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No. 4

Lipophilic organic material: An apparatus for extracting solids used
for their concentration from sea water

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LIPOPHILIC ORGANIC MATERIAL: AN APPARATUS FOR EXTRACTING SOLIDS USED FOR THEIR CONCENTRATION FROM SEA WATER

1 INTRODUCTION

Lipophilic organic substances, whether man-made, mobilized by human activities, or of recent natural origin, are usually dissolved in sea water at such minute concentrations that the chemical characterization and quantitative determination of single compounds are possible only after a sufficient quantity has been collected by concentration from relatively large (of the order of 100-1000 litres) volumes. Essentially two techniques have found widespread application in marine organic chemistry and pollution research, i.e., extraction, either batchwise or continuous, with a suitable water-immiscible solvent (Duinker and Hillebrand, 1983, and references cited therein) or sorption onto solids (Duinker and Hillebrand 1983, *loc. cit.*; Ehrhardt, 1983). Described below is a new apparatus¹ and technique for purifying sorbant material from substances interfering with ultra-trace analyses and for desorbing analytes.

The apparatus (Fig. 1) depicted without solvent flask (usually 250 cm³)

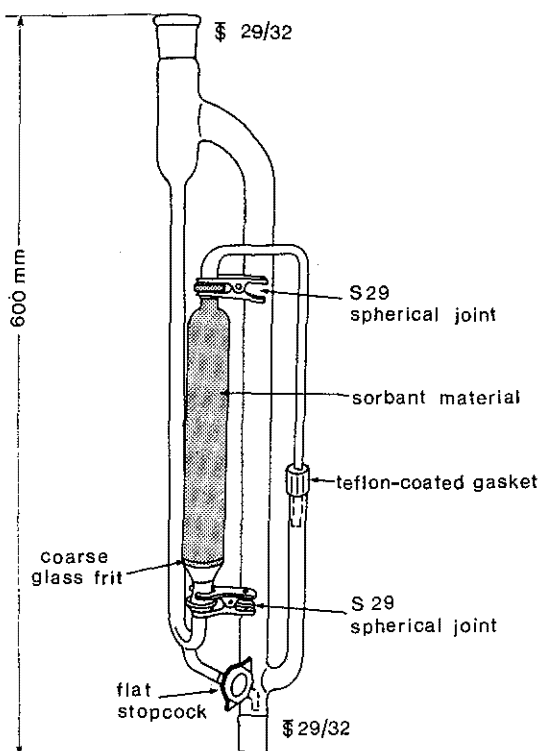


Figure 1. Extraction apparatus with cartridge inserted.

¹Patent pending.

and reflux condenser, permits the continuous percolation of a refluxing solvent through a bed of solid sorbant contained in a glass cartridge. Fresh solvent enters the cartridge from the bottom, and, in rising through the interstices between the sorbant particles, removes any air pockets after a few minutes of operation. In contrast to a Soxhlet extractor, the solvent is not siphoned off periodically but flows continuously, which, because of the exclusion of air pockets, results in very efficient extraction.

2 APPLICATION OF THE APPARATUS

2.1 Purification of XAD-2 resin

A glass cylinder is filled to approximately one-fifth of its volume with XAD-2 resin not of proven ultra-trace analytical quality and thus in need of cleaning. The cylinder sits in a bucket standing in a sink. Through a glass tube, tap water is added slowly to the cylinder from the bottom. If the resin does not remain at the bottom but floats on the rising water, the water flow is stopped and some acetone is added. After some time, depending upon the degree of dehydration of the resin beads, the latter will sink to the bottom, thus indicating that their internal pores are filled with water. This is important, because shrunk resin beads have a much lower sorption capacity.

Some resin beads may be carried away with the water flowing over the rim of the cylinder, but they are trapped in the bucket from which the water finally escapes into the sink. The flow of water through the resin is maintained until the supernatant is perfectly clear.

The resin, thus superficially cleaned, is placed in the glass cartridge shown in Figure 1. Drawing the resin slurry into the submerged cartridge by applying aspirator vacuum at its fritted end is a convenient way of doing this, because, after filling, excess water may be drawn into the vacuum pump trap. The resin bed is secured with a plug of glass wool and the filled cartridge connected with the extractor. With the flat stopcock (see Fig. 1) in the closed position, acetonitrile plus 10 % water (v/v) is refluxed through the resin bed for approximately three hours. This removes fine particles and colloidal material as well as a large proportion of substances contaminating the resin, in the case of XAD-2 mostly naphthalene.

Extraction is resumed with fresh acetonitrile plus 10 % ultra-pure water (v/v) for at least six hours (if possible, over night). This procedure is repeated until an acceptable blank is obtained (see below). The used acetonitrile may be reclaimed by first percolating it through a bed of activated charcoal and subsequent distillation over a suitable column.

2.2 Blank determination

The heat is switched off and the solvent left standing in the resin cartridge for approximately two hours to effect equilibration. The flask with the solvent is replaced with a 100-ml conical flask and the solvent in contact with the resin is drained into it by opening

the flat stopcock. Most of the acetonitrile is evaporated under reduced pressure on a rotary evaporator. The aqueous residue is shaken twice with small portions of n-hexane, and is then dried over anhydrous sodium sulphate. The volume of the hexane solution is reduced further to approximately 100 μ l, 1 μ l of which is injected in the splitless mode into a gas chromatograph equipped with a capillary column.

The repeated extraction with acetonitrile plus 10 % ultra-pure water (v/v) has been found to lead eventually to a resin sufficiently clean even for analyses of chlorinated hydrocarbon contaminants at ultra-trace levels. Finally, some ultra-pure water is filled into the cartridge to prevent shrinking of the resin beads. The cartridge is capped and stored in a refrigerator until use. Storage periods of a few days do not result in unacceptable blanks, but further experiments are needed to determine how stable the resin is under these conditions.

2.3 Common contaminants of XAD-2 resin

To enable users of XAD-2 resin to recognize material eluting from sorption columns not properly cleaned and thus contaminating samples, the first acetonitrile extract of XAD-2 as purchased was analysed by GC and GC-MS.

A 50-ml portion of the extract (about 200 ml) was diluted with an equal quantity of ultra-pure water and extracted with 20 ml n-hexane. The hexane phase was dried over anhydrous sodium sulphate and 1 μ l was injected into the GC-MS (Hewlett-Packard 5993C).

2.3.1 GC conditions

Column: 12 x 0.3 mm SE 54.

Temperature program: sample injected in the splitless mode at 40⁰ C (0.5 min), maintained for 1 min; 40⁰ C to 60⁰ C at 20⁰ C/min; 60⁰ C to 290⁰ C at 4⁰ C/min.

As evidenced by the mass spectra (see Figs. 3-8), TIC peaks Nos. 1-3 (Fig. 2A-C) are caused by isomeric C₄-alkylbenzenes. TIC peaks Nos. 4-6 most probably represent ethylstyrenes, TIC peak No. 6 a methyldihydroindene, and TIC peaks Nos. 11-13 C₆-alkylbenzenes. Lack of authentic reference compounds prevented unambiguous identifications. The intense TIC No. 10 is caused by naphthalene. For the structures of compounds causing the very low-intensity TIC peaks Nos. 14-17 no suggestions are made other than that they probably contain two benzene rings.

2.4 Concentration of dissolved lipophilic organic material with XAD-2 resin

An XAD-2 sorption cartridge, the blank value of which has been determined immediately before use, is connected, at the upstream end, with an inert filter holder containing a pre-combusted glass-fibre filter (e.g., Whatman GF/C). Water is drawn through filter and cartridge at a rate of 4 to 5 bed volumes per minute. After passage of a sufficient

volume of water, depending upon the concentration of the solute under investigation, the cartridge is disconnected from the filter holder, excess water is removed, and the cartridge inserted into the extractor. If volatile and/or sensitive compounds are to be analysed, the overflow tube is not inserted into the teflon-coated gasket but positioned in such a way that the effluent may be collected in a separate flask. The open side-tube of the extractor then has to be capped, of course. Most of the sorbed material is desorbed with the first column volume of solvent. This is a very clean and careful way of eluting sorbed material; clean, because the solvent is distilled in the same apparatus, and careful, because the effluent is not refluxed with the solvent. Any material remaining on the sorbant is desorbed in the continuous mode as described above.

If applied for analyses of hydrocarbons dissolved and/or finely dispersed in sea water, it should be noted that XAD-2 resin is a relatively poor sorbant for aliphatic hydrocarbons. Tests with spiked sea water led to recoveries of the order of 10 % for added n-alkanes (Derenbach *et al.*, 1978).

2.5 Extraction of particulate matter

The same apparatus may also be used for extracting particulate matter, e.g., collected on glass-fibre filters. The filter is disintegrated in a Virtis homogenizer under the solvent used for extraction. An empty glass cartridge is connected at its lower end with the extractor, the flat stopcock is closed, and the filter slurry filled into the cartridge. The overflow tube is connected either for discontinuous or for continuous extraction and the flow velocity of the refluxing solvent adjusted so that no filter fibres are washed out of the cartridge.

Cartridges, better suited for extracting solid materials such as tissue or sediments, which can be opened via a conical glass joint and have frits at both ends, are available from the same supplier as the extractor.²

2.6 Distillation

In the discontinuous mode, the extractor may be used for solvent distillation. A cartridge filled with alumina or silica gel may be inserted for additional purification or drying of the solvent immediately after condensation.

2.7 Chemical reactions in refluxing solvents

With the spherical ground joint of the extractor capped and a dropping funnel inserted into its side-arm, chemical reactions may be carried out in refluxing solvents, the volatile products of which may be distilled from the same apparatus simply by exchanging the spherical ground plug with an overflow tube and closing the flat stopcock.

² The extraction unit is available from Erich Eydam KG, Holzkoppelweg 101, D-2300 Kiel, Federal Republic of Germany. Telex: 292961.

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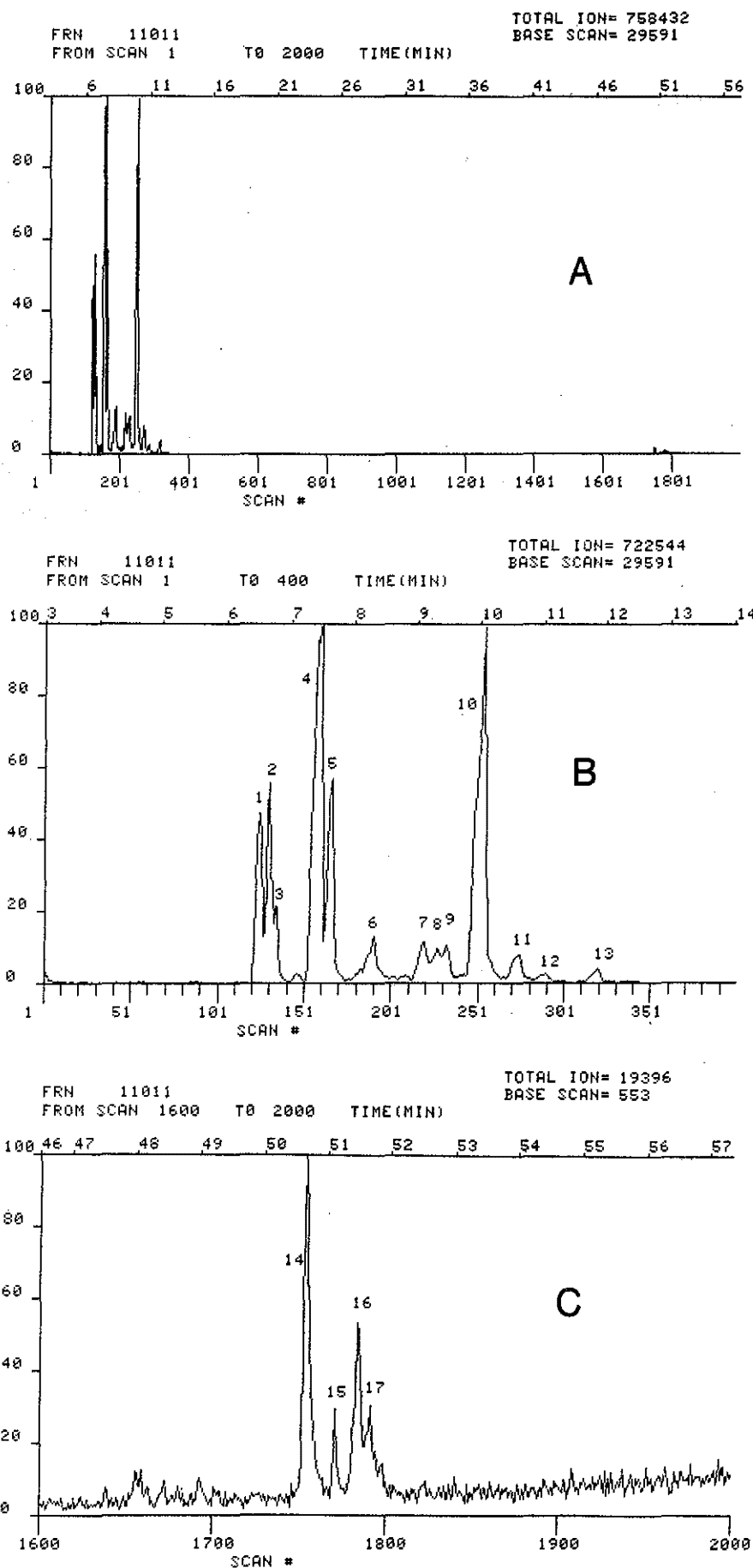


Figure 2. A) Total ion chromatogram of acetonitrile extract of commercial XAD-2 resin; B) normalized to most intense peaks between scans 1-400; and C, normalized to most intense peak between scans 1600-2000.

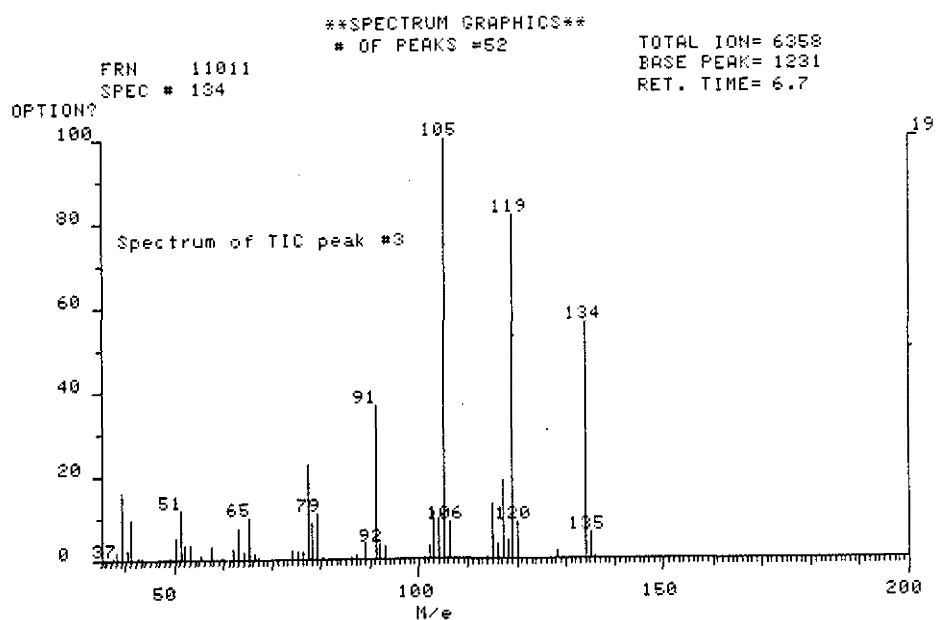
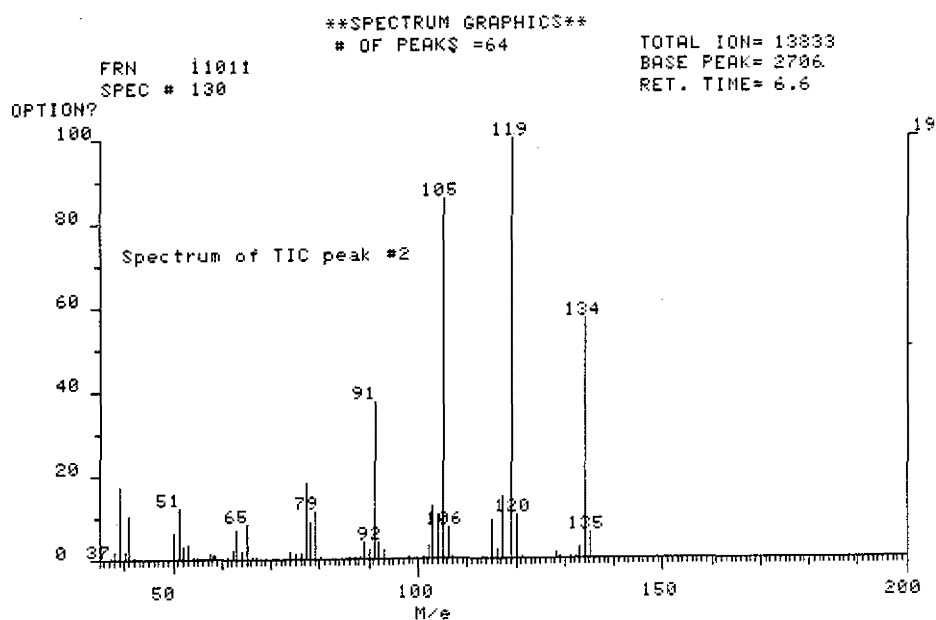
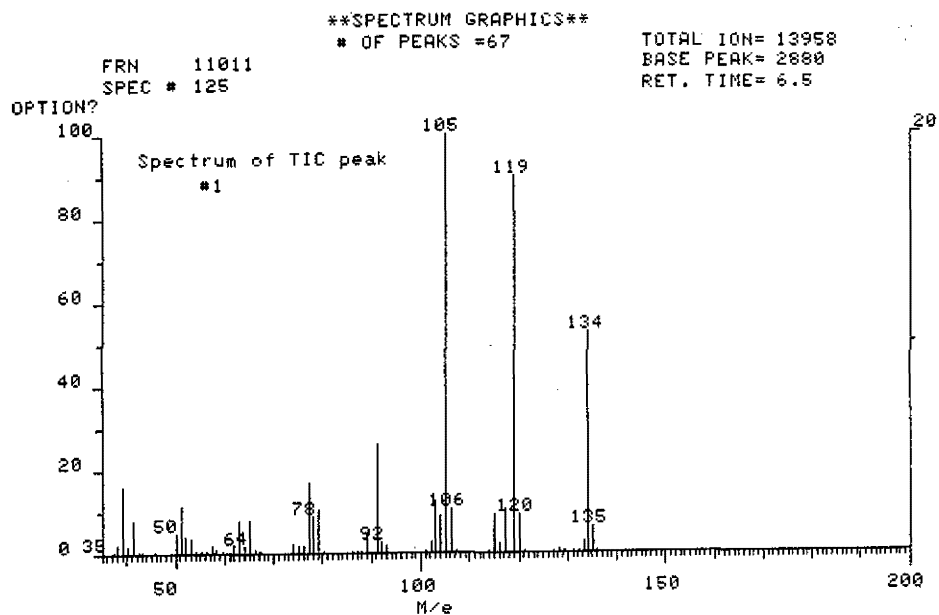


Figure 3. Mass spectra of TIC peaks Nos. 1, 2, and 3.

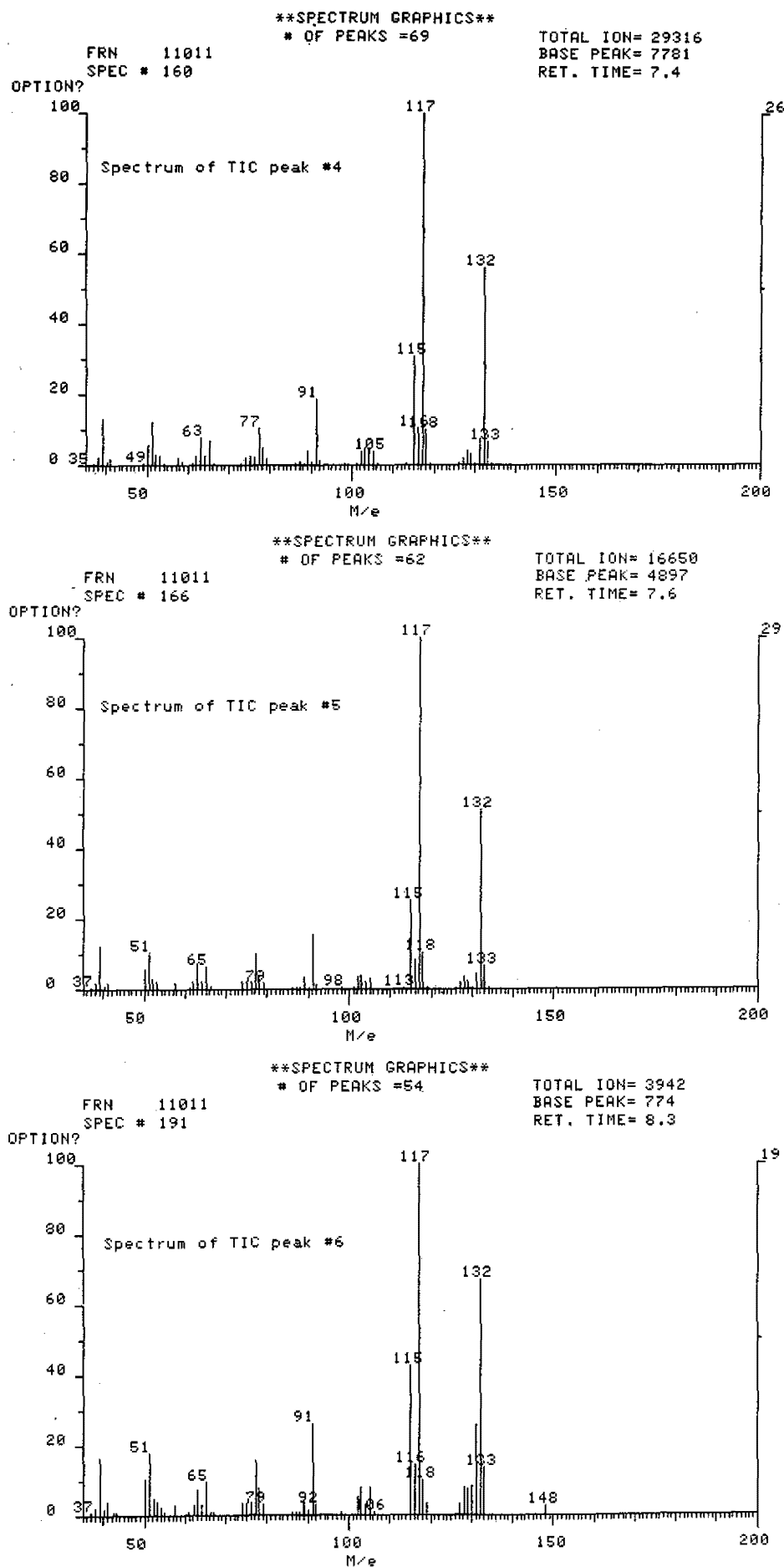


Figure 4. Mass spectra of TIC peaks Nos. 4, 5, and 6.

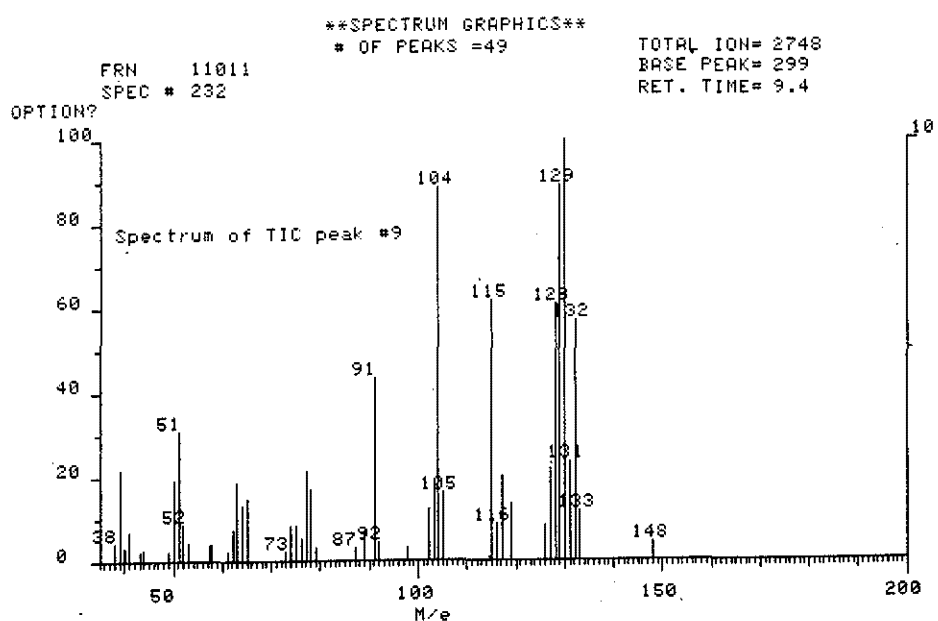
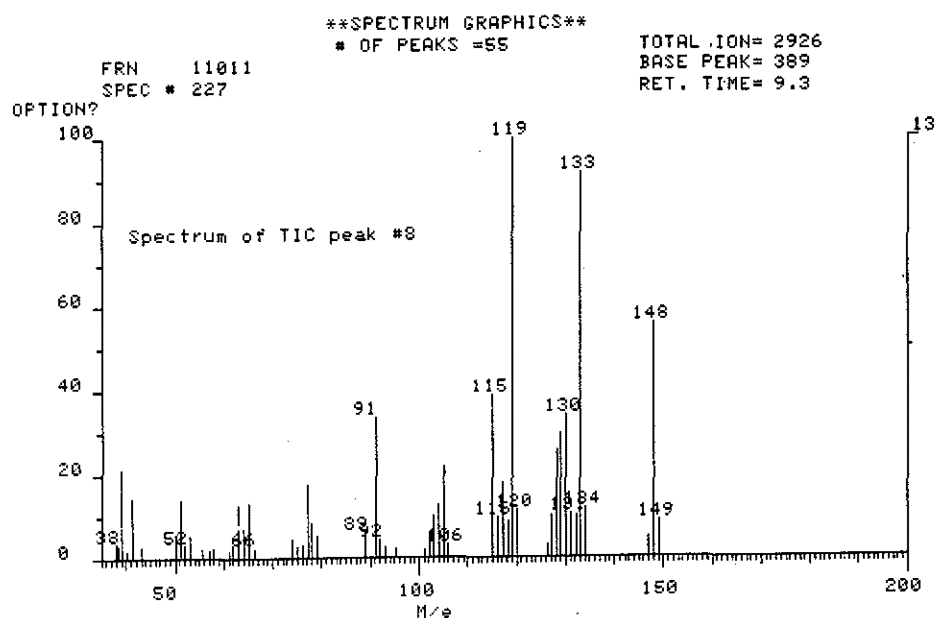
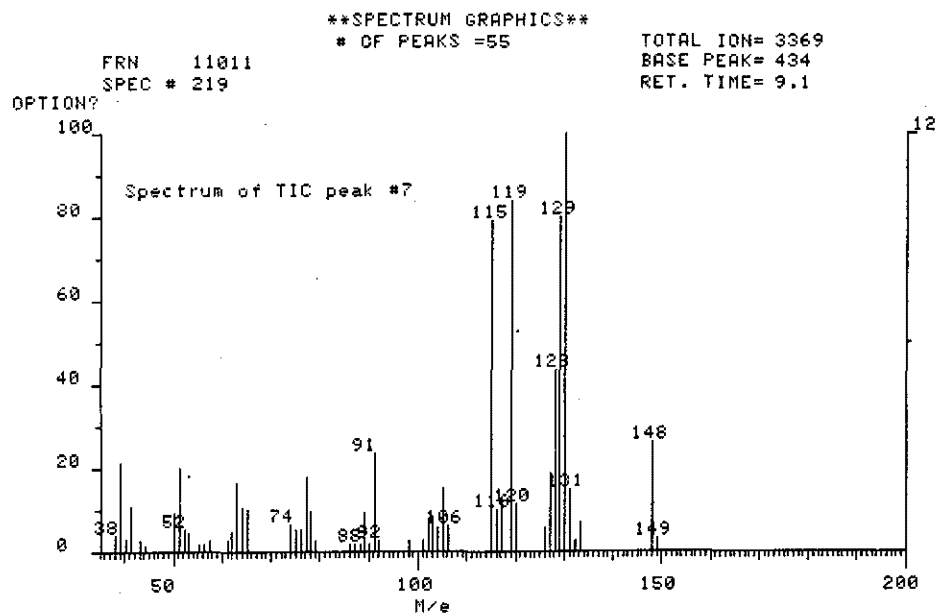


Figure 5. Mass spectra of TIC peaks Nos. 7, 8, and 9.

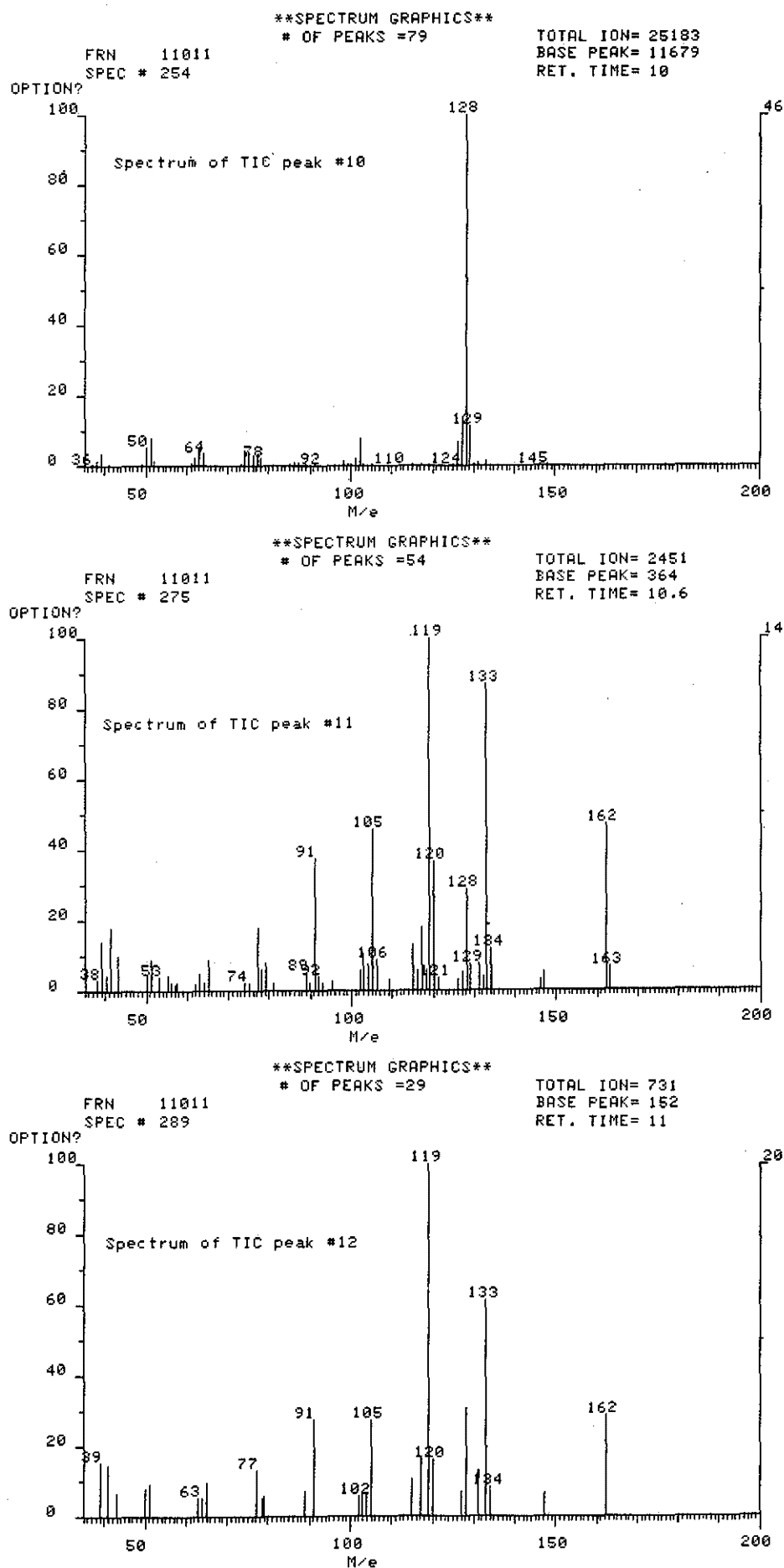


Figure 6. Mass spectra of TIC peaks Nos. 10, 11, and 12.

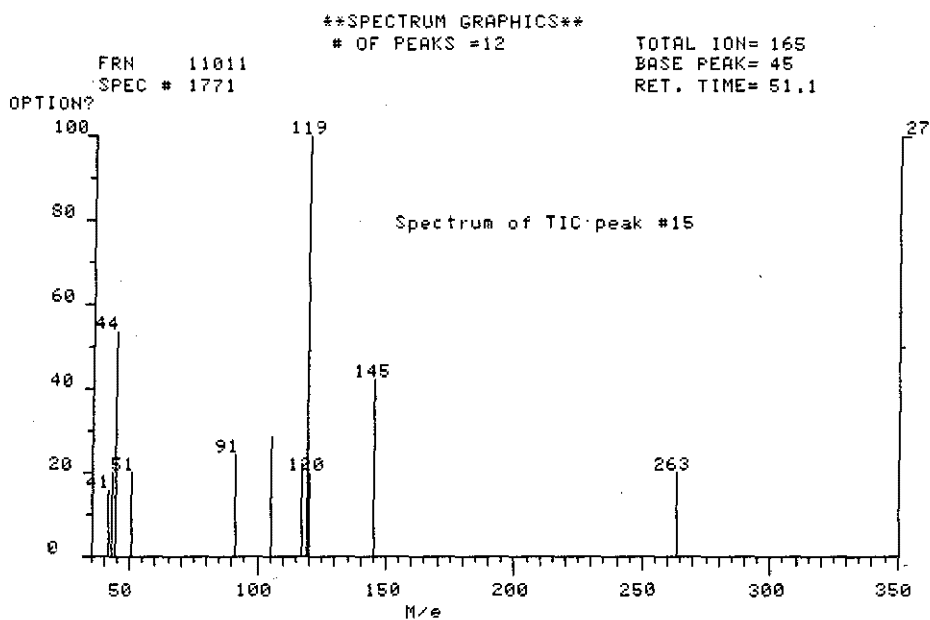
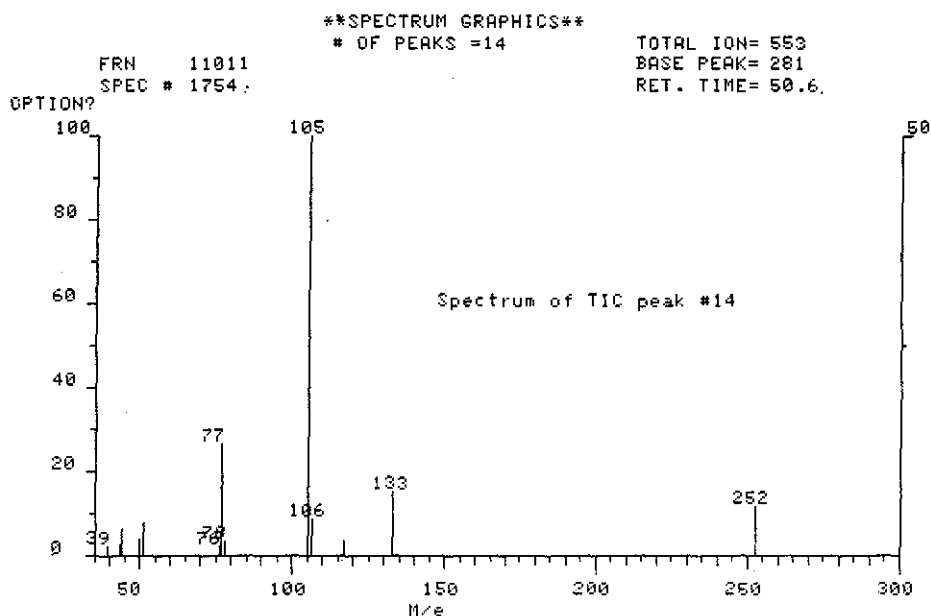
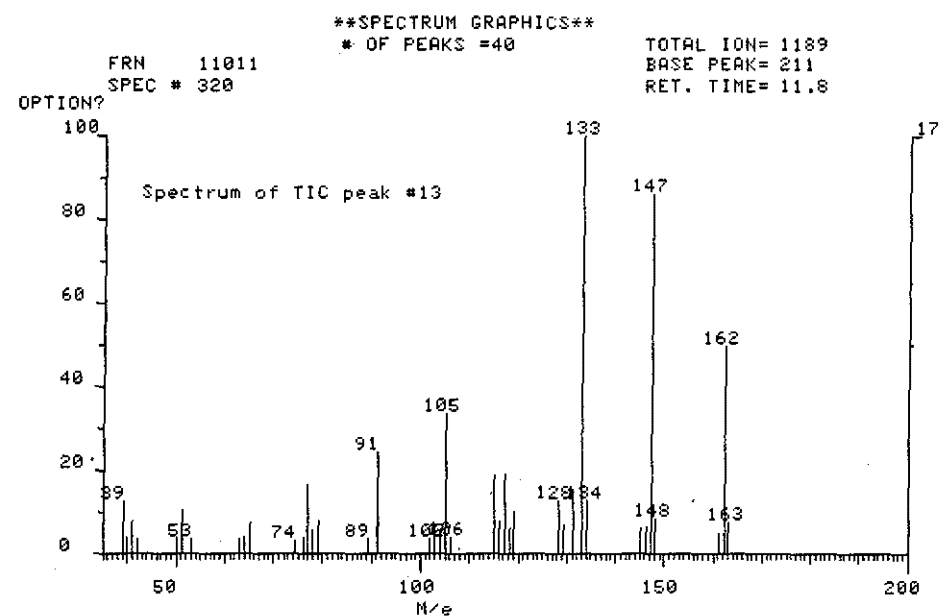


Figure 7. Mass spectra of TIC peaks Nos. 13, 14, and 15.

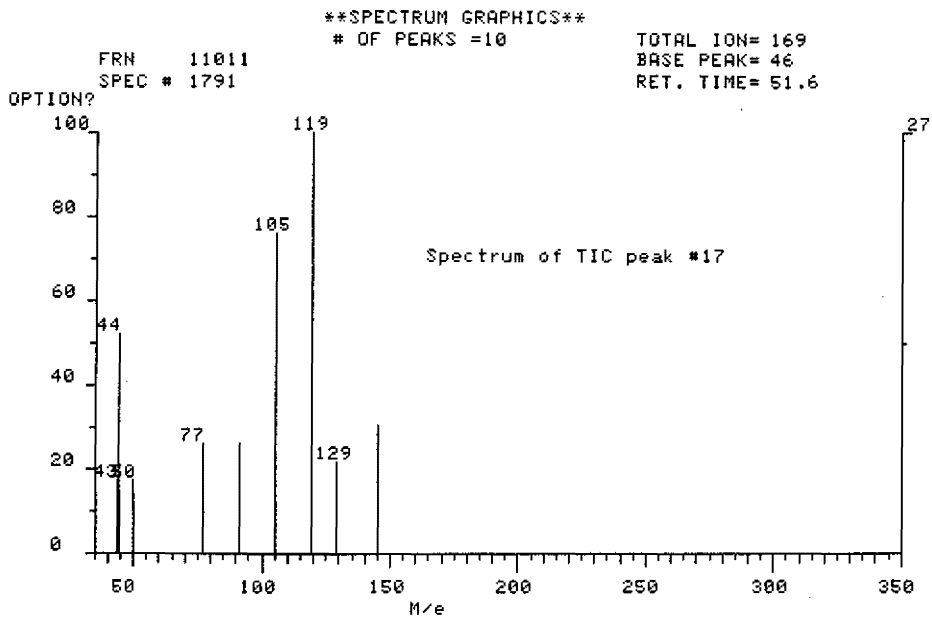
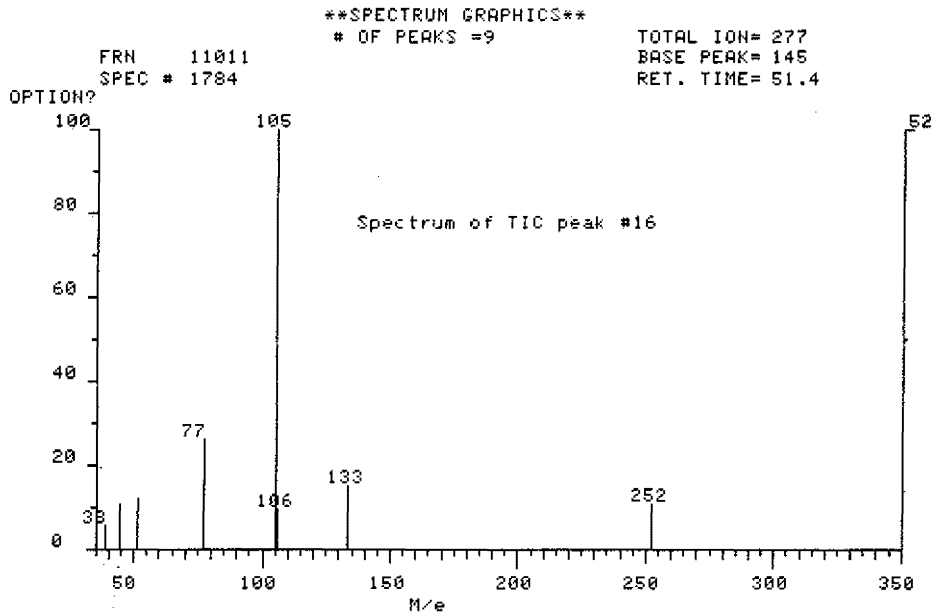


Figure 8. Mass spectra of TIC peaks Nos. 16 and 17.