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Supercritical fluid chromatography–mass spectrometry and matrix-assisted laser-desorption ionisation mass spectrometry of cyclic siloxanes in technical silicone oils and silicone rubbers

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Abstract

Supercritical fluid chromatography in combination with mass spectrometry is used for determining cyclic siloxanes beside linear methyl and hydroxyl "end-capped" siloxanes. Electron impact ionisation and chemical ionisation techniques are utilized for identifying cyclic siloxanes in technical silicone oils and silicone rubber. Ammonia as reagent gas is preferred in the higher-molecular-mass range. Matrix-assisted laser-desorption ionisation mass spectrometry can be useful as a supplementary method for characterizing smaller amounts of both cyclic and linear siloxanes as well as silanols in the higher-molecular-mass range.

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1. Introduction

Siloxanes have widely been used over the past 40 years. Methylsiloxanes, especially polydimethylsiloxanes (PDMSs), make up a major part of organo-silicon compounds. Silicone oils (low-molecular-mass PDMSs) are the basic materials for most silicone additives and silicone rubbers. Desired properties of silicone oils are a great range of fluidity, a low freezing point and low temperature dependence of viscosity. Therefore the preparation requires inhibition of cyclic siloxane formation or augmentation of linear "end-capped" siloxanes in final products [1].

Gel permeation chromatography and ^{29}Si NMR spectrometry may give information about the average molecular mass, but they cannot provide the resolution required to determine the amount of cyclic siloxanes in technical silicone oils [2]. By means of high-temperature gas chromatography substances of high molecular mass do not elute or they elute with great peak broadening. Supercritical fluid chromatography (SFC) has proven to be a method of choice for analysing cyclic siloxanes in technical silicone oils [3,4]. It is possible to couple SFC with mass spectrometry (MS), too [5–11]. We used this combination to determine cyclic siloxanes as well as linear methyl and hydroxyl "end-capped" species in technical silicone oils.

Other techniques used are direct exposure probe (DEP) and matrix-assisted laser-desorption ionisation (MALDI) MS which complements SFC in characterising siloxanes [12,13].

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2. Experimental

2.1. SFC

Equipment: SFC 602-D (Dionex); injector: pneumatic time-programmable switching valve (Valco), internal volume 0.5 μl, injection time: 1 s; samples were dissolved in toluene; retention gap: 1 m × 50 μm uncoated fused silica; column: 10 m × 50 μm fused silica, SB-Methyl-100; detection: flame ionization detection (FID) (350–380°C), integral or frit restrictor, MS (see Section 2.2)

Programmes: (a) Synchronized linear temperature and density programme; initial temperature: 100°C, hold for 10 min, then increase with a ramp rate of 0.6°C/min to 150°C; initial density: 0.2 g/ml, hold for 10 min, then increase with a ramp rate of 0.0065 g/ml to 0.6 g/ml. (b) Isothermal "asymptotic" pressure programme: temperature: 120°C; initial pressure: 10 MPa, increase with a ramp rate of 2 MPa/min to 16 MPa, then with a ramp rate of 1 MPa/min to 22 MPa, then with 0.5 MPa/min to 28 MPa, with 0.25 MPa/min to 34 MPa, and then with 0.12 MPA/min to 40 MPa, hold for 20 min. (c) "Fast" synchronized linear temperature and pressure programme: initial temperature: 120°C, increase with a ramp rate of 1.5°C/min to 150°C, hold for 40 min; initial pressure: 10 MPa, increase with a ramp rate of 1.5 MPa/min to 40 MPa, hold for 40 min.

2.2. MS

Equipment: SSQ 700 (Finnigan MAT), mass range 10–4000 u, emission current 200 μA, electron multiplier −1500 V, scan time 1 s; SFC–MS interface: option for Finnigan SSQ 700 with transfer line, flange and heater assembly [14]; temperature of the transfer line: 120°C; SFC–MS restrictor: 1 m uncoated 50 μm I.D. fused-silica tubing with a 2 cm frit (Dionex); restrictor temperature: 260°C, by controlling the heater tip via the MS software; ion source temperature: 170°C (chemical ionisation, CI), 150°C (electron impact ionisation, EI); manifold heater temperature: 70°C; initial CO_2 velocity at 10 MPa and 120°C about 2 cm/s; manifold pressure: $1.6 \cdot 10^{-6}$ Torr (1 Torr = 133.322 Pa); manifold pressure with ammonia: $2.1 \cdot 10^{-6}$ Torr; manifold pressure with ammonia (and with 35 MPa CO_2 pressure/145°C in SFC system): $1.4 \cdot 10^{-5}$ Torr; spectra: EI mode, tuning automatically with perfluorotributylamine (FC-43) in the range 50–650 u, from 650–1400 u tuning manually via insertion probe, manual change of resolution (molecular mass range > 1500 u) intensifies peak masses; CI mode with methane, isobutane and ammonia as reagent gases, ammonia was preferred in the high molecular mass range; DEP: Finnigan MAT DEP system; voltage: 0 to 10 V d.c.; output current: 0 to 1350 mA; initial current: 25 mA, hold for 0.4 min; increase with a ramp rate of 40 mA/min to 300 mA, hold for 10 min.

2.3. MALDI-MS

Equipment: Kratos Kompact MALDI III, positive ion mode, reflectron time-of-flight, 20 kV accelerating voltage; matrix: dihydroxybenzoic acid (10 mg/ml in acetone); samples: 5 μl in 1 ml acetone.

2.4. Materials and reagents

The supercritical CO_2 was SFC grade (Scott). The silicone rubber was laboratory tubing material. Specially prepared substances to identify linear siloxanes were provided by Dr. U. Scheim, Institute of Organic Chemistry, TU Dresden, Germany. Technical silicone oils were obtained from Merck and Chemiewerk Nünchritz, Germany.

The molecular masses of linear siloxanes exhibit the general formula M_2D_n or $Si(CH_3)_3$–O–$[Si(CH_3)_2$–O–$]_nSi(CH_3)_3$; the general formula of the corresponding cyclic siloxanes is D_m, where M is $(CH_3)_3Si$–$O_{0.5}$, D the monomer unit $Si(CH_3)_2$–O–and m and n the degree of polymerisation, where $m = n + 2$.

3. Results and discussion

EI mass fragmentation is the first technique to try for any sample that can be vaporized into the mass spectrometer. For siloxanes containing only

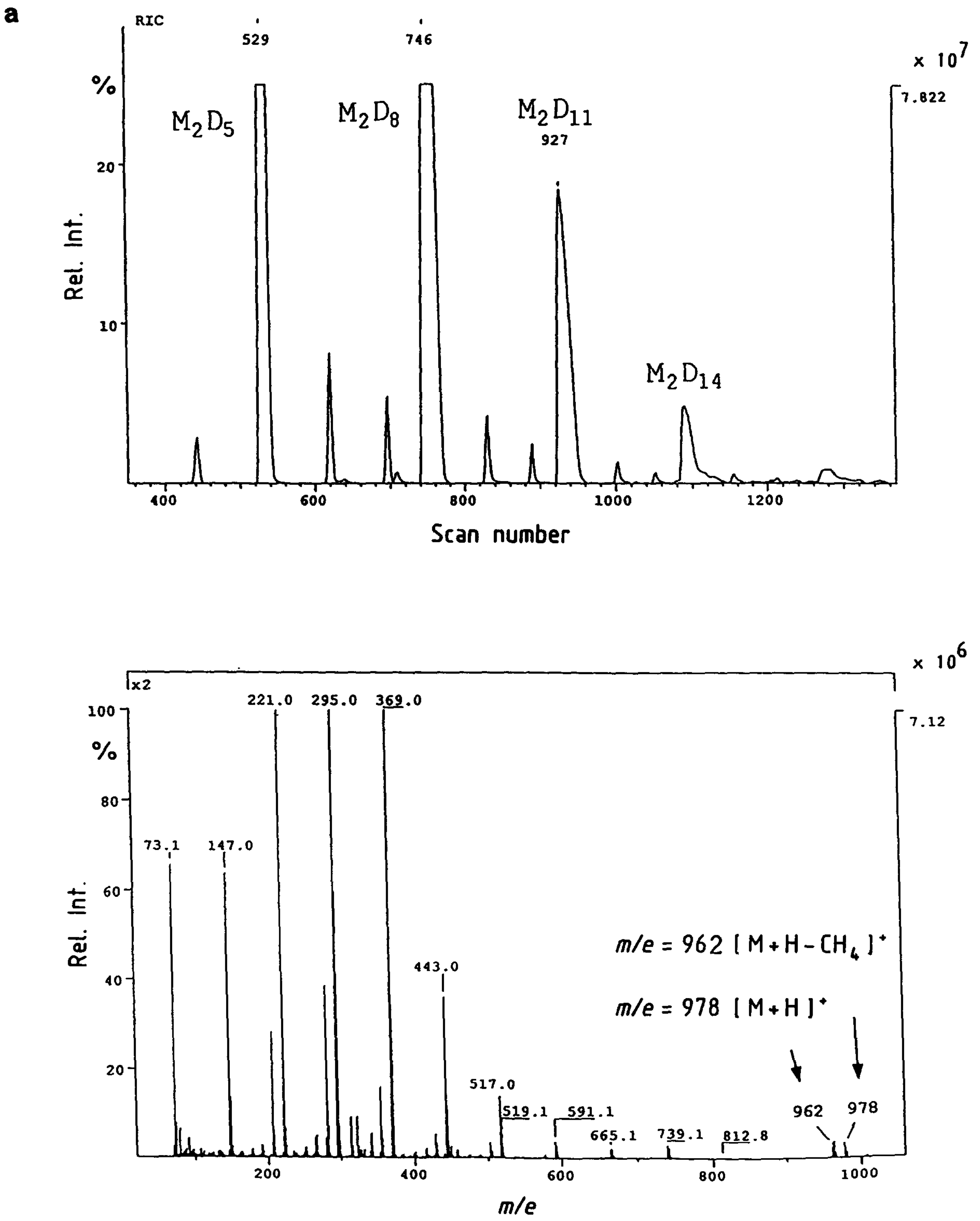

Fig. 1. *(Continued on p. 108)*

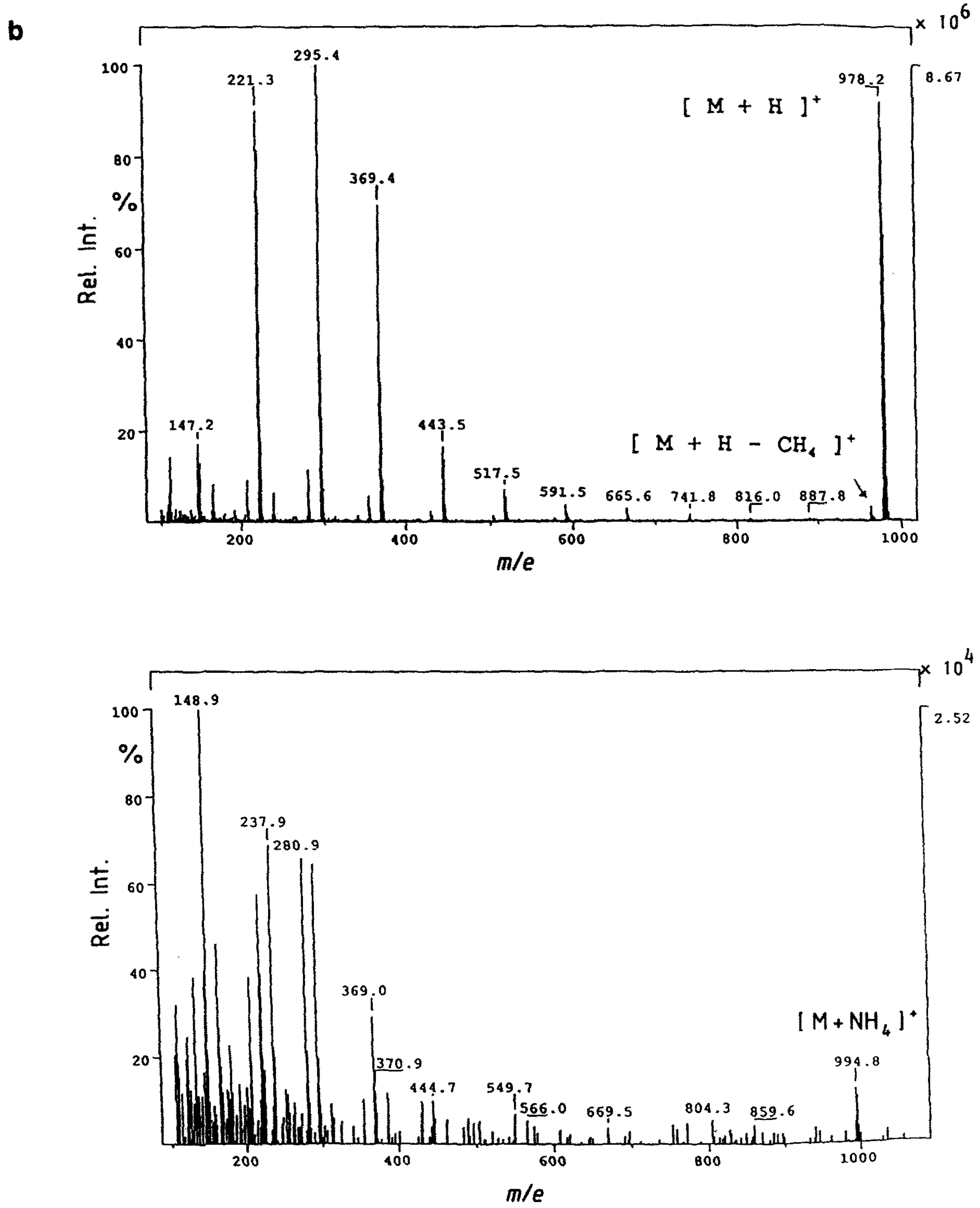

Fig. 1. (a) SFC–MS chromatogram of a mixture of mainly linear PDMS (top); CI (CH_4) mass spectrum of M_2D_{11} (bottom). (b) CI (iso-C_4H_{10}) mass spectrum of M_2D_{11} (top), CI (NH_3) mass spectrum (bottom).

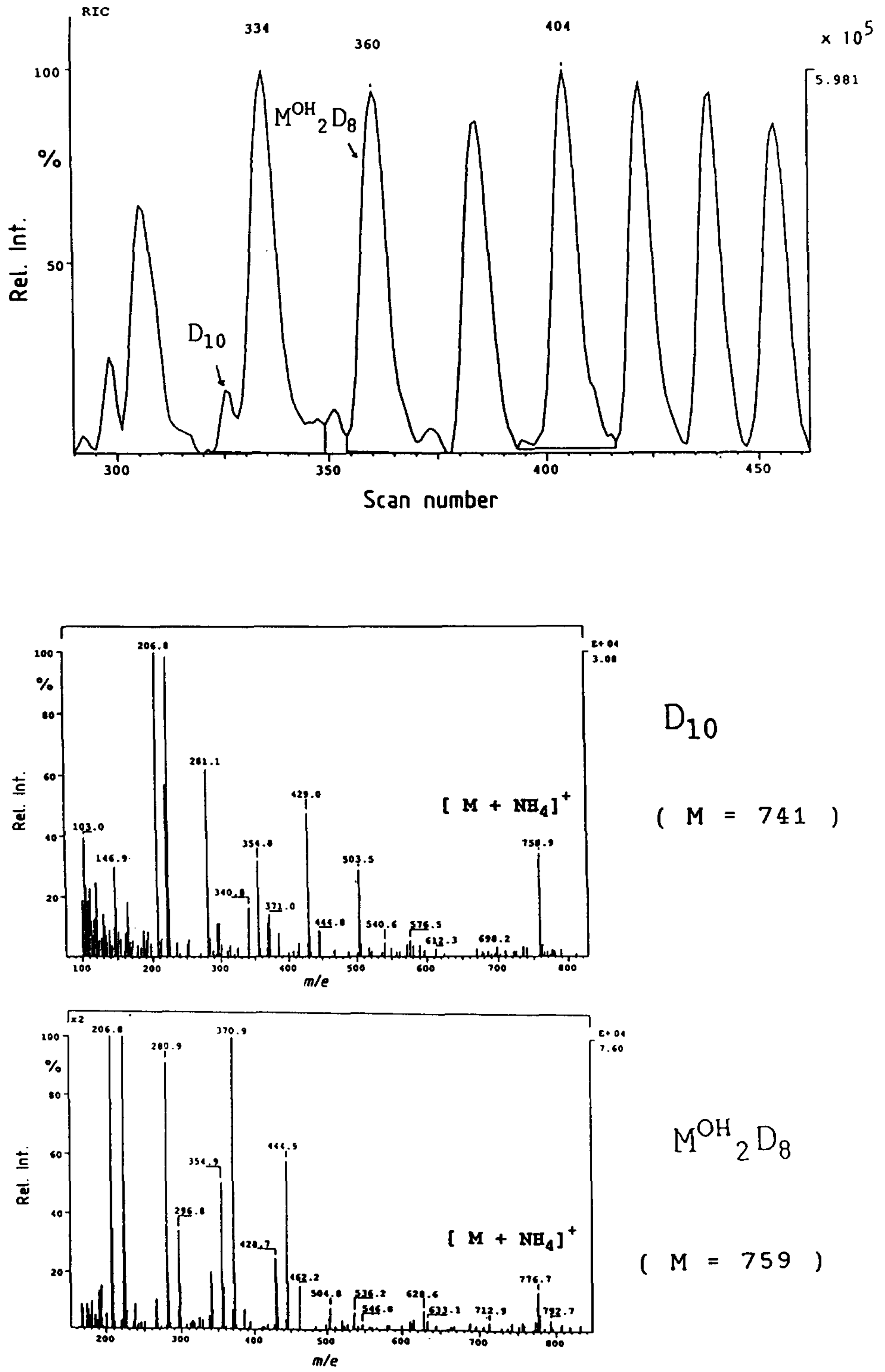

Fig. 2. SFC–MS chromatogram of a silanol sample containing methyl end-capped and cyclic siloxanes (top); CI (NH_3) mass spectra of D_{10} (middle) and $M_2^{OH}D_8$ (bottom).

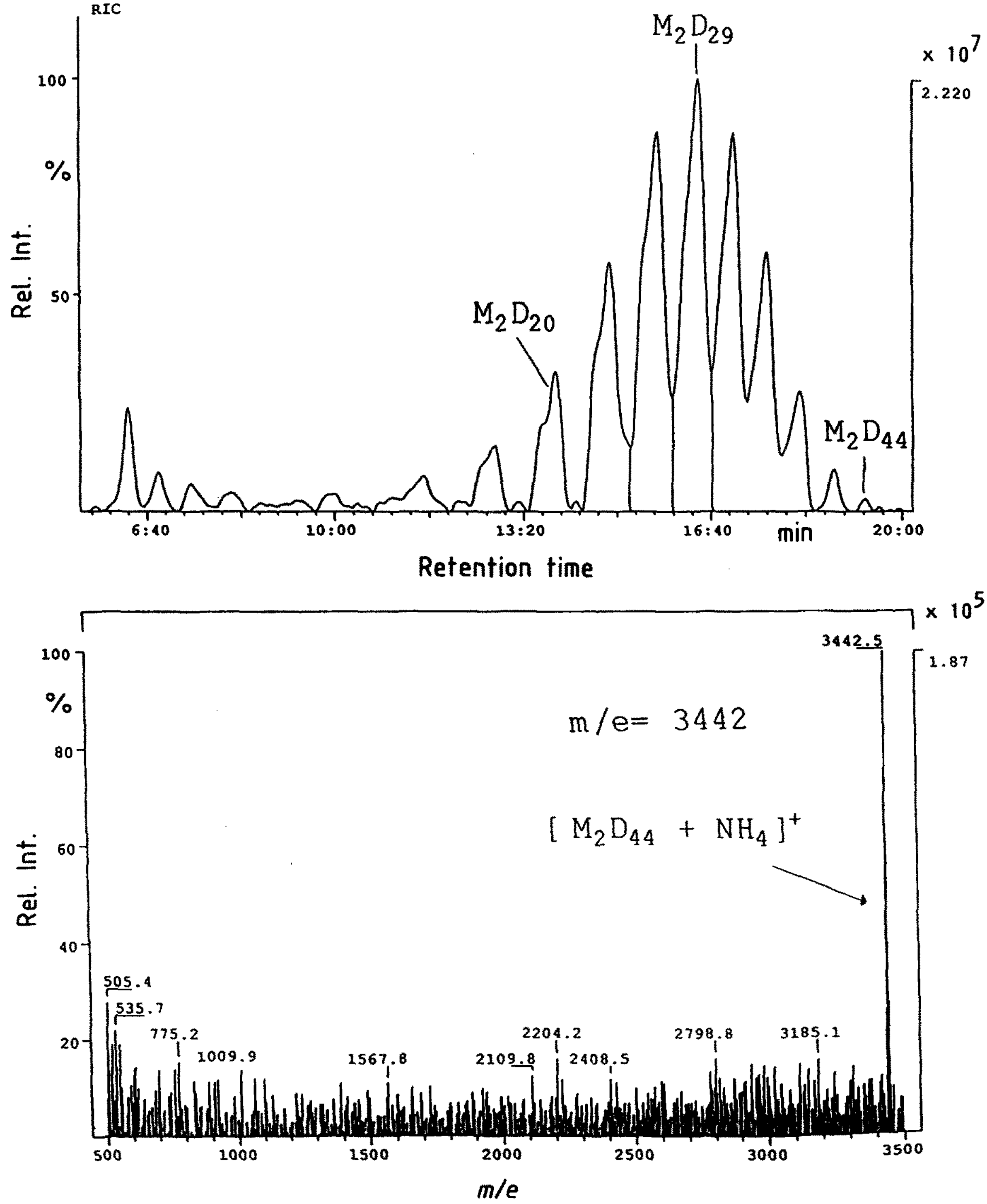

Fig. 3. SFC–MS chromatogram of a siloxane mixture with linear methyl end-capped components (top); CI (NH_3) mass spectrum of M_2D_{44} (bottom).

few silicon atoms, EI is informative. When the chain length increases, EI does not provide information on the complete molecule anymore, but it gives clues helping to identify the repeat unit from characteristic ions [15]. By coupling SFC with MS using SFC method b, a slow isothermal "asymptotic" pressure programme, we got normal EI mass spectra with intensive fragmentation (molecular mass difference 74 u). Molecular ions could not be observed, but cleavage of a methyl group from the molecules, e.g. octacyclosiloxane (D_8) losing CH_3. Library searchable spectra were obtained up to M_2D_4 or D_6.

Our first CI experiments were done with methane as the reagent gas. We analyzed the same sample used in the previous EI experiments consisting of mainly linear PDMSs. Fig. 1a (top) shows the SFC chromatogram of this oil and (bottom) the mass spectrum of a linear component in this siloxane mixture with its molecular mass of 977 u. The mass spectrum indicates the $(M + H)^+$ peak *m/z* 978 in this case of M_2D_{11}; it is significant in the relation to the isotope cluster of the silicon-containing ions. Some fragmentation takes place, and the mass spectrum shows the molecular ions losing methane (= 16 u), *m/z* 962, too. When the molecular masses of the compounds increase, no molecular or quasimolecular ions can be obtained with methane as reagent gas.

Softer ionization media are isobutane (C_4H_{10}) or ammonia (NH_3) [16]. With isobutane mass spectra can be obtained which show the $(M + H)^+$ ion; if ammonia is used as reagent gas the mass spectra show the $(M + NH_4)^+$ ion (Fig. 1b). In the latter case not much fragmentation can be observed even in high-molecular-mass range. In the low-molecular-mass range a triplet structure occurs with ammonia as reagent gas. Quasimolecular ions are formed either by hydrogen or ammonium ion addition, then losing methane. Thus, ions can be observed at M + 18 and M + 2 (18 − 16), and also at M + 1 and M − 15.

With ammonia as reagent gas, Si–OH components can be identified, too. Fig. 2 shows a silicone oil which contains cyclic and linear siloxanes, the linear ones "end-capped" either with methyl or hydroxyl end groups. Interesting is the chromatographic retention of these species. The cyclic siloxane D_{10} is followed by M_2D_8 in the retention time scale; $M_2^{OH}D_8$, however, elutes later, at nearly the same retention time as the retention time of M_2D_9. Fig. 2 (bottom) shows the mass spectra (CI with ammonia as reagent gas) of D_{10} and $M_2^{OH}D_8$.

With ammonia as reagent gas cyclic and linear siloxanes are distinguishable in the mass spectra; in the EI mode this cannot be achieved because water is ejected from the linear diols after the methyl loss. Thus, in the EI mode cyclic siloxanes and silanol-ended linear ones show the same ions [15].

By coupling SFC with MS, we were able to get well defined "reference substances", siloxane mixtures specially prepared for this purpose. Using SFC program c we determined for example the linear component M_2D_{44} in such a siloxane mixture. The signal-to-noise ratio of the molecular ion $(M + NH_4)^+$ was about 5 (Fig. 3).

SFC is a method of choice to determine the amount of cyclic components of technical

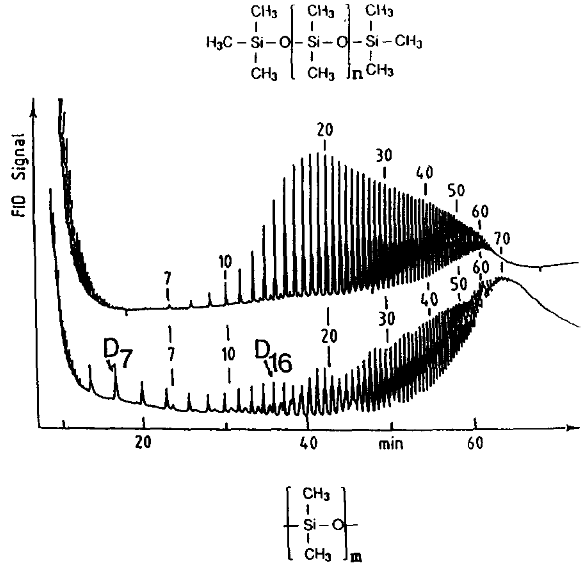

Fig. 4. SFC–FID chromatograms of a silicone oil with mainly linear components (top curve) and an oil with cyclic siloxane components (bottom curve).

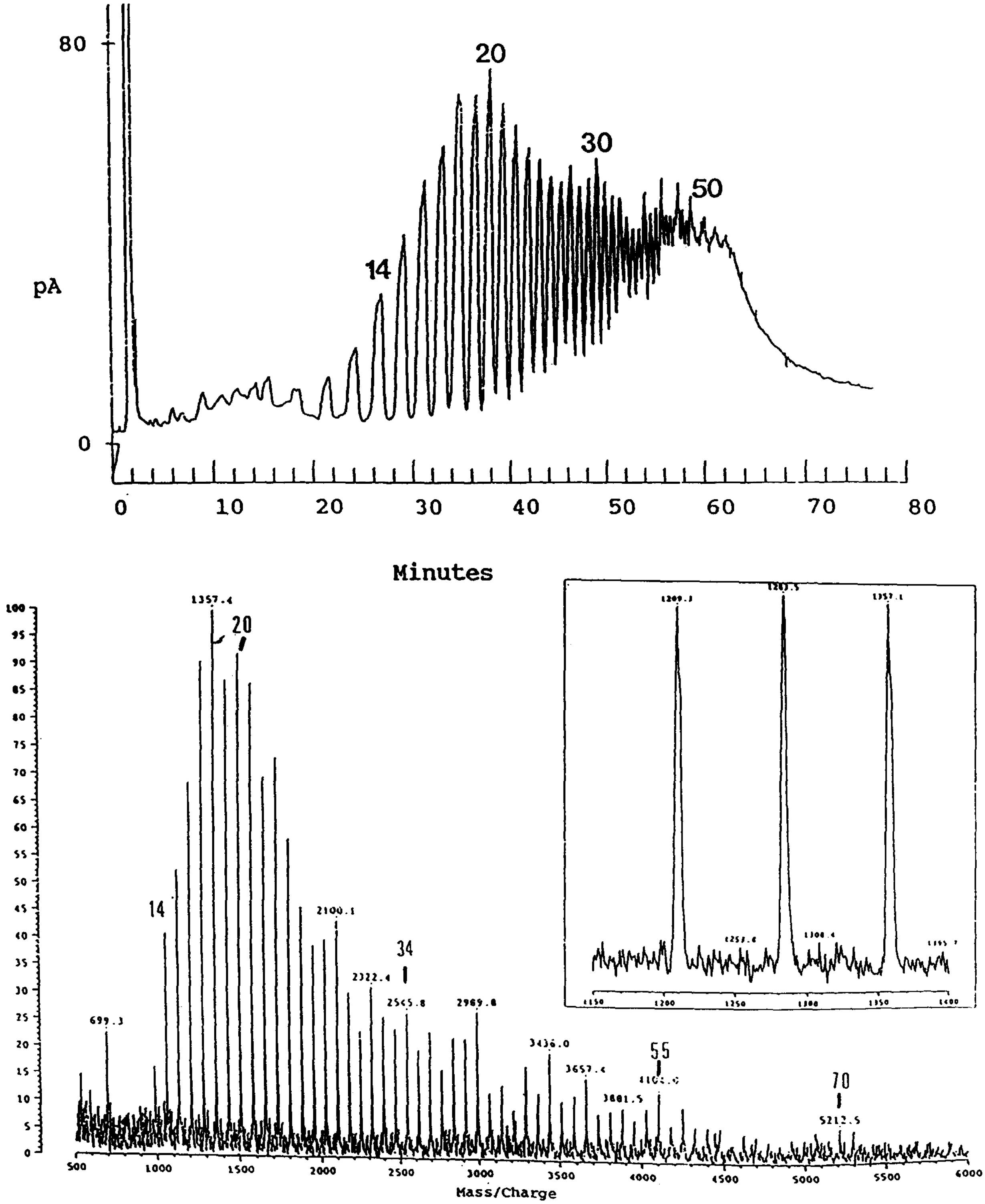

Fig. 5. SFC–FID chromatogram of cyclic siloxanes in silicone rubber, extracted with hexane (top); MALDI-MS spectrum (bottom), expanded plot shows molecular mass difference 74 u.

silicone oils in the low-molecular-mass range, important for the quality of the oils. Thus SFC can lead to a sufficient resolution in functionality and molar mass. Fig. 4 exhibits the SFC chromatograms of an oil consisting of mainly linear components (top) and of a silicone oil with a larger amount of cyclic components in the lower-molecular-mass range (bottom).

Using hexane we extracted cyclic siloxanes from silicone rubber, laboratory tubing material. The amount of extractable components by an 8-h Soxhlet extraction had been 2%. We analyzed the extract first by SFC. The molecular mass distribution of this extract is depicted in Fig. 5 (top). Additionally to coupling SFC with MS we also tried to use DEP as a screening method. Only a qualitative overview could be obtained showing that the components are cyclosiloxanes. DEP does not seem to be useful for quantitative measurements.

A faster and easier method used for characterising siloxanes in a qualitative manner is MALDI-MS. This method is based on the principle that the dissolved specimen is mixed with a matrix and then crystallizes. The specimen is desorbed and ionized by laser incidence. The molecular mass is determined by the time-of-flight (TOF). MALDI-MS may be used as a supplementary method to SFC of siloxanes. In the molecular mass range below 1000 u SFC has clear advantages; MALDI-MS does not provide for indication of smaller siloxane molecules in this range. On the other hand, the resolution in the higher-molecular-mass range is more pronounced than in SFC, as Fig. 5 shows. It is very difficult to identify traces of cyclosiloxanes with higher molecular masses by SFC–MS. The MS equipment used is also limited to the mass range of 4000 u. But with MALDI-MS we are able to determine cyclic and linear components with even higher molecular masses; nevertheless, the problem of discrimination remains in the lower-molecular-mass range. Thus, it is not yet possible to use MALDI-MS for quantitative data, but in a qualitative manner MALDI-MS may be used as a supplementary method to SFC–MS in the higher-molecular-mass range.

Further work is done by us to separate completely cyclic and linear components in technical silicone oils by "critical chromatography" (chromatography at the critical point of adsorption where the species are separated not by molecular mass but by functionality) and then analyse the separated compounds in a second dimension by SFC–MS and MALDI-MS.

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