

Performance evaluation of a TG/MS system

M. Statheropoulos^{*}, S. Kyriakou, N. Tzamtzis

National Technical University of Athens (NTUA), Department of Chemical Engineering, Sector I, 9 Iroon Polytechniou Str., Athens 157 73, Greece

Received 20 April 1998; received in revised form 22 June 1998; accepted 22 July 1998

Abstract

A procedure for the evaluation of the performance of a TG/MS system is proposed. This procedure includes tests for monitoring the mass-flow stability, the gas transfer delay, the evolved-gas condensation effect and the interferences of the coupling system on TGA and MSD specifications. The procedure was applied on an in-house constructed TG/MS system. The results of such evaluation procedure can be used for monitoring the performance of a specific TG/MS system and, thus, can be a basis for design improvements. In addition, they may be used for comparison of the results of different TG/MS systems, or for interlaboratory comparisons. © 1998 Elsevier Science B.V.

Keywords: Coupling; Evaluation; Performance; TG/MS

1. Introduction

The study of compound degradation by thermogravimetry (TG) can be greatly enhanced when evolved-gas analysis is used [1–4]. This can be achieved by combination of TG with other techniques capable of providing qualitative (evolved-gas detection – EGD), or both qualitative and quantitative information (evolved-gas analysis – EGA) [1,5–9]. It appears that the most popular technique used in combination with TG, is mass spectrometry (MS) on account of its sensitivity, versatility and fast analysis time.

In a TG/MS system, the thermobalance provides, among other things, with precise and reproducible heating conditions. The gaseous products generated by volatilisation, sublimation or chemical reaction, are flushed out of the furnace chamber with the help of a

purge gas. The evolved gases are introduced in the MS detector (MSD) through a coupling system, which acts both as an MSD inlet and a pressure-reduction system [6,10]. The coupling system should meet several specifications such as: rapid evolved-gas transfer from the sample pan in the TG analyser (TGA) to MSD; no memory effects; no degradation or condensation of evolved gases, no interferences on the specifications of the TGA and the MSD; no air insertion during TGA furnace opening; simplicity in construction; easy system decoupling and cleaning; low cost; and continuous monitoring and versatility with respect to TGA and/or MSD [6,10]. In addition, if the system is used for EGA, then high sensitivity and repeatable flow conditions are necessary.

A great variety of TG/MS systems have been presented in the literature during the past decade [6]. Therefore, a need appears for the development of a procedure for quantitatively estimating the specifications of a TG/MS system. The purpose of this work

^{*}Corresponding author. Tel.: +30-1-7723109; fax: +30-1-7723188; e-mail: stathero@orfeas.chemeng.ntua.gr

was to develop and apply various performance evaluation criteria on an in-house constructed TG/MS system. The results of such evaluation procedure can be used for monitoring the performance of a specific TG/MS system and, thus, can be a basis for design improvements. Furthermore, it may be used for comparing the results of different TG/MS systems, or for interlaboratory comparisons.

2. Experimental

2.1. Instruments

The TGA used was a TA Instruments TGA 2050, using the 1.5B Universal data analysis system. The MSD used was a Hewlett–Packard 5972. The TG/MS

coupling system used was an in-house constructed one-stage type capillary system [11]. The TG/MS system configuration is shown in Fig. 1(a). The system consists of (1) a computer-controlled TGA, (2) a heated coupling system and (3) a computer-controlled MSD. A rough diagram of the TG/MS coupling system is shown in Fig. 1(b). It consists of a TG/MS interface and a transfer line. The transfer line consists of a deactivated 2.17 m×0.15 mm i.d. Chrompack capillary and a heating thermomantle. The TG/MS interface and the transfer line can be heated up to 250°C. The TG/MS interface operates as a split system. Port A is connected to vacuum. Port B has two modes of operation: (i) the sampling mode, when port B is connected to vacuum in order to direct evolved gases to the head of the capillary during the TG/MS analysis and (ii) the idle mode, when port B is

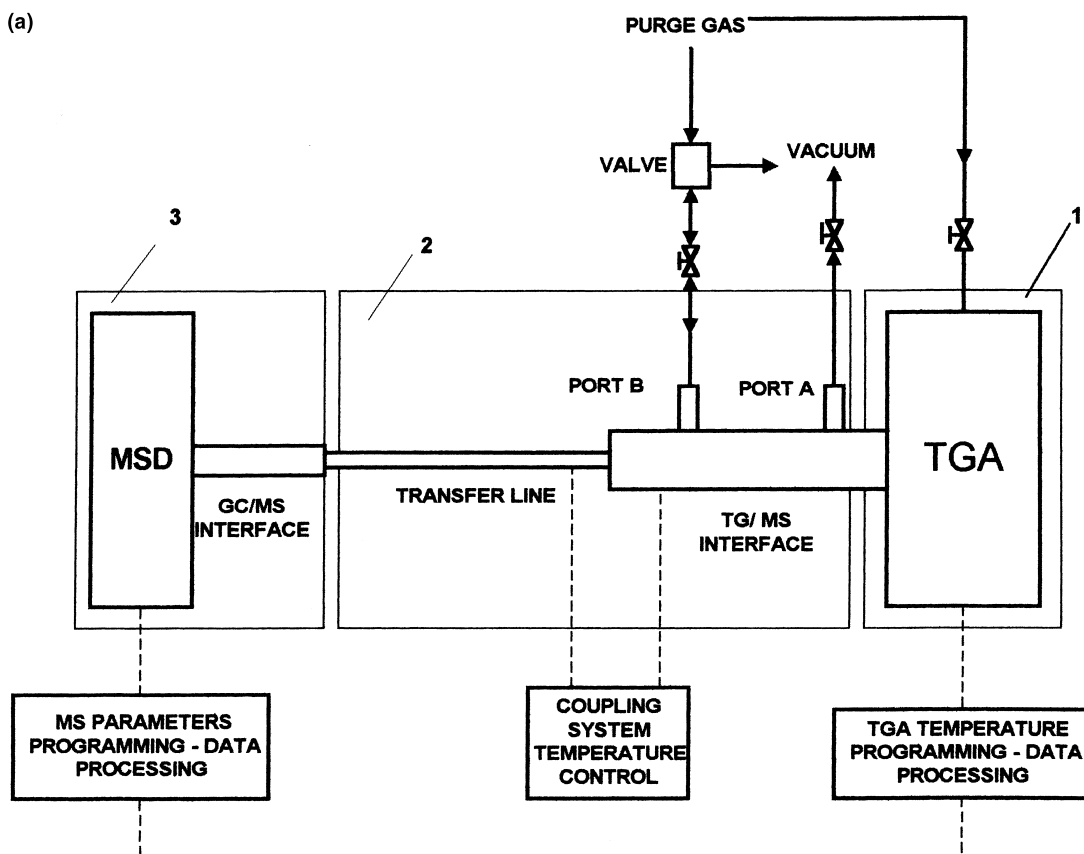


Fig. 1. (a) TG/MS system configuration: (1) thermogravimetric analyser; (2) coupling system; and (3) mass spectrometric detector. (b) TG/MS coupling system consisting of a TG/MS interface and a deactivated capillary with a thermomantle (transfer line).

(b)

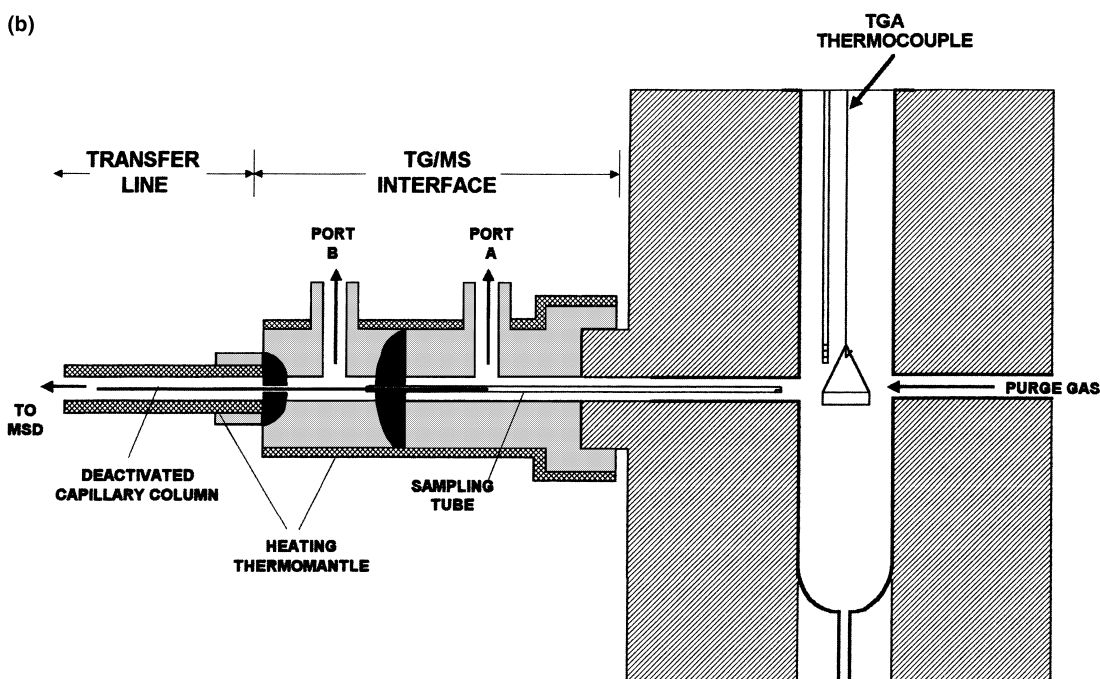


Fig. 1. (Continued)

connected to a gas purge in order to prevent air insertion during TGA furnace opening. The vacuum in ports A and B establish laminar flow conditions through the interface. In this way, evolved-gas mixing is avoided, thus resulting in a narrow, initial sample mass distribution [10].

2.2. Materials

The following compounds were used: KHCO_3 , CaCO_3 , and flakes of NaOH (pro analysis Merck), calcium oxalate standard (TA), LDPE standard (CDS pyrolysis unit), and benzoic acid 98% (Fluka).

2.3. Methods

2.3.1. Evaluation of mass-flow repeatability and evolved-gas transfer delay

Three different quantities, ranging from 1 to 15 mg from each of KHCO_3 and CaCO_3 , were heated in TGA under the following conditions: heating rate $20^\circ\text{C}/\text{min}$ up to 300° and 900°C , respectively. Mass loss generates a differential thermogravimetry (DTG) curve of positive sign.

2.3.2. Evaluation of the interferences of the coupling system on TGA and MSD performance

(a) Calcium oxalate samples, with 10 mg weight, were analysed with, and without, the coupling system for the evaluation of possible TGA deterioration of performance. TGA was weight calibrated using TA standard weights, and the temperature calibrated using TA nickel and Alumel Curie-point standards. The calibration was performed under the actual experimental conditions. Heating rate was $50^\circ\text{C}/\text{min}$ up to 900°C . A mixture of benzoic acid and NaOH in a 1/3 mole ratio was analysed for monitoring MSD performance. The mixture was heated with a heating rate of $50^\circ\text{C}/\text{min}$ from ambient up to 600°C .

2.3.3. Evaluation of evolved-gas condensation

Low-density polyethylene (LDPE) was heated at a heating rate of $50^\circ\text{C}/\text{min}$, from ambient to 700°C .

In all the foregoing cases, the coupling system was heated at 190°C . The volumetric flows through ports A and B were adjusted to 60 and 39 ml min^{-1} , respectively, and TGA furnace was purged with Helium at

100 ml min⁻¹ under 0.5 bar. The mass-spectrometric detector was operated in a total ion-current mode (TIC) at 6.1 scans/s, while GC/MS interface was maintained at 200°C.

3. Results and discussion

3.1. TG/MS system

The TGA furnace has a vertical configuration with a horizontal purge gas flow. The presence of a quartz liner minimises memory effect problems. As evolved gases are purged out of the TGA furnace, their temperature decreases rapidly. This might result in a severe condensation problem. Gas condensation may be partially avoided by properly heating the TG/MS coupling system, using a heating thermomantle.

The described TG/MS system presents several advantages, such as: low cost; versatility with respect to MSD; and simplicity in construction. However, fractionation of some compounds in the evolved-gas stream may occur in the capillary. This sets some limitations to the applications of the system, especially when a gas mixture with high molecular-weight compounds is analysed [5,10]. Table 1 summarises the built-in characteristics of the TG/MS system for meeting certain specifications.

3.2. Evaluation of mass-flow repeatability and evolved-gas transfer delay

Mass-flow repeatability is an important factor in quantitative determinations. It is influenced by volumetric flow and evolved-gas density stability [9,10].

Volumetric-flow repeatability depends on the temperature and pressure control of the coupling system. The estimated standard deviations of the time values corresponding to the maximum of the DTG curve and MSD signal, when CO₂ was monitored from KHCO₃ and CaCO₃ decomposition, are presented in Table 2. Both compounds decompose in one stage, with KHCO₃ simultaneously liberating H₂O and CO₂. The results of an F-test on these values show that there is no significant variance introduced in the presence of the coupling system, at a 95% confidence level. This is indicative of repeatable temperature and pressure conditions in the coupling system. Evolved-gas density depends on parameters such as: weight loss rate; nature of gas eliminated from the sample; and the nature and flow rate of purge gas. The repeatability of these parameters can be assessed by the evaluation of the interferences caused of the coupling system on TGA performance, as presented below.

The ability of the MSD in the TG/MS system to monitor on-line the TGA events can be measured by the time hysteresis of the MSD signal in relation to the DTG signal. An estimation of the time delay can be made by calculating the difference between the time at the maximum of the DTG curve and the maximum of the MSD signal. A mean time difference of 0.1 min was determined for both, CaCO₃ and KHCO₃ TG/MS analysis. The time difference is the sum of the times required for the gases evolved to be transferred: (a) from TGA sample pan to the entrance of the capillary; and (b) to the MSD ion source through the capillary. In the first case, the time needed depends on port B vacuum, sampling-tube inner diameter, and the distance between the sample pan and the capillary. In the second case, the time needed depends on the capillary

Table 1
TG/MS system characteristics for meeting certain specifications

Specifications	TG/MS system characteristics
Quick transfer from TGA to MSD	coupling system with small dead volumes
No memory effects	TGA quartz liner
No evolved-gas condensation or degradation	heated coupling system. Use of inert materials
No air insertion during furnace opening	inert-gas insertion from Port B
Simplicity of construction, easy decoupling, low cost	one-stage coupling system
Continuous monitoring	MSD triggered by TGA event switch
Versatility with respect to MSD	easy capillary connection to any GC/MS interface
High sensitivity	small evolved-gas dilution. No evolved-gas mixing
Repeatable flow conditions	stable temperature and pressure conditions in the TG/MS coupling system

Table 2

Standard deviations of time values corresponding to the maximum of DTG and MSD curves

Compound	Standard deviation of time at DTG curve maximum (min)	Standard deviation of time at MSD curve maximum (min)
CO ₂ (KHCO ₃)	1.580	1.550
CO ₂ (CaCO ₃)	1.009	0.975

length and inner diameter, the pressure at the entrance of the capillary and the dynamic viscosity of evolved gases [12].

3.3. Evaluation of the interferences of the coupling system on TGA and MSD performance

The deterioration of the TGA performance can be evaluated by monitoring the precision and accuracy of weight loss and decomposition temperatures of a standard compound, in the presence of the coupling system. Calcium oxalate can be used as a standard, as it decomposes in three well-resolved stages ranging from 180° up to 720°C. Table 3 shows the mean values and estimated standard deviations of weight loss and decomposition temperatures, in the presence, and absence, of the coupling system. The values of weight loss and decomposition temperatures without the coupling system were used as standard values. The results of a *t*-test and *F*-test, at 95% confidence level, indicate that there is no significant systematic error or variance introduced in TGA weight and temperature measurements in the presence of the TG/MS coupling system.

Mass-spectrometer electron impact (EI) ionisation-mode performance can be evaluated by monitoring carbon-isotope abundances in the spectrum from various compounds. Benzene was selected for various reasons, such as strong molecular ion and sufficient

number of carbon atoms. The sample used was a mixture of benzoic acid and sodium hydroxide in a 1 : 3 mole ratio. The general appearance of the benzene mass spectrum, resulting from the decarboxylation reaction at 390°C, is in agreement with those presented in various mass-spectra compilations [13]. The calculated value for the number of carbon atoms, based on *M*+1 and *M* isotopic abundances, is in good agreement with the theoretical value. This indicates that the coupling system does not affect the ion-source performance.

3.4. Evaluation of evolved-gas condensation

Evolved gas condensation is possible when high boiling point compounds are present in the evolved-gas stream. In order to evaluate the extent of condensation in a TG/MS system, a compound which produces a long range of known thermal degradation compounds is needed. Low-density polyethylene decomposition results in a series of normal paraffin and olefin products with known boiling points [14]. By monitoring the mass spectra of those compounds, it is possible to identify the product with the highest *m/z* ratio that has been successfully recorded. Fig. 2(a) shows the weight loss, DTG and temperature curves recorded from LDPE thermal degradation. Fig. 2(b and c) show the corresponding MS signal curve and

Table 3

Mean and estimated standard deviations of % weight loss and temperatures of calcium oxalate decomposition in the presence, and absence, of the TG/MS coupling system

Calcium oxalate decomposition stage	% Weight loss (without coupling system)		% Weight loss (with coupling system)		Decomposition temperature (°C) (without coupling system)		Decomposition temperature (°C) (with coupling system)	
	mean	SD	mean	SD	mean	SD	mean	SD
1	12.59	0.088	12.66	0.021	180.3	1.830	182.8	2.304
2	19.56	0.080	19.80	0.110	500.0	1.990	500.7	1.147
3	29.85	0.083	29.92	0.056	714.9	2.250	722.1	5.790

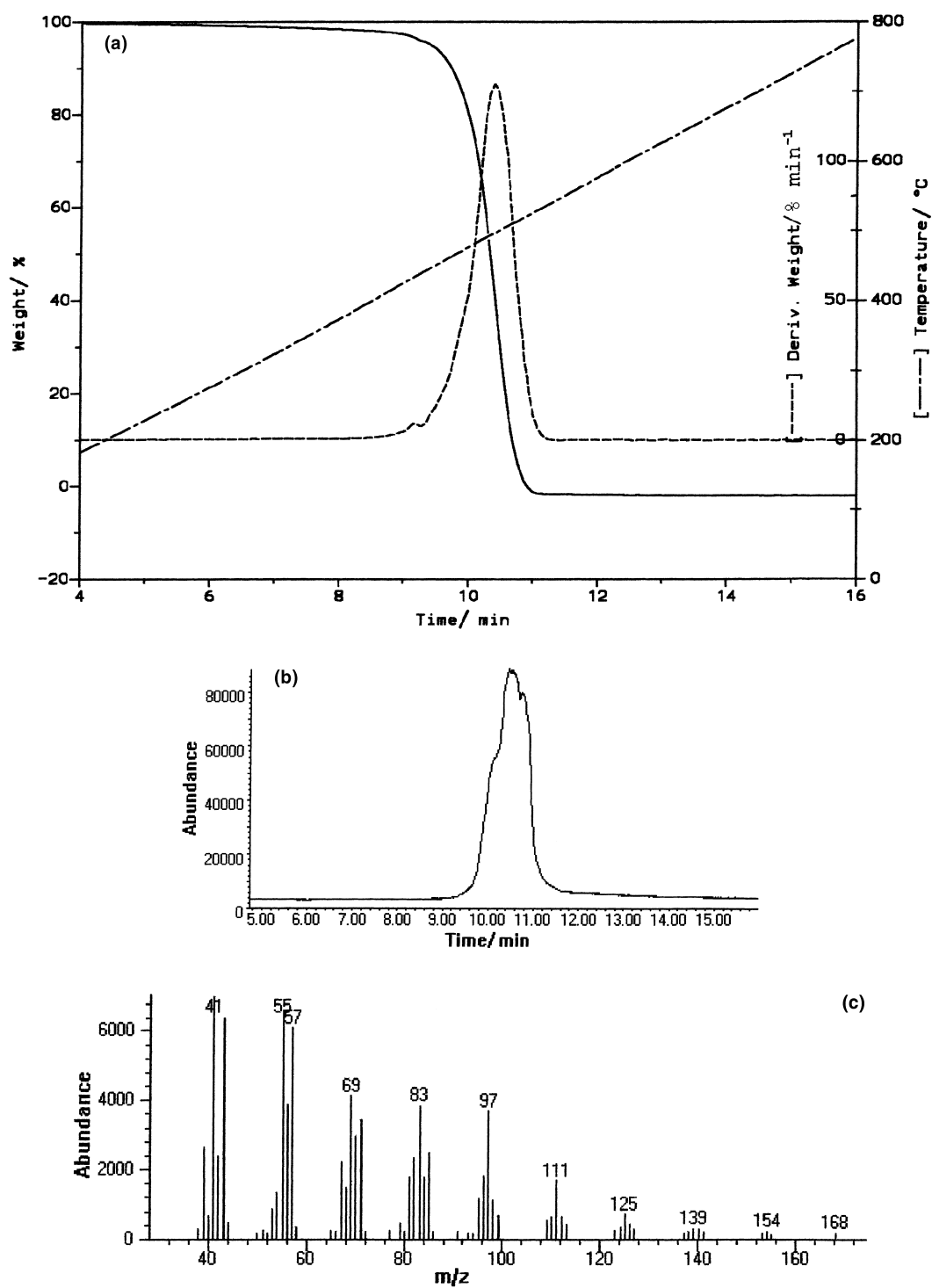


Fig. 2. (a) Weight loss, DTG and temperature curves from LDPE thermal degradation. (b) MS signal from thermal degradation of LDPE. (c) Mass spectrum at 10.50 min, corresponding to dodecene.

the mass spectrum at 10.50 min, respectively, using the TG/MS coupling system. The mass spectrum corresponds to dodecene, indicating that the coupling system allows the detection of compounds with boiling points nearly up to 214°C [15]. However, it should be emphasised that the results of this test can be greatly affected by parameters such as electron multiplier voltage, electron impact voltage, ion-source pressure, as well as by MSD maintenance.

4. Conclusions

It is possible to evaluate quantitatively the performance of a TG/MS system. The evaluation procedure includes measurements on various parameters such as the mass-flow stability, the evolved-gas transfer delay and the evolved-gas condensation effect. The procedure can also quantitatively determine the extent of interferences of the TG/MS coupling system on TGA and MSD specifications. It appears that the evaluation procedure can be used for monitoring the performance of a specific TG/MS system and, thus, can be a basis for design improvements. In addition, it may be used for comparing the results of different TG/MS systems or for interlaboratory comparisons.

References

- [1] G. Szekely, M. Nebuloni, L.F. Zerilli, *Thermochim. Acta* 196 (1992) 511.
- [2] T. Leskelä, M. Lippmaa, L. Niinistö, P. Soininen, *Thermochim. Acta* 214 (1993) 9.
- [3] M.R. Holdiness, *Thermochim. Acta* 75 (1984) 361.
- [4] D. Dollimore, G.A. Gamlen, T.J. Taylor, *Thermochim. Acta* 75 (1984) 59.
- [5] K. Jaenicke-Rößler, G. Leitner, *Thermochim. Acta* 295 (1997) 133.
- [6] K.G.H. Raemaekers, J.C. Bart, *Thermochim. Acta* 295 (1997) 1.
- [7] W.M. Groenewood, W. de Jong, *Thermochim. Acta* 286 (1996) 341.
- [8] M. Mittleman, *Thermochim. Acta* 166 (1990) 301.
- [9] M. Maciejewski, A. Baiker, *Thermochim. Acta* 295 (1997) 95.
- [10] E. Kaisersberger, E. Post, *Thermochim. Acta* 295 (1997) 73.
- [11] W.H. McClennen, R.M. Buchanan, H.L.C. Meuzelaar, *Anal. Chem.* 65 (1993) 2819.
- [12] C.A. Cramers, G.J. Scherpenzeel, P.A. Leqlerq, *J. Chromatogr.* 203 (1981) 207.
- [13] *Eight Peak Index of Mass Spectra*, 1st edn., 1970, Vol. 1, Table 1.
- [14] M.P. Stevens, *Techniques and Methods of Polymer Evaluation, Characterization and Analysis of Polymers by Gas Chromatography*, Chap. 4, Marcel Dekker, New York, 1969.
- [15] *CRC Handbook of Chemistry and Physics*, 52th edn., Section C, 1971.