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Analysis of Ferrocenyl Compounds by LR and HR Field Desorption Mass Spectrometry

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Abstract

Tris-ferrocenyl-substituted benzenes, s-tricyanobenzenes and s-triazine aromatic compounds have been synthesized by stepwise substitution of halogen atoms by ferrocenylethinyl groups.

For this FD-MS study seven compounds representing the structural types of ferrocenyl compounds under investigation have been examined.

In order to know about the limitations of the method, e.g., in case of extremely low solubility of potential analytes, the detection limits have been determined. They were found to be in the low nanogram range for scanning spectra.

A procedure for scanning mode HR-FD-MS has been developed. Despite its inherent difficulties, HR-FD-MS turned out to yield reliable mass values within a 5–7 mmu error range.

FD-MS was employed starting from a first evidence for a successful synthesis, reaching to control of purity and to the establishment of elemental composition.

Field desorption mass spectrometry (FD-MS) proved to be the method of choice for the mass spectrometric characterization of these ferrocenyl compounds.

Keywords

Field Desorption, Ferrocenyl Compounds, High Resolution MS, Mixture Analysis

1 Introduction

Tris-ferrocenyl-substituted aromatic compounds are of great interest because of their potential non-linear optical activity. Based on benzene, s-tricyanobenzene and s-triazine such systems have been synthesized by stepwise substitution of halogen atoms by ferrocenylethinyl groups (Fig. 1).

Matrix or solvent dependent techniques like FAB (LSIMS) [1], MALDI [2] and ESI [3] are currently the most widespread soft ionization methods. During recent years, field desorption mass spectrometry (FD-MS) [4] has lost much popularity because it is generally assumed to be an experimentally more demanding technique [5].

Nevertheless, due to its good sensitivity and its clean background, FD-MS proved to be the method of choice for the mass spectrometric characterization of the ferrocenyl compounds starting from a first evidence for a successful synthesis, reaching to control of purity and to establishment of elemental composition.

For this FD-MS study seven compounds representing the different structural types under investigation have been examined in detail (Fig. 2, Table 1). The aim was to optimize the mass spectrometric procedure and to get an estimate of its limitations.

2 Results and discussion

2.1 Comparison to FAB-MS

The ferrocenyl compounds of interest are usually of low solubility in all solvents. Especially, typical matrices used for FAB-MS like 3-nitrobenzyl alcohol or glycerol are not suited for this purpose. This gave rise to relatively poor FAB spectra and in several cases even prevented the use of FAB-MS. Fig. 3 shows FAB spectra of 4 and 6 which represent a relatively good and a bad case, respectively.

2.2 LR-FD-MS scanning spectra

By scanning the instrument over a mass range from m/z 100 to m/z 1500, LR-FD-MS yielded the basic information about reaction products. Examples are the spectra of 2 and 5 (Fig. 4 and Fig. 5, respectively). All samples selectively formed radical cations, $M^{+\cdot}$, under FD conditions. The experimentally observed isotopic patterns perfectly match the calculated ones. The isotopic patterns are clearly reproduced in the weak M^{2+} signals.

2.3 Mixture analysis

FD-MS did only allow for the analysis of mixtures on a qualitative level. Unfortunately, quantitative results could not be obtained due to differences in desorption behavior. It turned out that repeated measurements of artificial mixtures under virtually identical conditions yielded significantly different ratios of these components for different runs (Table 2).

While quantitative results could not be obtained from FD-MS spectra, the qualitative decission whether another compound is present or not could be made down to the 1% level. Especially the clean background of FD proved to be useful for the detection of impurities. Fig. 6 shows the mixture consisting of 1 + 2 + 4 in the ratio 15:15:1000. The minor components may be identified; isotopic patterns are fully resolved. Fig. 7 gives an example of a “real-life” mixture. It is worth to compare this with the corresponding FAB spectrum (Fig. 3b).

2.4 Detection limits

In unfortunate cases, the solubility might become so low that it is helpful to know about the detection limits of the method. The detection limits have been determined using compound 4. The measurements have been repeated on different days. The graph of Fig. 8 clearly demonstrates that compound 4 can be detected even at the 0.1 ng level with a signal-to-noise (S/N) better than 10. In Fig. 9 two levels of S/N are visualized. According to the moderate quantitative reproducibility of the measurements, S/N varies over a relatively wide range. But nevertheless, detections limits may be considered to be in the low nanogram range for scanning spectra in any case.

2.5 High-resolution FD-MS

A procedure for HR-FD-MS of the ferrocenyl compounds has been developed. While older approaches used the peak matching technique [6], this approach makes use of the co-desorption of internal standard and analyte. By use of polyethylen glykols, scanning spectra can be obtained. Fig. 10 shows a portion of the FD-HR-MS of 1. Despite its inherent difficulties that are mainly caused by the low ion currents, HR-FD-MS turned out to yield reliable mass values within a 5–7 mmu error range. Both, medium range magnet scans and accelerating voltage scans have been tested for this purpose.

3 Experimental

We used a Jeol JMS-700 sector instrument (Jeol, Tokyo, Japan) of BE geometry, equipped with an FD/FI ion source.

For FD-MS the analytes were dissolved in CH_2Cl_2. 1–2 μL of theses solutions were applied to the activated 13 μm tungsten emitters (Linden Chromaspec, Leeste, Germany) using a microliter syringe. During the measurements, the emitters were heated at a rate of 4–8 mA/min until the analyte had been completely desorbed. To prevent thermal degradation of the analyte as well as emitter damage by field-induced discharge, sometimes the rate of heating was reduced when a good level of desorption/ionization had been reached.

For routine LR-FD-MS resolution was set to R=1500 by tuning the instrument in the FI mode on the molecular ion of toluene. The magnet was scanned from m/z 100–1500 in about 10 s.

For sensitivity determinations compound 4 has been used. At R=1000 the magnet was scanned from m/z 100–1000 in about 10 s.

For HR-FD-MS resolution was set to R=5000 in the same way. The scan range was reduced to about M±200 u and the scanning rate was lowered. Alternatively, HV scanning with comparable scanning rates was employed.

Polyethylene glycol (PEG 400 or PEG 600) was used for internal calibration. For this purpose, a solution of PEG in ethanol was applied together with the analyte to the field emitters. The analyte/PEG ratio was adjusted as to obtain signals of similar intensity for both compounds. Between measurements readjustment of the signal was achieved by fine tuning on peaks from field desorbing PEG close to the expected molecular mass.

Due to the changing PEG spectrum during the desorption process, not only $[PEG+Na]^+$ but also $[PEG+H]^+$ signals had to be incorporated into the mass reference file.

4 Conclusion

FD-MS is still a very valuable ionization method. FD represents the only desorption/ionization technique that allows desorption of the analyte without interference with any matrix compound or solvent effects.

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Table 1: **Elemental composition and molecular weight of 1–7.**

Sample	Formula	Basepeak of isotopic pattern	Average isotopic mass
1	$C_{18}H_{12}FeBr_2$	443.8637	444.0
2	$C_{30}H_{21}Fe_2Br$	571.9529	573.1
3	$C_{30}H_{21}Fe_2I$	619.9388	620.1
4	$C_{42}H_{30}Fe_3$	702.0398	702.2
5	$C_{45}H_{27}Fe_3N_3$	777.0256	777.3
6	$C_{39}H_{27}Fe_3N_3$	705.0256	705.2
7	$C_{33}H_{37}F_3N_3$	633.0255	633.1

Table 2: **Theoretical and experimental ratios found from artificial mixtures.**

Mixture	Ratio theor.	Ratio exp.
2+4	2/4	2/4
	1/10	1/3.7
	1/10	1/12
	1/2	1/1.5
	1/2	1/1.2
	1/1	1/2.6
	1/1	1/1
1+3	1/3	1/3
	1/10	1/11
	1/2	1/3.6
	1/1	1/1.2
	1/1	1/2.9
	1/1	1/3.9
	2/1	1.64/1

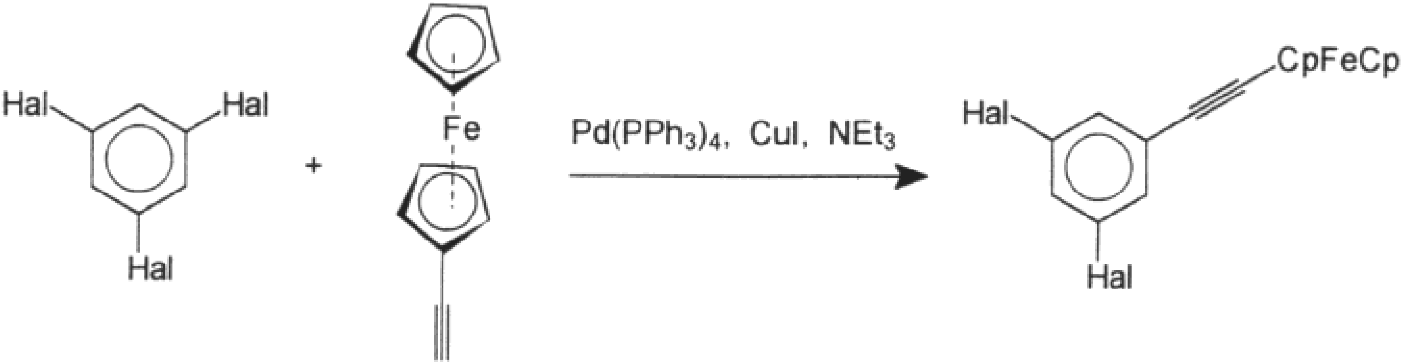

Figure 1 Synthesis by Hagihara reaction.

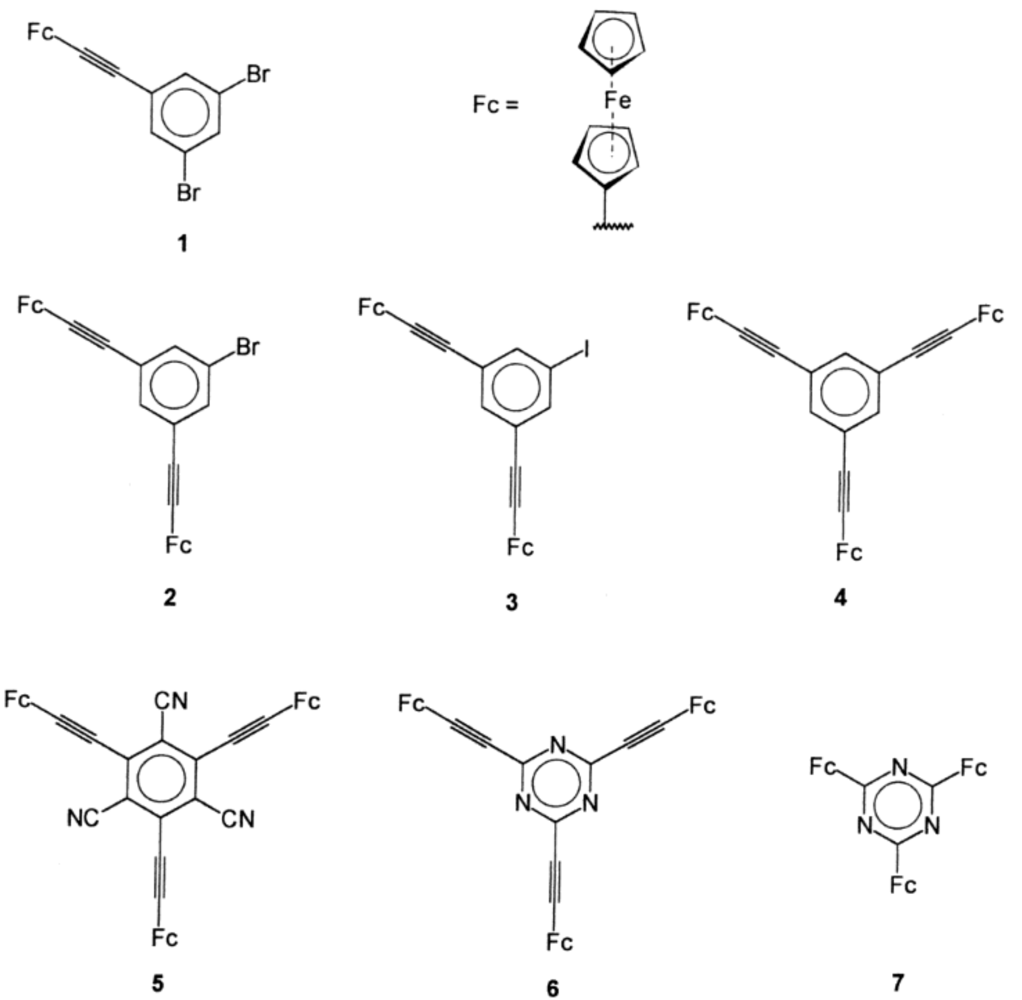

Figure 2 The ferrocenyl compounds used in this study.

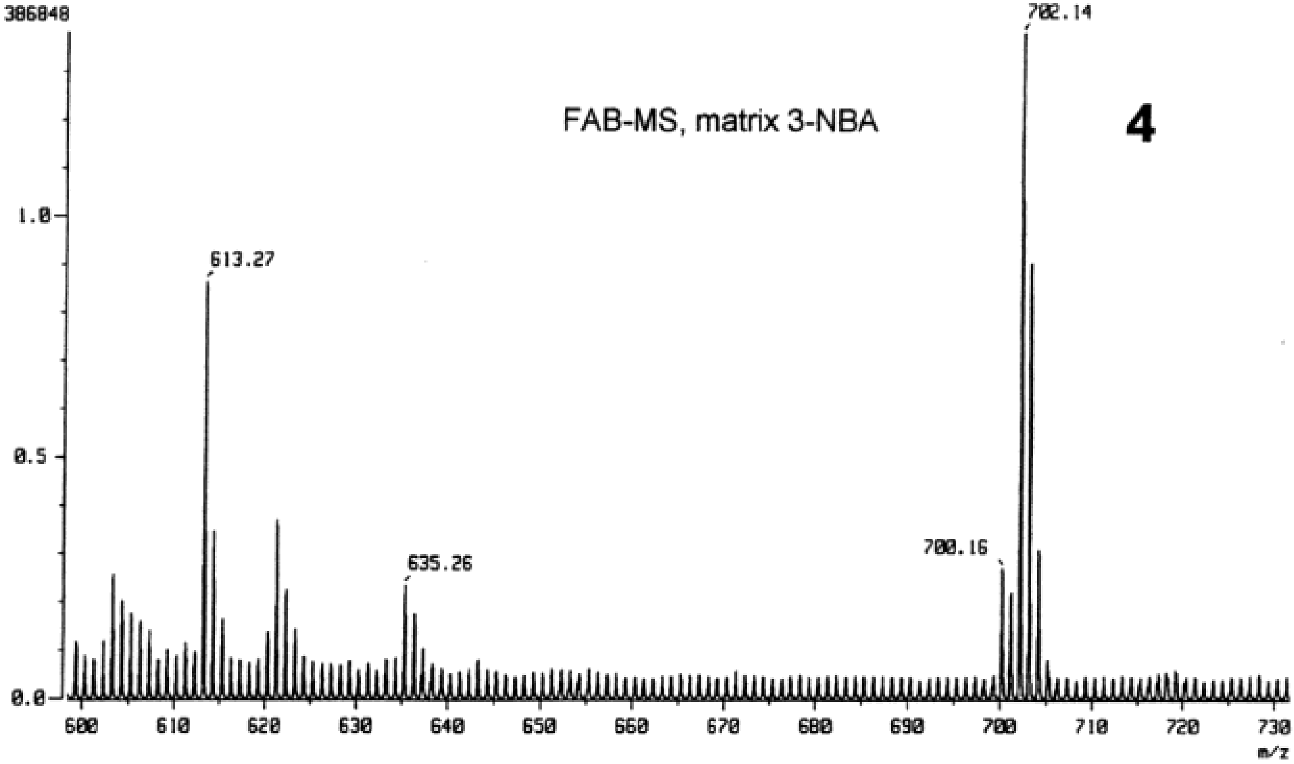

Figure 3 FAB spectra of 4 and 6 which is badly soluble in 3-NBA.

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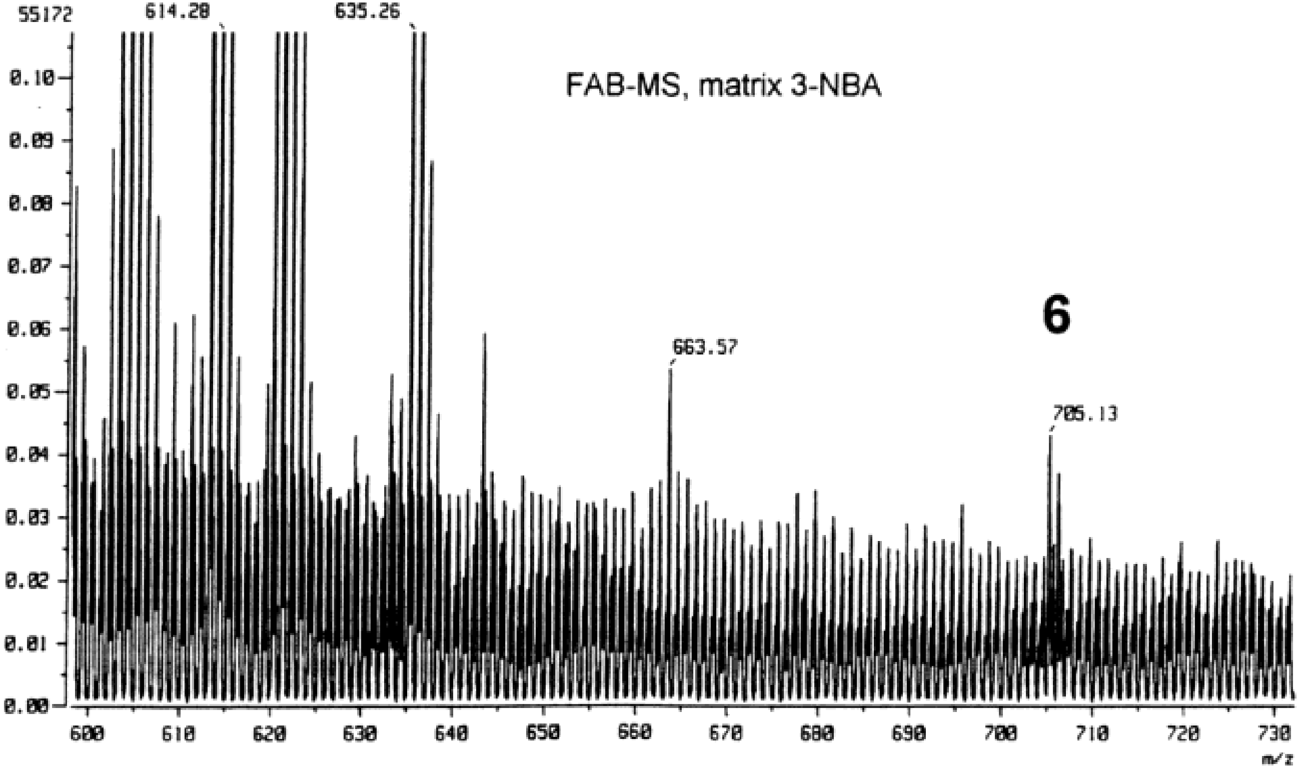

Figure 3. (cont.)

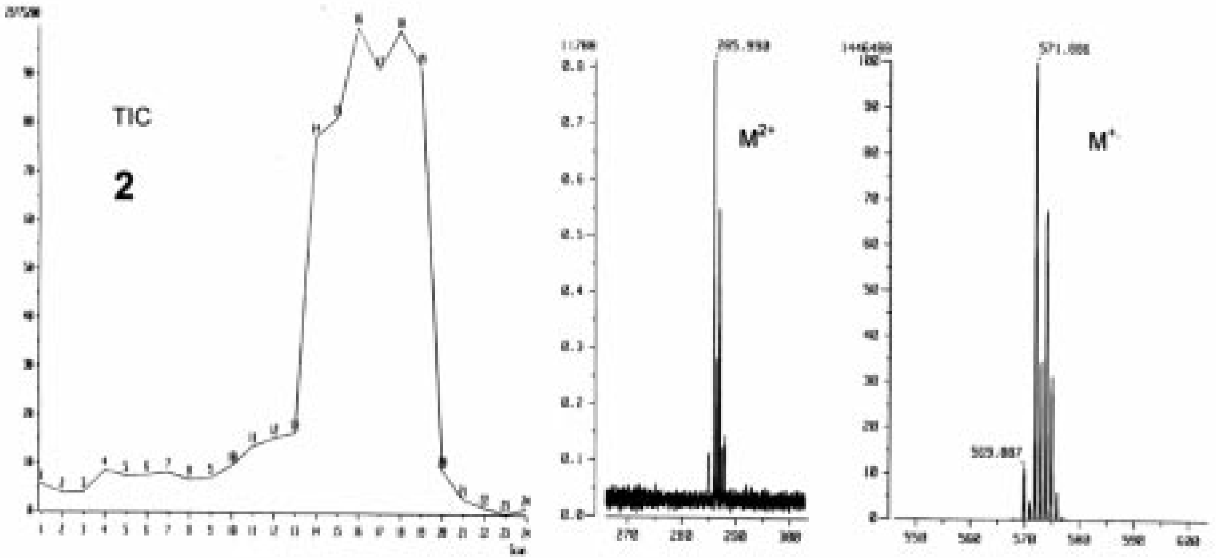

Figure 4 FD spectrum of 2.

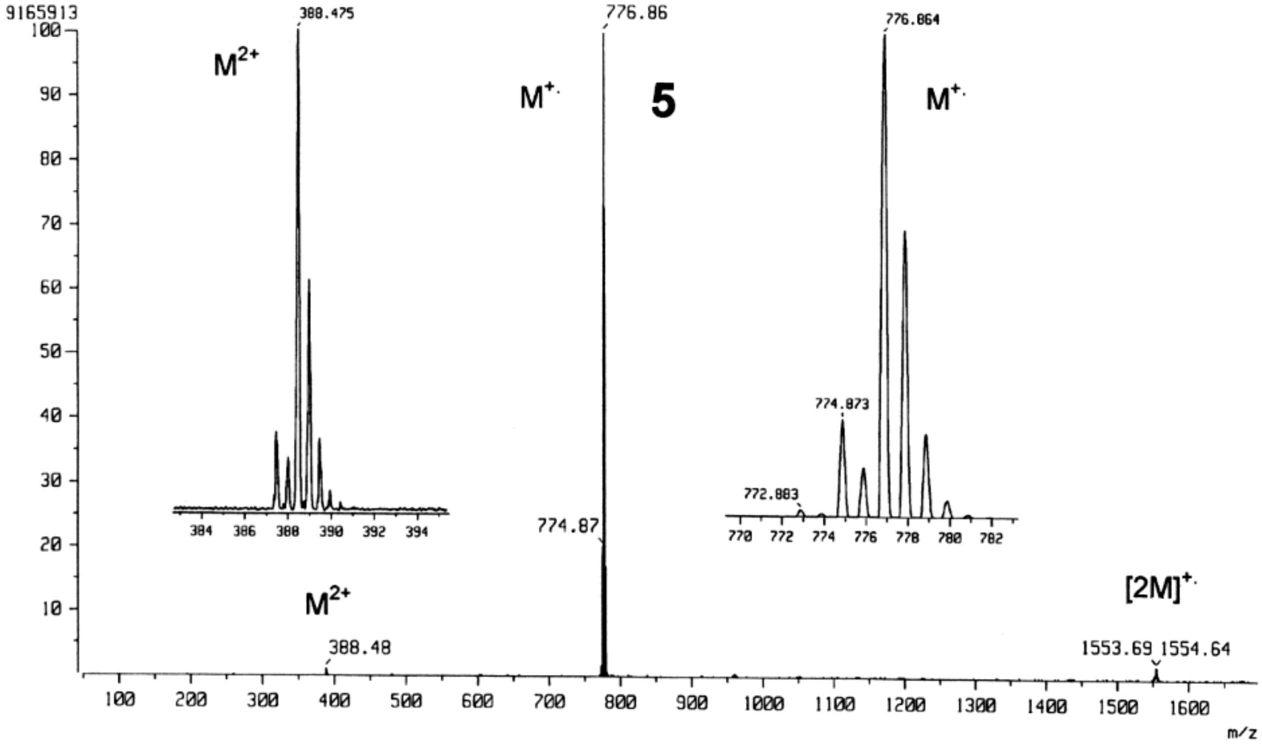

Figure 5 FD spectrum of 5.

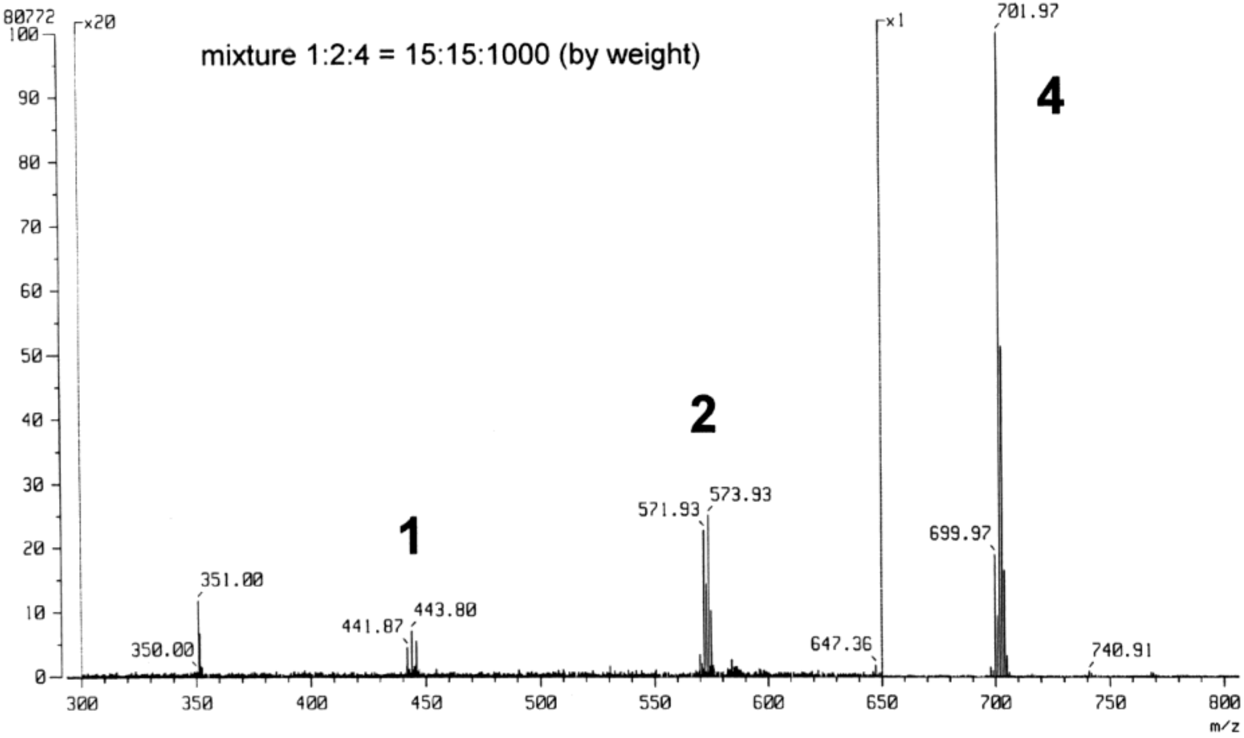

Figure 6 FD spectrum of an artificial mixture consisting of 1, 2 and 4.

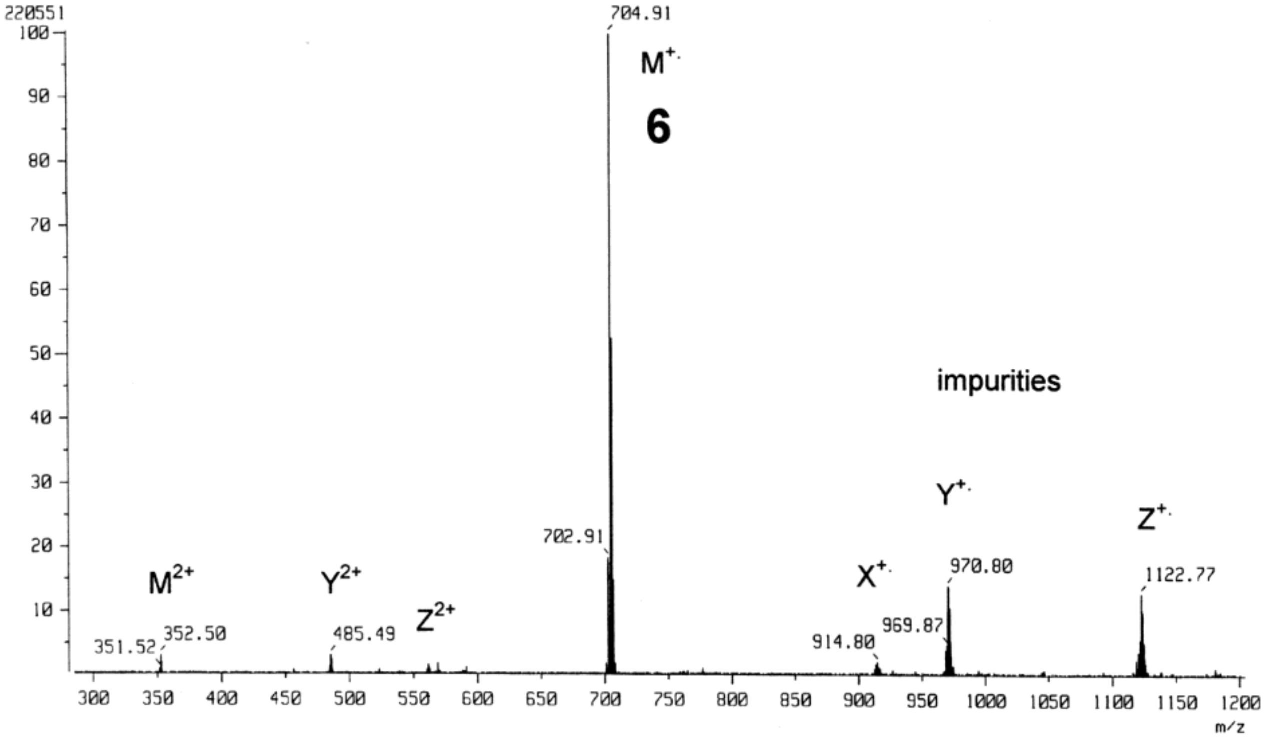

Figure 7 FD spectrum of a “real-life” mixture from a reaction that was intended to yield 6.

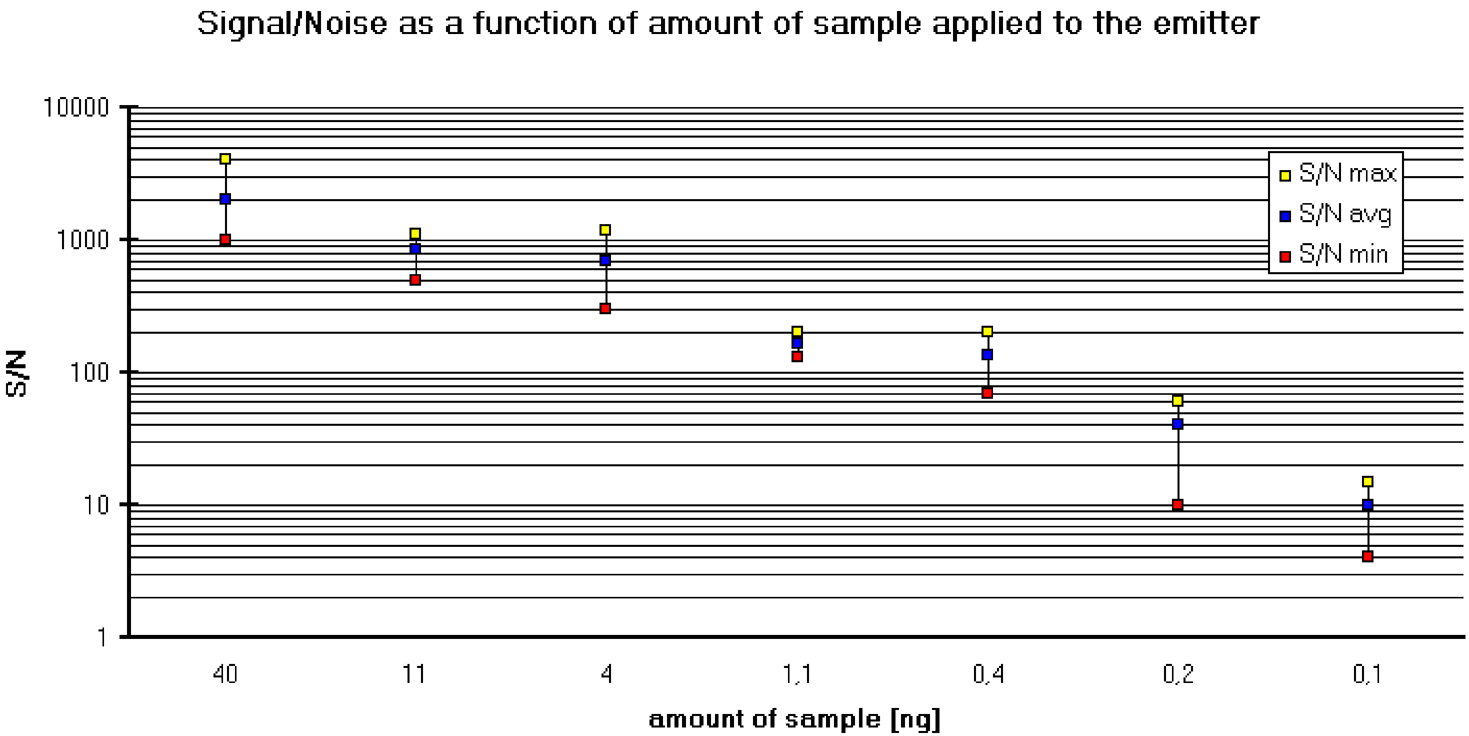

Figure 8 Plot of signal-to-noise ratio vs. amount of sample.

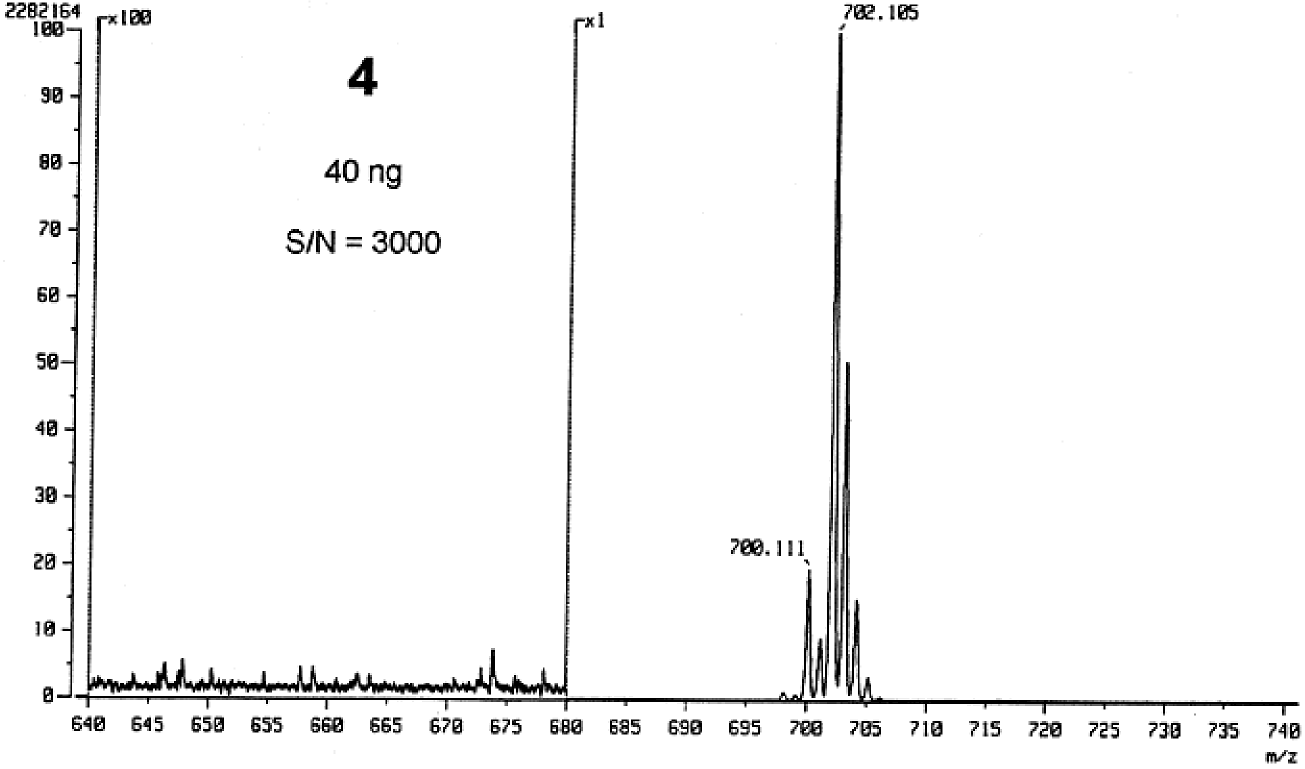

Figure 9 Visualization of two S/N ratios (cf. preceeding page for part 1).

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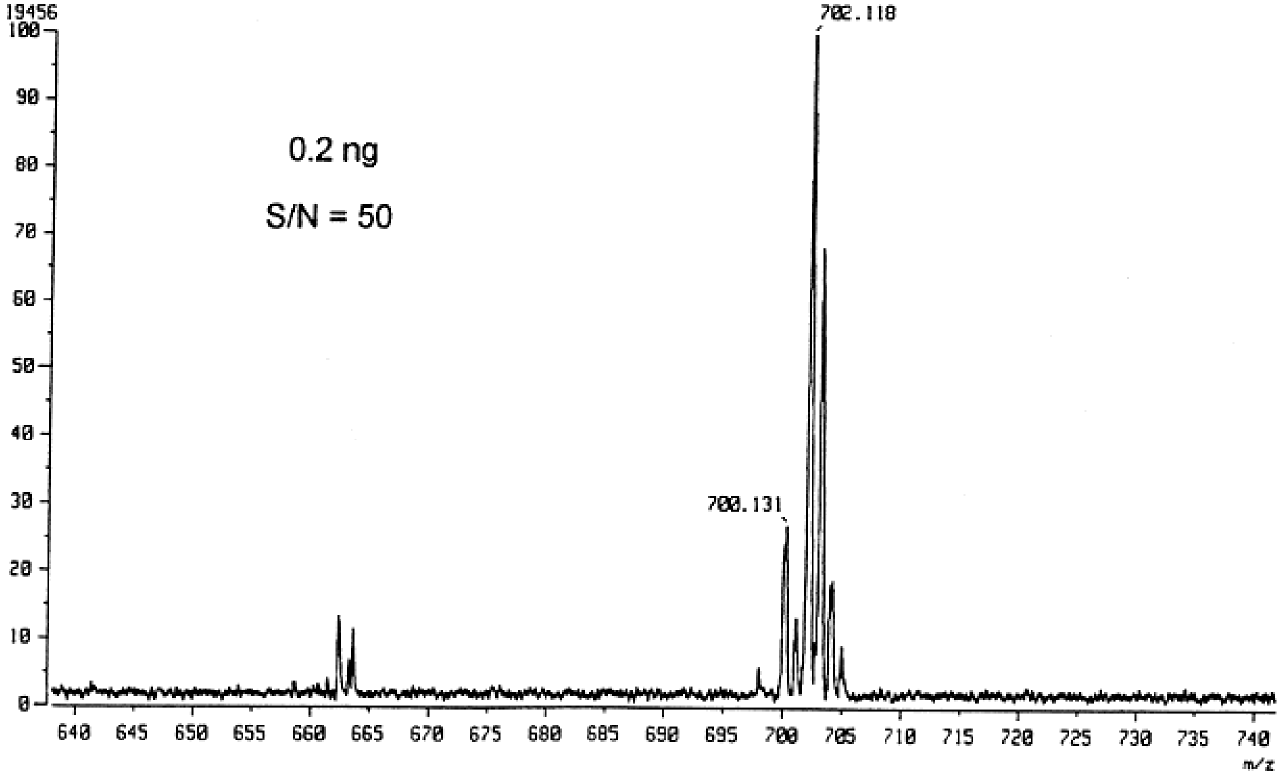

Figure 9 (cont.)

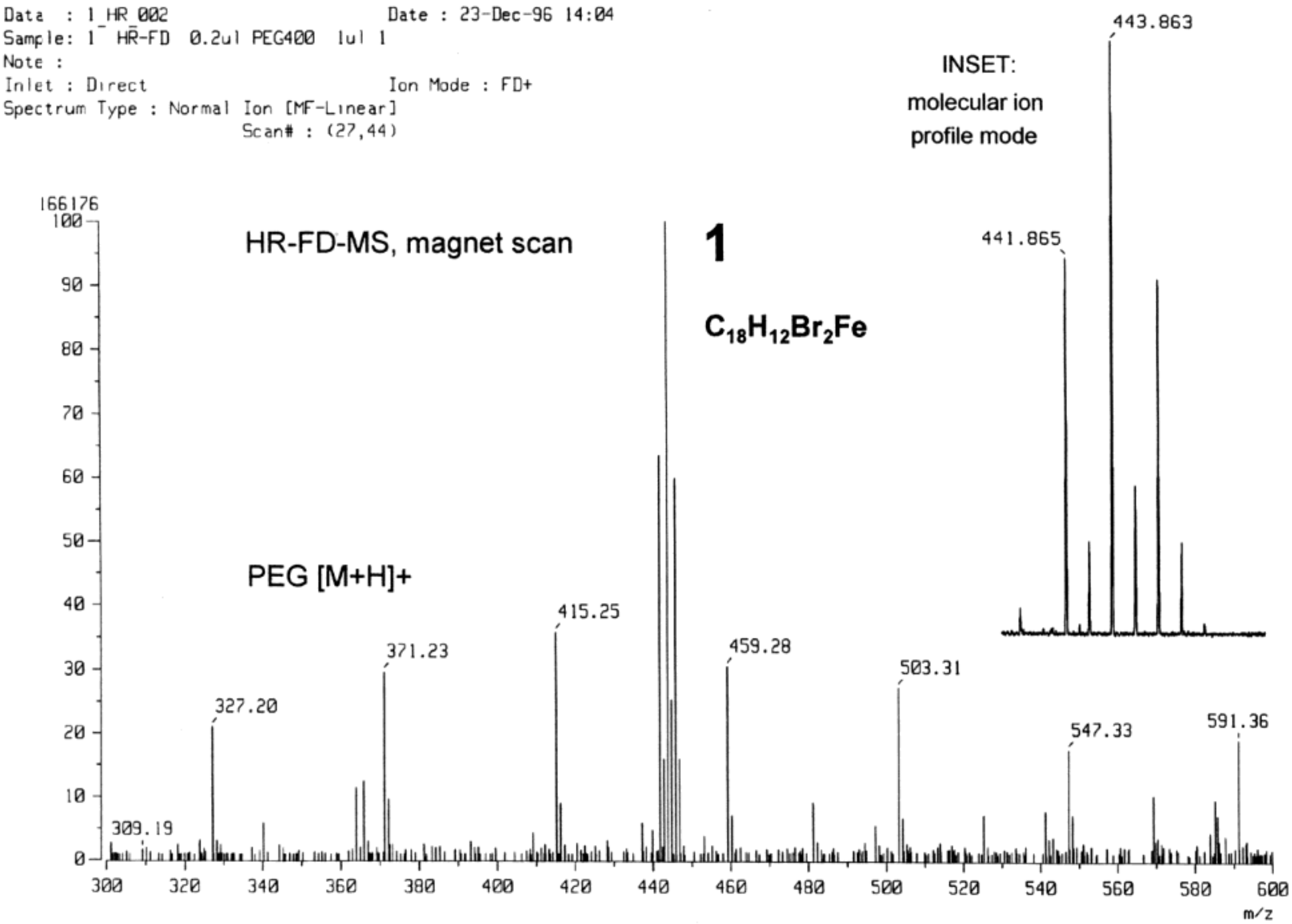

Figure 10 HR-FD-MS scanning spectrum of 1.