas chromatographic analysis of the vapour phase, which is in thermodynamic equilibrium with the sample to be analysed in a closed system. By analysing the vapour phase we can avoid the above problems, and in some cases a higher analytical sensitivity can be obtained because a larger amount of sample can be injected into the column.

In our experiments, because the graft component does not dissolve in any solvent and the impurities in a common solvent cause interference, we have used special solvents and selective detectors. The use of distilled dimethylformamide (DMF) as solvent allowed us to obtain a very fine and homogeneous dispersion of graft, and to avoid the presence of solvent impurities. Moreover, the addition of 10% water[5] to the solution allowed us to modify the solubility and activity coefficient of acrylonitrile in the solution, thus increasing its concentration in the vapour phase. We used the nitrogen-selective detector (NPSD)[6] and dimethyl sulphoxide (DMSO) as solvent to obtain a dramatic increase in the detection sensitivity.

EXPERIMENTAL

Apparatus

A Carlo Erba (Milan, Italy) gas chromatograph Fractovap Model 2450, equipped with the automatic head-space accessory (HS sampler Model 250), flame ionization detector (FID) and NPSD, was used. The HS Model 250 consists of a thermostatted sampling module mounted on the top of the gas chromatograph to equilibrate the sample (up to 40 samples) and to inject the vapour phase with a Hamilton 1002N gas-tight syringe. All functions are programmed on an external control module. Facilities are provided for separate temperature controls of the gas-tight syringe and turntable. To avoid cross contamination due to residues of low volatility, the syringe can be flushed automatically with ambient air.

A Leeds & Northrup (North Wales, Pa., U.S.A.) recorder Model FB Mark II and glass vials (10 ml) with rubber PTFE-laminated discs and aluminium seal rings, were also used.

Chemicals

Analytical grade DMF, DMSO, acrylonitrile and propionitrile were obtained from Carlo Erba.

Methods

Determination of acrylonitrile in resin using an FID. A sample of 1 g of resin was dissolved in a septum-sealed vial containing 4.5 ml of carefully distilled DMF.

When a fine dispersion was obtained 0.5 ml of water was injected with a syringe, through the septum, into the polymer dispersion. The vial was stirred for 5 min and then equilibrated at 80° for 60 min.

The analyses were carried out under the following conditions: column: 3 m × 2 mm I.D. stainless-steel tubing packed with 10% Carbowax 20 M on Chromosorb W AW (60–80 mesh); temperatures: thermostatted sample turntable 80°, injector/detector 170°, syringe 90°, column 95°; sample size: 2 ml; carrier gas: nitrogen, at a flow-rate of 30 ml/min; the syringe was flushed three times with ambient air. Fig. 1 shows a chromatogram obtained under these conditions.

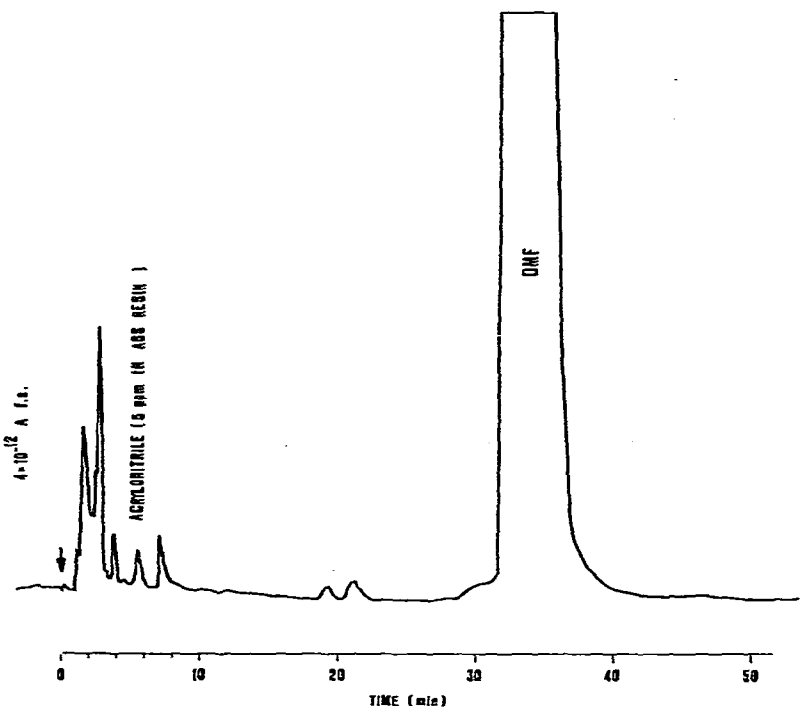

Fig. 1. Chromatogram of the head space above the solution of ABS resins, containing 5 ppm of acrylonitrile, dissolved in DMF solvent (FID).

Determination of acrylonitrile in olive oil using an FID. Four plates (25 × 100 × 0.5 mm)[7] were prepared for each sample and put on a stainless steel holder, which was placed inside a glass tube with a glass stopper. The plates were covered with 100 ml of olive oil and the tube was sealed and put into an oven at 40°. After 10 days 5 ml of migration liquid were pipetted into a 10-ml vial which was then tightly sealed and equilibrated at 80° for 60 min.

The analyses were carried out under the following conditions: column: 2 m × 2 mm I.D. stainless-steel tubing packed with Chromosorb 102 (100–120 mesh); temperatures: thermostatted sample turntable 80°, injector/detector 180°, syringe 90°, column 140°; sample size: 2 ml; carrier gas: helium, at a flow-rate of 30 ml/min;

the syringe was flushed five times with ambient air. Fig. 2 shows a chromatogram obtained under these conditions.

Determination of acrylonitrile in resin using an NPSD. 0.5 g of ABS resin was dissolved in a septum-sealed vial containing 5 ml of DMSO. When a fine dispersion was obtained 10 μl of a standard solution, containing propionitrile (as internal standard) in DMSO in the ratio 0.04:100 was injected into the polymer dispersion. The vial was stirred for 5 min and then equilibrated at 80° for 60 min.

The analyses were carried out under the following conditions: column: 4 m × 2 mm I.D. stainless-steel tubing packed with 10% Carbowax 1500 on Chromosorb W AW (60–80 mesh); temperatures: thermostatted sample turntable 80°, injector/detector 150°, syringe 90°, column 80°; sample size: 2 ml; carrier gas: nitrogen, at a flow-rate of 30 ml/min; the syringe was flushed three times with ambient air. Fig. 3 shows a chromatogram obtained under these conditions.

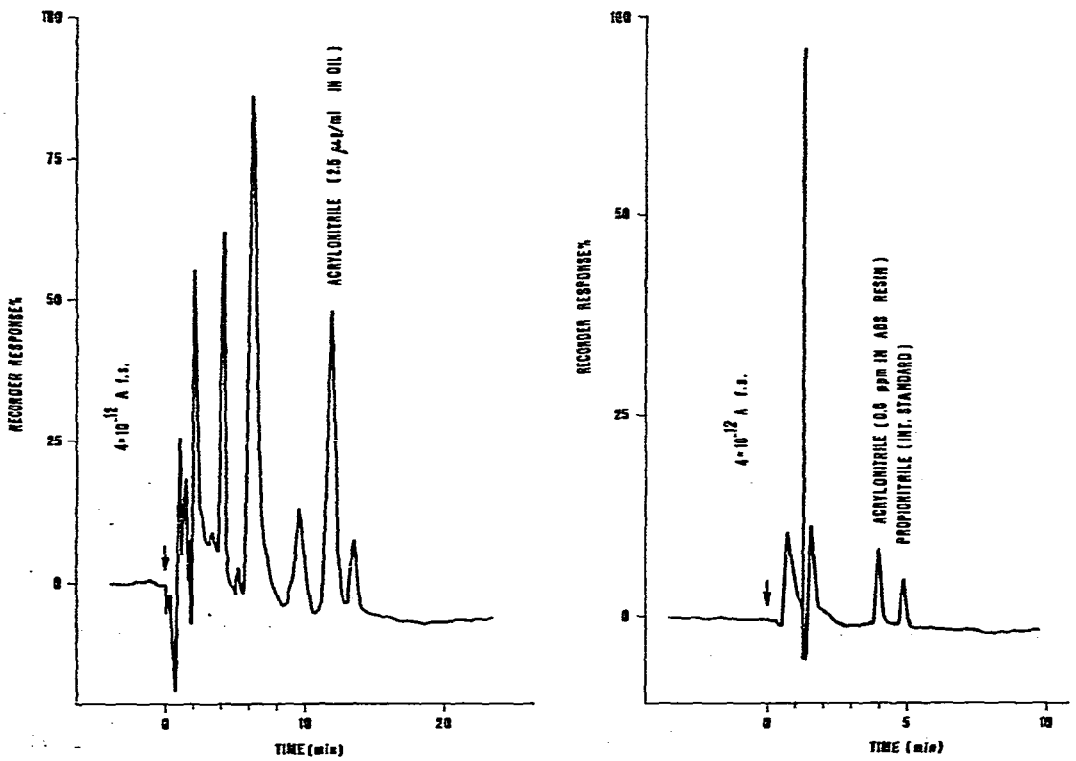

Fig. 2. Chromatogram of the head space above olive oil containing 2.5 ppm of acrylonitrile (FID).

Fig. 3. Chromatogram of the head space above the solution of ABS resins, containing 0.6 ppm of acrylonitrile, dissolved in DMF solvent with the addition of propionitrile internal standard (NPSD).

Determination of acrylonitrile in olive oil using an NPSD. 5 ml of migration liquid, obtained as before, was pipetted into a 10 ml vial, which was tightly sealed and equilibrated at 80° for 60 min. The analyses were carried out under the following conditions: column: 4 m × 2 mm I.D. stainless steel tubing packed with 10% Carbo-

wax 1500 on Chromosorb W AW (60–80 mesh); temperatures: thermostatted sample turntable 80°, injector/detector 150°, syringe 90°, column 80°; sample size: 2 ml; carrier gas: nitrogen at a flow-rate of 30 ml/min; the syringe was flushed five times with ambient air. Fig. 4 shows a chromatogram obtained under these conditions.

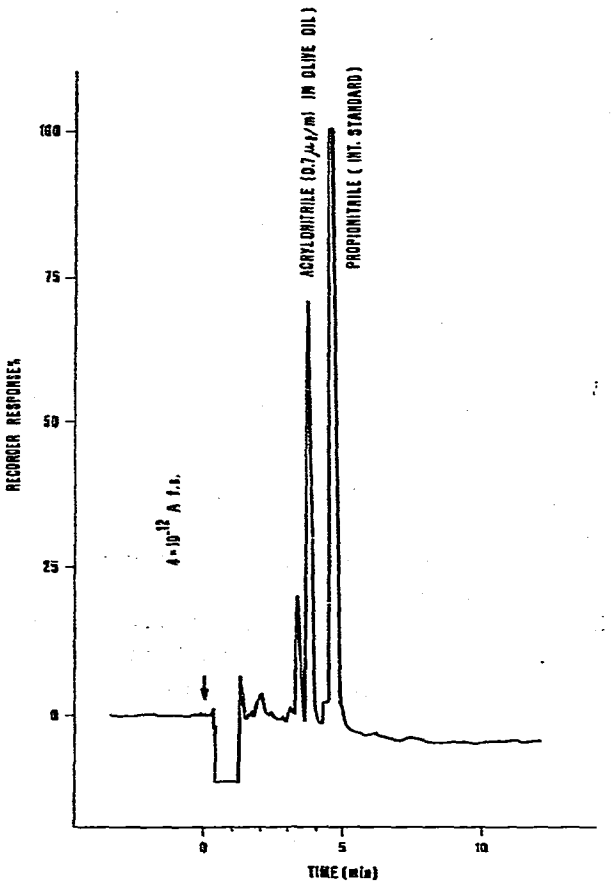

Fig. 4. Chromatogram of the head space above olive oil containing 0.7 ppm of acrylonitrile with the addition of propionitrile internal standard (NPSD).

RESULTS AND DISCUSSION

The quantitative determination using FID was carried out by plotting the peak area of acrylonitrile against the corresponding calibration curve obtained with standard solutions of pure acrylonitrile. The results are shown in Figs. 5 and 6. The concentration, X, of acrylonitrile in the resin was determined from the following formula:

$$X = \frac{C}{p} \cdot 10^6$$

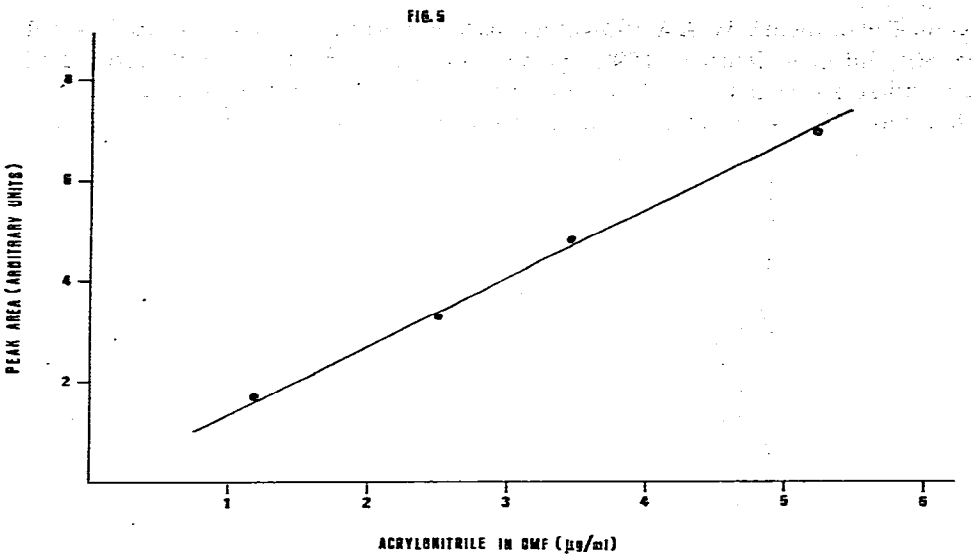

Fig. 5. Calibration curve of peak area ratio versus the amount of acrylonitrile added to the ABS resin standard solution.

where X = ppm of acrylonitrile in the resin; C = μg of acrylonitrile plotted in the calibration curve; p = μg of resin analysed.

The concentration of acrylonitrile in the olive oil was determined by plotting the peak area of acrylonitrile on the corresponding calibration curve.

For each series of analyses a blank was tested to verify the absence of interference due to the solvent or olive oil. The research on olive oil made evident the need to work with a column that could separate the peak of the monomer from

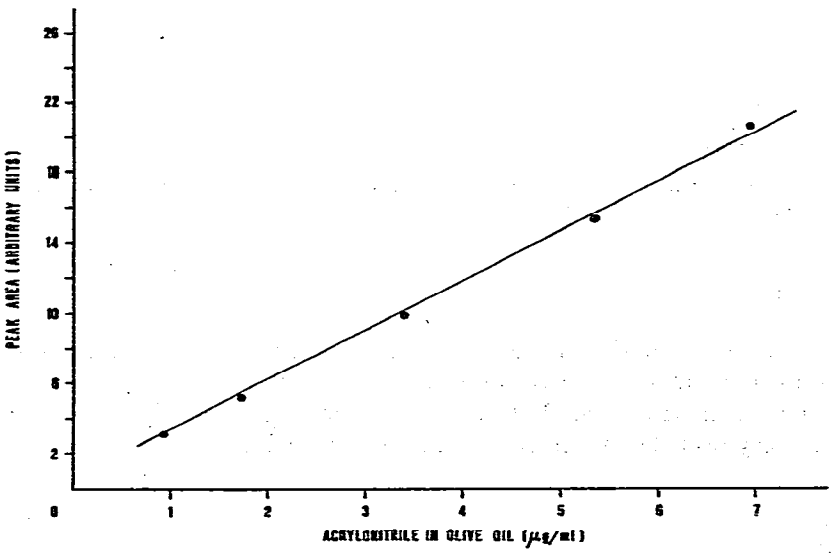

Fig. 6. Calibration curve of peak area ratio versus the amount of acrylonitrile added to olive oil.

those of the other substances present in the vapour phase. The best results were obtained with a column packed with Chromosorb 102.

The detection levels of the FID were not low enough to provide the accuracy needed by the resin industry: for food packaging, and for environmental safety also. The use of NPSD resulted in a dramatic increase in the monomer detection because, as Fig. 7 shows, the interference due to the vapour phase compounds of the olive oil is reduced as the NPSD is less sensitive to nitrogen-free organic compounds.

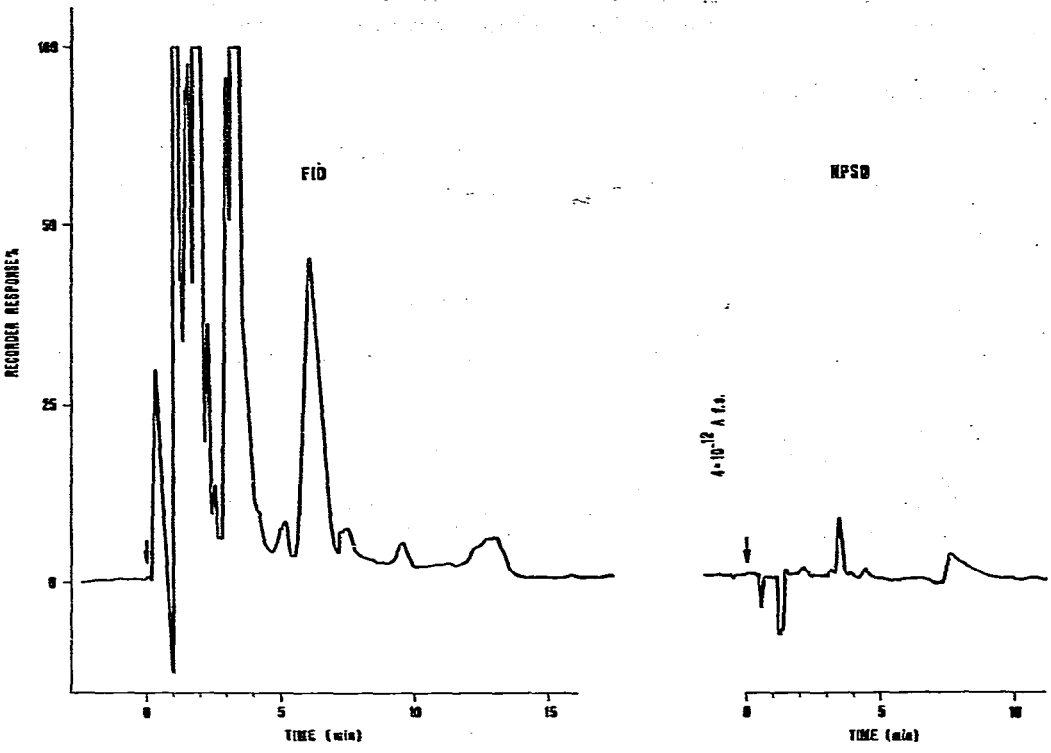

Fig. 7. Chromatograms of blank olive oil with FID and NPSD.

As a consequence the same column (Carbowax 1500) utilized previously was used for the determination of the monomer in the resins. The results, with NPSD, were 0.3 ppm of acrylonitrile in the resins and 30 ppb* in olive oil. Moreover, the type of solvent used for the resin dissolution did not require special purification. For the quantitative determination the so-called internal standard method was used, and this gave better results than standard calibration owing to the characteristics of this type of detector. Propionitrile was used as an internal standard. With NPSD, a linear plot passing through the origin was obtained for monomer determination both in the resin and in olive oil in the concentration range of greatest interest (up to 10 ppm). The standard deviation in the quantitative determination, obtained under the experimental conditions described above, was less than 6%.

* Throughout this article the American billion (10^9) is meant.

CONCLUSIONS

We have developed an analytical method for the determination of acrylonitrile in ABS resins and in olive oil, which simulates fatty foodstuffs. This problem is very important particularly because the ratio between the amount of migrated monomer and monomer contained in the resin is a constant determined by the polymer system and the contact liquid[9].

The reliability and the sensitivity characteristics of the analytical instrumentation proposed permit the use of this method for routine control.

ACKNOWLEDGEMENTS

The authors wish to thank Drs. N. Ercoli Malacari and L. Turri (ANIC) for many helpful discussions.

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