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Identification of novel synthetic organic compounds with supersonic gas chromatography–mass spectrometry

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Abstract

Several novel synthetic organic compounds were successfully analyzed with a unique type of GC–MS titled Supersonic GC–MS following a failure in their analysis with standard GC–MS. Supersonic GC–MS is based on interfacing GC and MS with a supersonic molecular beam (SMB) and on electron ionization of sample compounds as vibrationally cold molecules while in the SMB, or by cluster chemical ionization. The analyses of novel synthetic organic compounds significantly benefited from the extended range of compounds amenable to analyses with the Supersonic GC–MS. The Supersonic GC–MS enabled the analysis of thermally labile compounds that usually degrade in the GC injector, column and/or ion source. Due to the high carrier gas flow rate at the injector liner and column these compounds eluted without degradation at significantly lower elution temperatures and the use of fly-through EI ion source eliminated any sample degradation at the ion source. The cold EI feature of providing trustworthy enhanced molecular ion (M^+), complemented by its optional further confirmation with cluster CI was highly valued by the synthetic organic chemists that were served by the Supersonic GC–MS. Furthermore, the provision of extended mass spectral structural, isomer and isotope information combined with short (a few minutes) GC–MS analysis times also proved beneficial for the analysis of unknown synthetic organic compounds. As a result, the synthetic organic chemists were provided with both qualitative and quantitative data on the composition of their synthetic mixture, and could better follow the path of their synthetic chemistry. Ten cases of such analyses are demonstrated in figures and discussed.

Keywords: Supersonic molecular beam; Cluster chemical ionization; Synthetic organic compounds; Sample identification

1. Introduction

Gas chromatography–mass spectrometry (GC–MS) is a central analytical technique that serves a broad range of applications [1,2]. One important application of GC–MS is its use for the identification of new organic compounds and as a service tool for synthetic organic chemists. This area of GC–MS application is characterized by several specific challenges. The use of the extensive libraries of electron ionization (EI) is limited since most novel organic compounds are by definition not included in any library. The identification of novel organic compounds can be further confronted by frequent absence of the molecular ion (M^+), which in view of the fragile nature of many of these compounds is a frequently encountered problem. Since the availability of the molecular ion cannot be trusted, even if it is observed as a small peak further independent confirmation could be required. As a result, an additional analysis with chemical ionization (CI) [3–5] is often required, which could necessitate a lengthy procedure of ion source replacement and is not universally applicable. An additional major problem is that many of these novel organic compounds are thermally labile and as a result, are not amenable to standard GC–MS analysis. Furthermore, LC–MS despite its higher cost provides only limited structural mass spectral information, its response is sometimes too weak for small and relatively non polar samples and it is not semi-quantitative as GC–EI–MS. Consequently, an advanced novel GC–MS system is required, that should extend the range of compounds amenable to GC–MS analysis, and that should always provide a trustable molecular ion plus dependable mass spectral structural and isomer information in a rapid analysis.

In the last decade we developed and explored the performance capabilities of a new type of GC–MS, based on the use of a supersonic molecular beam (SMB). SMB was used

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for interfacing the GC to the MS [6–8] and as a medium for ionization of sample compounds while in the SMB, either by EI [9–11] or by hyperthermal surface ionization (HSI) [10,12,13]. SMB (with helium as carrier gas) is characterized by intra-molecular vibrational supercooling of its seeded sample molecules due to relatively low collision energies of sample compounds and carrier gas species during the supersonic expansion. Consequently, the M^+ intensity is enhanced in EI with SMB (named "cold EI") and it is practically always exhibited [10,11,14]. The feature of enhanced molecular ion and its anticipated appearance is important for sample identification, since with it, our confidence level in having the molecular ion as the highest mass spectral ion is much greater in comparison with standard 70 eV EI. However, the ionized sample compound could be so unstable that even with cold EI the molecular ion could be weak, or in rare cases missing.

In order to obtain molecular ions for the few compounds that did not show it in cold EI, Dagan and Amirav [15] developed a new ionization method named cluster chemical ionization (cluster CI or CCI). Fialkov and Amirav [16] further explored the use of cluster CI for obtaining increased confidence level in the identity of the molecular ion. Cluster CI is based on the addition of methanol or another solvent vapor into the helium make-up gas that serves for the supersonic expansion. The mixture of helium make-up gas, sample compounds and methanol vapor expands from the supersonic nozzle, it is super-cooled, and various species of sample compounds embedded within clusters of a few solvent molecules are formed. Upon the electron ionization of the sample molecule in such small cluster, a hydrogen atom, is or could be, transferred from the solvent molecule such as methanol to the molecular ion resulting in $(M + 1)^+$ ion. If the cluster is ionized via its solvent molecules, a proton can be transferred from it to the sample molecule, driven by its higher proton affinity, resulting in $(M + 1)^+$ ion as well. After ionization, most of the solvent molecules dissociate since the van der Waals bonds of the cluster are usually weaker than the chemical bonds in the sample molecular ion. Then, the sample molecular ion or protonated molecular ion may further dissociate as in cold EI but with somewhat less intra-ion energy. This intra-ion energy could be insufficient for full cluster dissociation, thus, satellite mass spectral peaks of protonated or non-protonated clustered molecular ion with one, two or a few methanol molecules are observed, alongside with fragments [15,16]. Their observation serves as a very strong evidence that the mass spectral peak in question is actually the molecular ion.

Another important fact is that the degradation of thermally labile compounds can be significantly reduced by lowering the GC elution temperatures with the Supersonic GC–MS. Such lower GC elution temperatures (by over 200 °C) can be achieved through the reduction of the column length, increase of carrier gas flow rate, reduction of adsorption film thickness and lowering the temperature programming rate [17]. In addition, the use of cool-on-column injection or a temperature programmable injector with high liner flow rate results with lower temperature sample "elution" from the liner into the column, and the use of fly through EI ion source completely eliminates any ion source related sample degradation. The features of much lower elution temperatures and significantly reduced injector and ion source degradation were effectively used for the analysis of thermally labile and low volatility compounds. As a result, the range of compounds amenable to GC–MS analysis was significantly extended [17]. As will be demonstrated in this manuscript, such extension of the range of thermally labile compounds amenable to GC–MS analysis is very important for the analysis of novel synthetic organic compounds.

2. Experimental

We have incorporated GC–MS with SMB into a new instrument and approach, which we have titled "Supersonic GC–MS". This instrument has been described in detail previously [8,16]. In brief, its design involves the modification of a commercially available Agilent (Wilmington, DE) GC–MS system (6890 GC plus 5972 MSD) to include an SMB interface and ion sources. The Supersonic GC–MS transfer line, a 20 cm long piece of 0.53 mm i.d. deactivated fused silica capillary, was connected at the vacuum end with a nozzle (0.1 mm i.d.) and was operated at a typical temperature of 200–250 °C with 130 mL/min combined make-up and column He flow rate. After the supersonic expansion from the nozzle, the free jet was differentially pumped, skimmed and passed into a fly-through EI ion source (home-made, dual cage design, 10 mA ionizing electron emission current with 70 eV electron energy [18]) located perpendicular to the quadrupole MS inside the vacuum chamber of the original 5972 mass spectrometer detector (MSD) instrument. The original 5972 MSD was used essentially as is, except the original EI ion source that was replaced by our home-made 90° ion mirror and ion optics. An optional HSI ion source, combined with the ion mirror (for the EI-produced ions), was also fitted inside the quadrupole mass analyzer in lieu of the original EI ion source.

For enabling easy-to-use cluster CI we installed a single 1/4 in. valve connected to a glass vial containing methanol in its one side, placed in the path of the helium make-up gas. In order to increase the solvent vapor concentration at the helium make-up gas, the later was passed through an internal Teflon tube up to the 1/4 in. valve, and then upward back to a standard T fitting at the make-up gas line. Furthermore, we placed a piece of rope inside the solvent vial that acted as a wick in oil candles to "pump" the solvent via capillary action and increase its diffusion rate, hence partial vapor pressure, at the valve entrance. This wick also ensured a solvent delivery rate that is relatively independent on the liquid level at the vial. Using this arrangement, cluster CI is initiated simply by opening one valve (which can be automated). Equilibration of the methanol vapor was reached in a few seconds and its presence was indicated through the increase of the mass spectrometer vacuum pressure from typical reading value of

3.4×10^{-5} to 5–5.4×10^{-5} Torr. The dual cage ion source was used for cluster CI as in cold EI with only a slight change of its exit lens voltage due to the lower sample kinetic energy in the methanol-seeded SMB.

The vacuum system of the Supersonic GC–MS is based on the use of a 250 L/s turbo-molecular pump (Navigator 301 Varian, Torino, Italy) at the supersonic nozzle vacuum chamber and a 70 L/s turbo-molecular pump (TC TMH 071 Balzers Pfeiffer, Asslar Germany) at the mass spectrometer vacuum chamber, backed by a single 200 L/min rotary pump (RV12 BOC Edwards, Crawley, UK). All of the gas flow rates, heated zones, sampling, etc. are performed the same way as with the original system and are computer-controlled via the original Agilent Chemstation software. Data analysis was also performed with the Chemstation software in combination with the NIST 98 mass spectral library, using the NIST search algorithm. The Agilent 6890 GC was used either with its standard split/splitless injector or with an Optic-2 temperature programmable injector (Atas, Veldhoven, The Netherlands). Home-made ChromatoProbe devices [19] could also be coupled with this injector or with the Agilent standard injector. These ChromatoProbes are similar to our previous ChromatoProbe, which is available from Varian.

For the experiments described in this manuscript we typically used a 5 m long 0.25 mm i.d. column with 0.25 μm DB 5 ms film (Agilent, Folson CA) with 16 ml/min helium column flow rate (3 m long column and up to 64 ml/min for the more thermally labile compounds). The initial GC oven temperature was 50–120 °C, depending on the anticipated volatility of the sample and the temperature program of 20–30 °C/min started immediately after injection, up to 250–300 °C upper GC oven temperature. Typically split injection was employed with split ratio of 4–10 and the sample concentration was crudely adjusted to be around 1000 ppm through its dilution in methanol or another solvent as provided by the chemists. The Agilent split splitless injector temperature was typically 250 °C or as low as 100 °C and if the Optic injector was used it was temperature programmed from 100 to 350 °C at a rate of 10 °C/s. Sample specific variations of these conditioned are mentioned in the figure captions.

Our school of chemistry has also a Saturn 2000 ion trap based standard GC–MS (Varian, Walnut Creek CA) with CI, MS–MS and ChromatoProbe options plus a high resolution magnetic sector GC–MS (Autospec, VG Scientific, Manchester, UK) operated with either GC–MS (having both EI and CI options) or direct insertion probe or FAB ionization options. An electrospray ionization (ESI) LC–MS is also available either at our laboratory (model 1100 LC plus model 1946A MSD, Agilent, Palo Alto, CA) or ESI-LC–MS (LCQ of ThermoFinnigan, San Jose, CA) in another laboratory.

3. Results

The application of the Supersonic GC–MS for the analysis of novel synthetic organic compounds was offered to certain faculty members of our school of chemistry, provided that they first tried to use the available standard GC–MS (and sometimes LC–MS) instrumentation and failed with it so that we dealt only with challenging and demanding applications. Over the last 3 years we successfully analyzed about 50 such samples and in this manuscript we report the ten cases that we found as both interesting and representative. Typical challenges in the analysis of such samples are their thermal lability, low volatility, absence of molecular ion in standard EI and/or CI or incompatibility with LC–MS. Furthermore, the synthetic mixture can contain a set of compounds of interest (raw material, by-products, and desired compound) each of which can have a different challenge. On the other hand, high sensitivity is not required since concentrated samples are typically prepared made from almost neat material that is diluted to about 100–1000 ppm solution. The most important question to answer is typically whether the synthesis was successful, i.e. whether the desired compound is present in the sample vial. The subsequent questions of interest that can arise are: what is the approximate yield of the desired compound relative to other products, are there any isomers or homologous compounds, etc. Therefore the results of analysis which provides mass-spectra with trustworthy molecular ion and significant fragments are highly valuable for the synthetic chemists.

In Fig. 1 the analysis of the indicated synthetic sulfur compound is shown. That compound was an intermediate compound prepared by Hagooly and Rozen for its further selective partial fluorination [20]. The GC–MS analysis of this compound with Saturn 2000 in both EI and liquid CI is shown in the upper mass chromatogram and two mass spectra in Fig. 1. The compound (three homologous and two isomers of one of them, determined by the set and position of the methyl–ethyl groups) eluted at 16–17 min. Severe peak tailing is observed at the 200 °C ion source temperature used. In addition, no molecular ion was observed in both the EI and CI mass spectra of this compound. The high mass peak at m/z = 247 corresponds to the fragment of the shown molecule without EtOCO group. The analysis of this sample by standard GC–MS was considered as “disappointing” by those who did the synthesis and we were asked to try it with the Supersonic GC–MS. We note that the definition “disappointing” was in part adopted since without further information the chemists could not even assume that the compounds in question properly eluted from the GC, and in addition, the number of peaks was unexpectedly high. The GC–MS analysis of that compound (actually a mixture of four main compounds plus a few others) with the Supersonic GC–MS is demonstrated at the bottom total ion chromatogram trace and four 70 eV EI mass spectra that are included to the left of the peaks. The peak tailing was completely eliminated and a clean chromatogram was obtained despite the much shorter analysis time (less than five minutes hence lower GC resolution) obtained with a 5 m 0.25 mm i.d. column with 16 ml/min He column flow rate. We note that ion source related peak tailing is inherently eliminated in the Supersonic GC–MS through

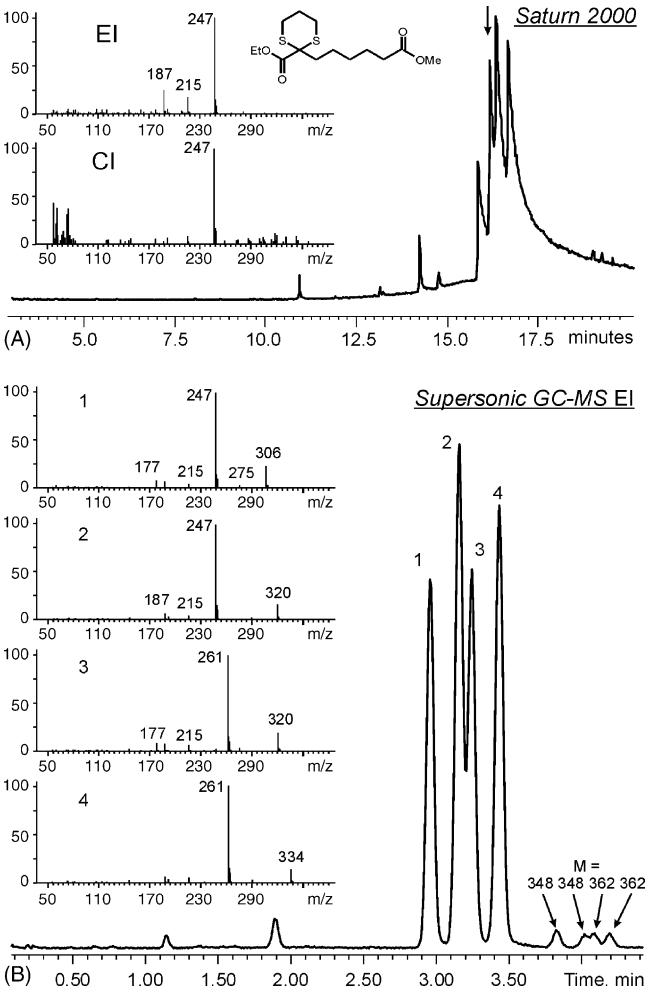


Fig. 1. The analysis of the indicated compound in its synthetic mixture with (A) Varian Saturn 2000 GC–MS using both EI and liquid methanol CI (upper trace and mass spectra of the indicated GC peak). (B) Supersonic GC–MS (bottom trace and cold EI mass spectra). Note the qualitative difference in information content of the mass spectra obtained with Saturn 2000 and Supersonic GC–MS with cold EI.

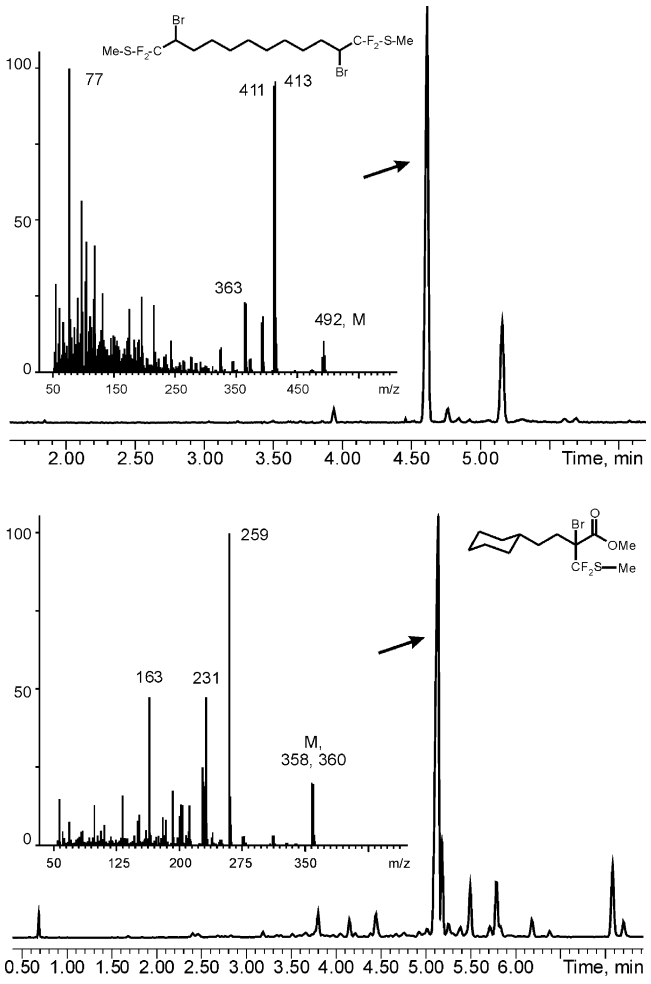


Fig. 2. The analysis (total ion mass chromatograms and 70 eV cold EI mass spectra) of the indicated synthetic compounds with the Supersonic GC–MS. The analysis of these compounds with standard GC–MS or MS probe failed to provide molecular ion in both EI and methane CI. "M" stands for molecular ion.

vacuum background filtration [9,10], in contrast to standard GC–MS ion sources. The latter may exhibit peak tailing due to lengthy cycles of intra-ion source thermal desorption of the sample molecules. This peak tailing could be reduced through increased ion source temperature but with a severe penalty of exponentially reduced abundance of the molecular ion [21,22] and increased intra-ion source degradation of thermally labile compounds. The mass spectra of all the four main compounds in the synthetic mixture are clean and all of them exhibit a relatively intense and trustworthy molecular ion. Even the weak peaks that followed had a trustworthy molecular ion as written above them. From these mass spectra it was clear that the synthesis suffered from having a few homologous compounds with increasing number of CH_2 in the side chain. However, a surprising finding (to the synthetic chemists) was that each compound had two GC peaks for the same molecular ion with clear isomer mass spectral effects. Through the use of simple mass spectral and chemical knowledge it became clear that the isomeric difference is in the location of the methyl and ethyl ester groups. The dominant high mass fragment originated through the fragmentation of the ester group near the secondary carbon atom that is stabilized by the two nearby sulfur atoms. Having this information the synthetic chemists quickly found the errors in their choice of solvent and further improved their synthetic method.

Another example for novel synthetic compounds that could not be properly analyzed by standard GC–MS is shown in Fig. 2 [23,24]. The indicated two compounds, each contained O, S, F and Br hetero atoms, possessed molecular weight of 358 and 490 amu, which is considered high on the GC–MS scale. These compounds were analyzed by the Autospec high resolution magnetic sector mass spectrometer system but it failed to provide a molecular ion in both EI (70 eV and low electron energy probe measurements) and methane CI. While other CI agents could have been explored, such studies are not practical for routine analysis of synthetic

organic compounds in "service" GC–MS instrumentation and were not attempted. These compounds were easily analyzed with the Supersonic GC–MS using 70 eV EI as demonstrated in Fig. 2 and each of these compounds gave a trustworthy molecular ion plus additional information about the other GC peaks (not shown) that belonged to additional synthetic by products.

As often happens many of the novel synthetic organic compounds are thermally labile thus cannot be analyzed by GC and/or GC–MS and 1,10-dioxo-phenanthroline is an example of such a delicate molecule. This compound has two oxygen atoms that cannot be situated in the aromatic ring plane. Thus, it has highly strained chemical bonds thereby it is unstable and had been considered as impossible for synthesis. Rozen and Dayan were the first to succeed in its synthesis through a unique action of $HOF{\cdot}CH_3CN$ using a novel synthetic method [25]. 5-Methyl derivative of this compound was later prepared by Rozen and Carmeli [26] and we were requested to analyze this highly strained thermally labile compound in its synthetic mixture. As shown in Fig. 3 we were able to analyze this compound and obtained a dominant molecular ion (mass spectrum number 2) plus further identify the singly oxidized compound (3) and raw material (1). This structure was later confirmed by NMR and we also found (through comparison with the NMR results) that intime this compound probably partially decomposed at room temperature, being thermally labile.

Epoxides is another family of highly strained compounds, which as a result are thermally labile and unstable. The analysis of the indicated tetra epoxide compound is demonstrated in Fig. 4. Again, this compound failed to be analyzed by standard GC–MS. Interestingly, even if the compound can be eluted from the GC but it fails to provide a molecular ion, the analyst usually determines that since it is thermally labile probably it did not elute. As observed in Fig. 4 we had no problem to elute these compounds using temperature programmed GC injector and low elution temperatures (below 70 °C) through the use of short (5 m) column with high column flow rate of 16 ml/min. Remarkably, we found two isomers of this tetra epoxide compound, each with significant molecular ion but with noticeably different relative ion intensities. The successful analysis of a similar tri epoxide compound is demonstrated in Fig. 5, helping the organic chemist with vital information [27].

Another even more challenging analysis was of the triangle hexavalent episulfone indicated in Fig. 6. This compound is highly thermally labile and failed to be analyzed by GC, GC–MS and probe MS. This situation is further exacerbated by the fact that even if it is purified, it cannot be analyzed by NMR since its NMR spectrum provides only one peak of all equal hydrogen atoms but it does not provide information about the atoms on the sulfur, which is the goal of the synthesis employed to convert a sulfur atom into sulfur dioxide (sulfone) using a novel synthetic method developed by Rozen and cowokers [28]. We also had initial problems with this compound but as demonstrated it could

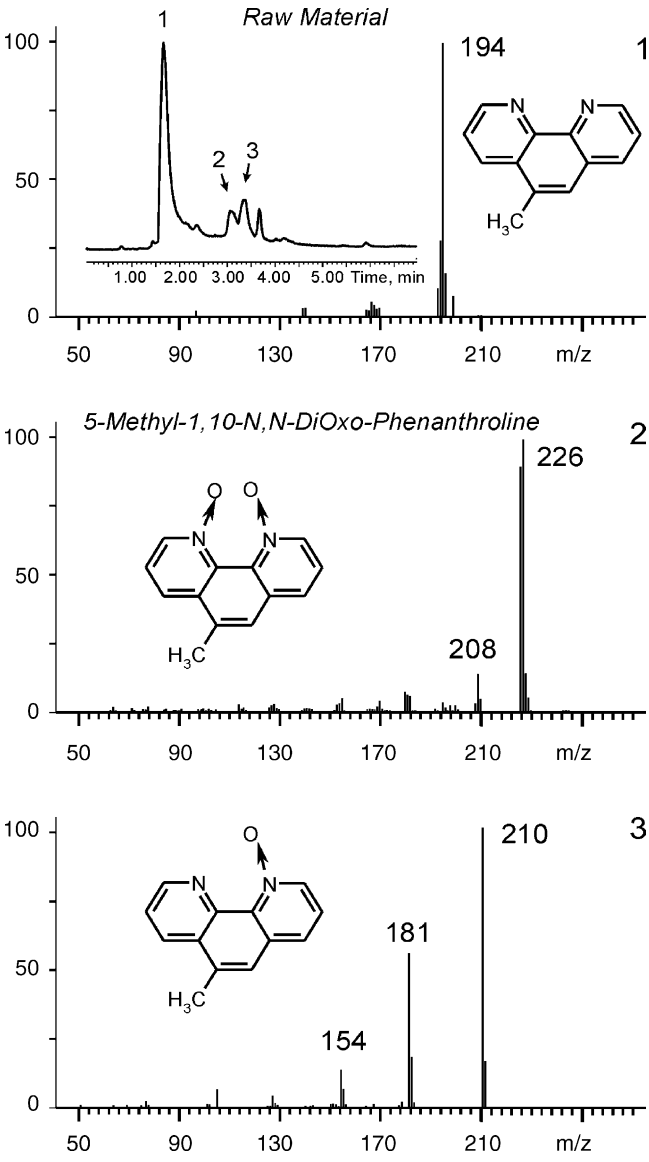


Fig. 3. Supersonic GC–MS analysis of the indicated 5-methyl-1,10-dioxo-phenanthroline in its synthetic mixture. Shown are cold EI mass spectra of the raw material (M = 194 amu (1)), target compound (M = 226 amu (2)) and one of the by-products (M = 210 amu (3). The total ion chromatogram with the indicated GC peaks is shown in the insert in the upper trace.

be successfully analyzed using a 5 m column with 32 ml/min column flow rate and low injector temperature of 100 °C. However, even cold EI failed to provide a molecular ion and to make the situation even more troubling a minor (∼1%) m/z = 93 was observed that could not be easily reconciled. We realized that this is a protonated molecular ion obtained through "residual" cluster CI with the tail of the methanol solvent and thus continued with cluster CI as shown at the bottom of Fig. 6. A dominant protonated molecular ion was obtained together with satellites of this compound with one and two methanol molecules plus a minor peak of the sample dimer. The appearance of satellites serves as an unambiguous evidence for the identity of the molecular ion as discussed in reference [16] while the m/z = 64 fragment

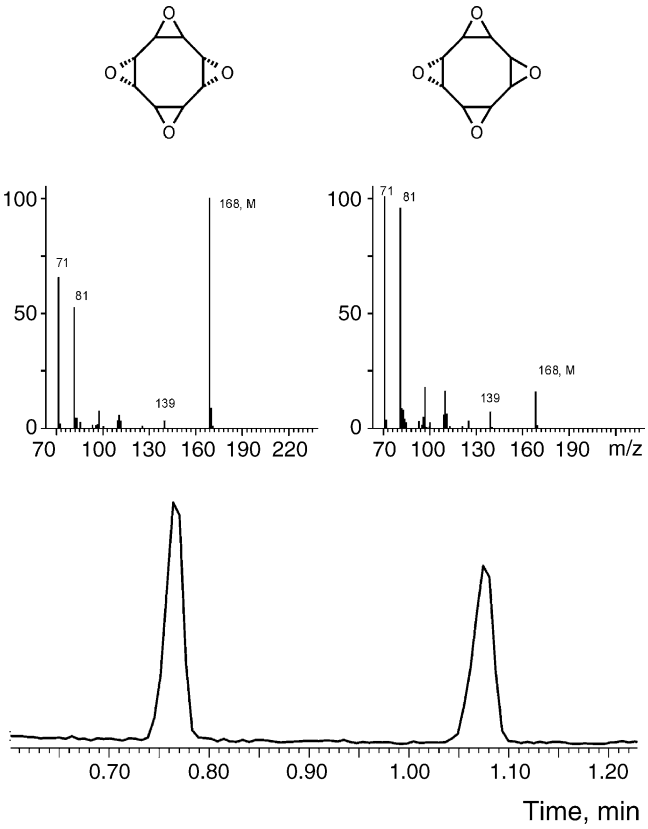


Fig. 4. Supersonic GC–MS analysis of the two indicated tetra-epoxide isomers. The bottom trace shows the total ion mass chromatogram while the upper inserts show the cold EI mass spectra of these compounds.

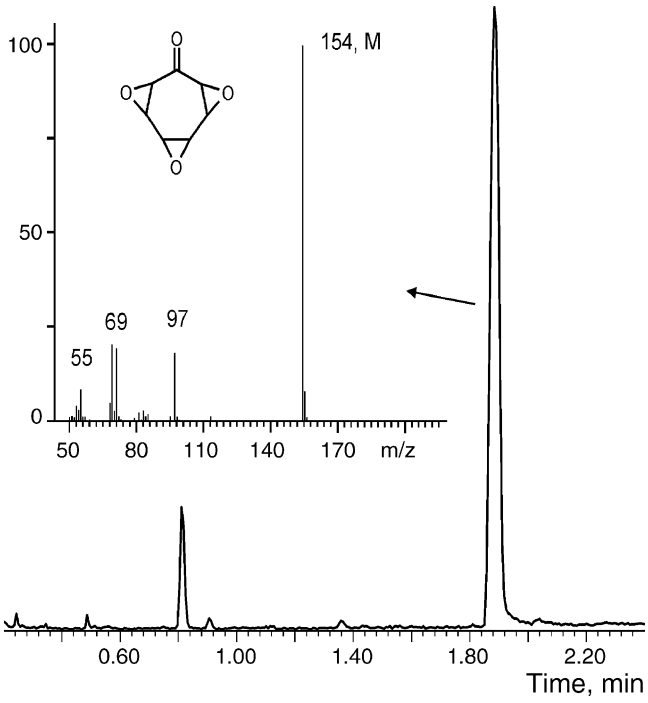
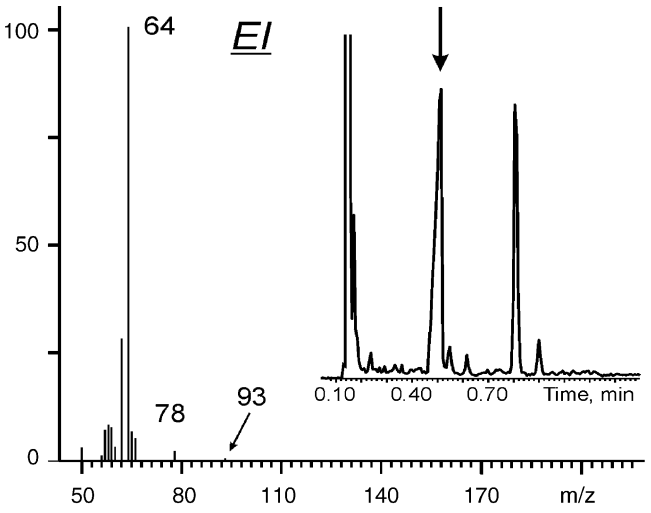


Fig. 5. Supersonic GC–MS analysis of the indicated tri-epoxide ketone compound. The bottom trace shows the total ion mass chromatogram while the upper insert show the cold EI mass spectrum of this compound.



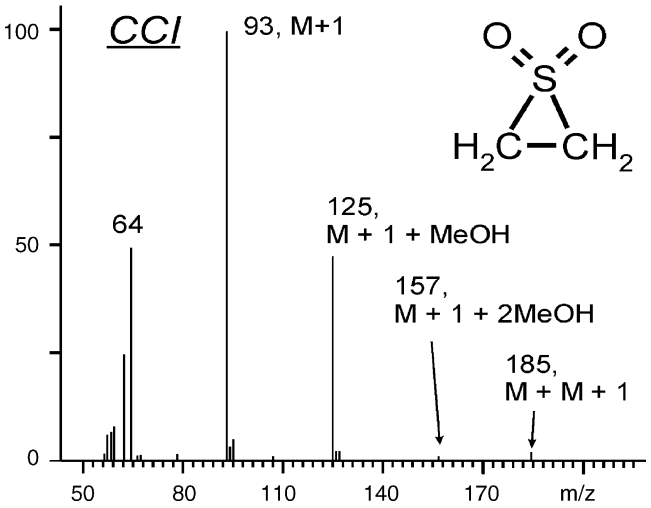


Fig. 6. Supersonic GC–MS analysis of the indicated highly strained sulfone in a three-membered ring compound. The upper trace shows the cold EI mass spectrum of this compound plus the total ion chromatogram in the insert, while the bottom trace is its methanol cluster CI mass spectrum; 32 ml/min helium column flow rate was used with 100 °C injector temperature.

provides further evidence for the presence of SO_2 in this compounds.

1,2-Dinitrocyclohexane (both with all ^{16}O and all ^{18}O) is a compound that is difficult to synthesize. A sample was given to us as a challenge by Rozen and Golan who made it through their unique amino oxidation method using an $HOF{\cdot}CH_3CN$ complex [29]. This compound did not produce a molecular ion in conventional EI and CI (Autospec magnetic sector GC–MS and Saturn 2000 ion trap GC–MS) as well as in cold EI as shown in the upper total ion chromatogram trace and mass spectrum in Fig. 7. The identification of the molecular ion of this compound was our first true test case of unknown identification with cluster CI [16]. As one can see in the cluster CI mass spectrum (middle trace) the protonated molecular ion of this vicinal dinitro compound is clearly observed together with its further con-

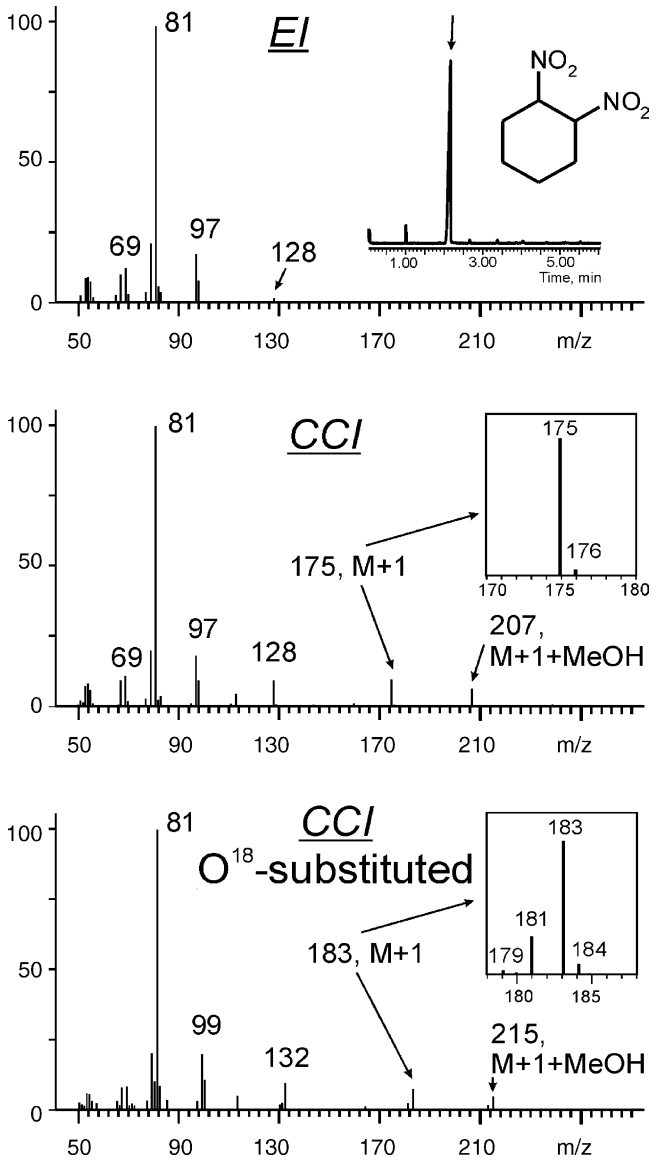


Fig. 7. Supersonic GC–MS analysis of 1,2-dinitrocyclohexane. The upper trace shows the cold EI mass spectrum plus the total ion mass chromatogram (in the insert). The middle trace shows the cluster CI mass spectrum of this compound while the lower trace shows the cluster CI of the fully O^{18} isotope labeled compound. The expanded mass spectra near the protonated molecular ion that demonstrate the isotope ratio, are shown in the inserts in the middle and bottom traces.

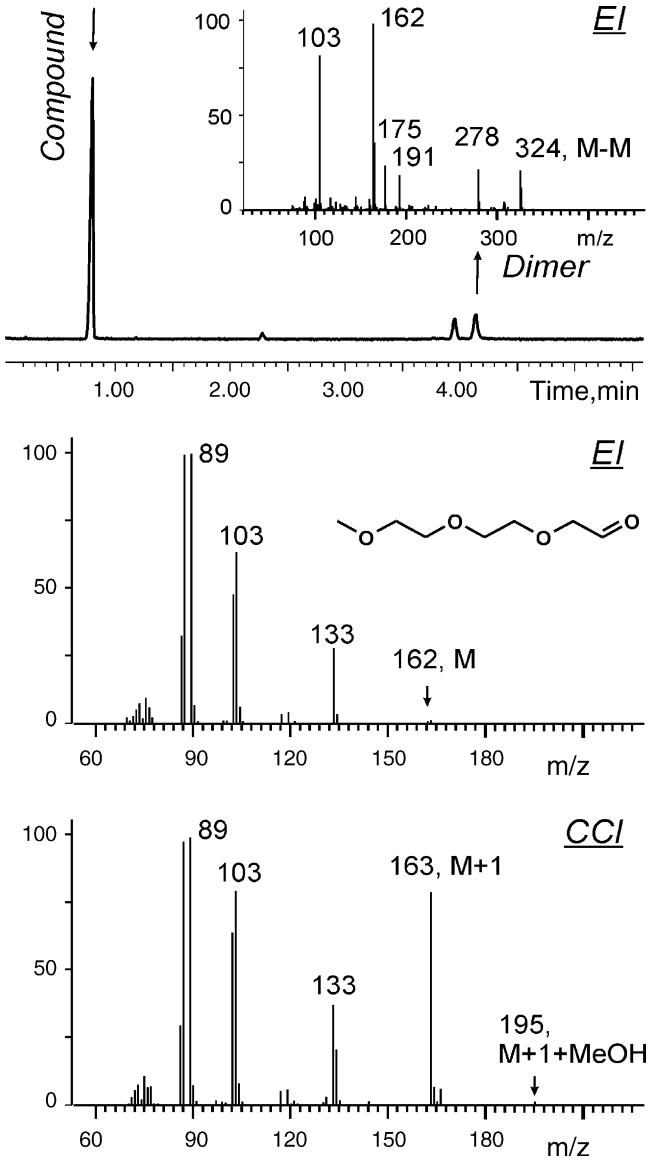


Fig. 8. Supersonic GC–MS analysis of the indicated $C_7H_{14}O_4$ compound (molecular weight of 162 amu). The upper trace shows the total ion mass chromatogram of the synthetic mixture plus the cold EI mass spectrum of the dimer of the desired compound (in the insert). The middle trace is the cold EI mass spectrum of this compound while the lower trace shows the methanol cluster CI mass spectrum of this compound.

firmation through the methanol cluster satellite mass spectral peak that is unique to the molecular ion (and not to any fragment ion [16]). The success of this synthesis was later confirmed by NMR, but with GC–MS we could provide its identification at an earlier synthetic stage in its impure synthetic mixtures. Moreover, the Supersonic GC–MS provided unique information that could not be obtained in any alternative way through the provision of ^{18}O isotope labeling information. This is demonstrated at the lower cluster CI mass spectrum that show the almost full isotope enrichment with mostly four ^{18}O and slightly with three ^{18}O and one ^{16}O. The demonstration of the success of isotope labeling provides important clues about the mechanism of the synthetic method [29].

$C_7H_{14}O_4$ (Fig. 8) is another example of a synthetic reagent that was given to us as a challenge by M. Gozin, a synthetic organic chemist at our school of chemistry [30]. This compound showed no molecular ion in standard EI (also only minor molecular ion with cold EI as shown in the middle EI mass spectrum in Fig. 8) while its standard CI produced only *m/z* = 163 protonated molecular ion. However, its NMR showed conflicting results, suggesting that its size is even doubled. With the Supersonic GC–MS using cold EI we found the presence of $C_{14}H_{28}O_8$ dimer and $C_{14}H_{28}O_7$ dimer deriva-

tive of this compound at the 10–15% concentration range (as demonstrated in the total ion mass chromatogram and mass spectrum insert shown in the upper trace in Fig. 8), thus explaining the NMR results. In this case, the ability of Supersonic GC–MS to extend the range of compounds amenable to analysis proved to be essential. Following the use of cluster CI as shown in the lower mass spectrum in Fig. 8, the identification of this unknown compound was enabled, as in the structure included in Fig. 8 that was later confirmed by NMR of a further purified sample.

In a few cases the analytical challenge is not significant but the synthetic organic chemist simply wants the best available analytical tool to ensure that their analytical results provide the most useful information. The analysis of polypropylene oligomers belongs to that category. The group of M. Kol at our school of chemistry is exploring the preparation of polypropylenes with novel zirconium and other organometallic based catalysts [31]. The provision of trustworthy accurate molecular ion for their reaction products was essential for that group, while isomer structural information is also desirable (tacticity of the oligomers, i.e. non statistical ratio of diasteroisomers with the implication of some stereo-control by that specific catalyst [32]). The results of this analysis are shown in Fig. 9, which shows the obtained total ion chromatogram plus a representative mass spectrum of one of the $(C_3H_6)_6$ isomers. This oligomer isomer mass spectrum reveals a strong m/z = 252 molecular ion, unlike in standard GC–MS in which the molecular ion could be much weaker or even absent, depending on the polymer size. In our case it was always a strong mass spectral peak even for larger oligomers [14].

Another type of challenge was provided by the group of A. Bar-Nun from the department of Geophysics and Planetary Sciences at our university. This group is attempting to explain the formation of aerosols in Titan's atmosphere [33,34] (Titan is one of Saturn's satellites, to be visited soon by the Cassini–Huygens spacecraft). Since acetylene is the major unsaturated species in Titan's atmosphere, its photolytic polymerization is probably a major source of formation of the observable aerosols in the atmosphere. Polymers formed by photolysis of acetylene have an expected atomic composition of C:H = 1:1. namely, mostly polyvinyls. The polyvinyl structure is chemically active, leading to cross-linking which makes these polymers insoluble in common organic solvents. Furthermore, these polymers are highly susceptible to oxidation by air.

The analytical challenge in the analysis of these polyvinyls began with the fact that the obtained brown/yellow powder could not be dissolved in any ordinary solvent. Consequently, we used our ChromatoProbe sample introduction device and placed some of this powder in a micro glass vial into a temperature programmable injector (Optic 2, ATAS, Veldhoven, The Netherlands) for intra injector sample thermal desorption followed by its Supersonic GC–MS analysis. Our typical results are shown in Fig. 10, which exhibits the obtained total ion mass chromatogram (upper trace) together with the cold EI

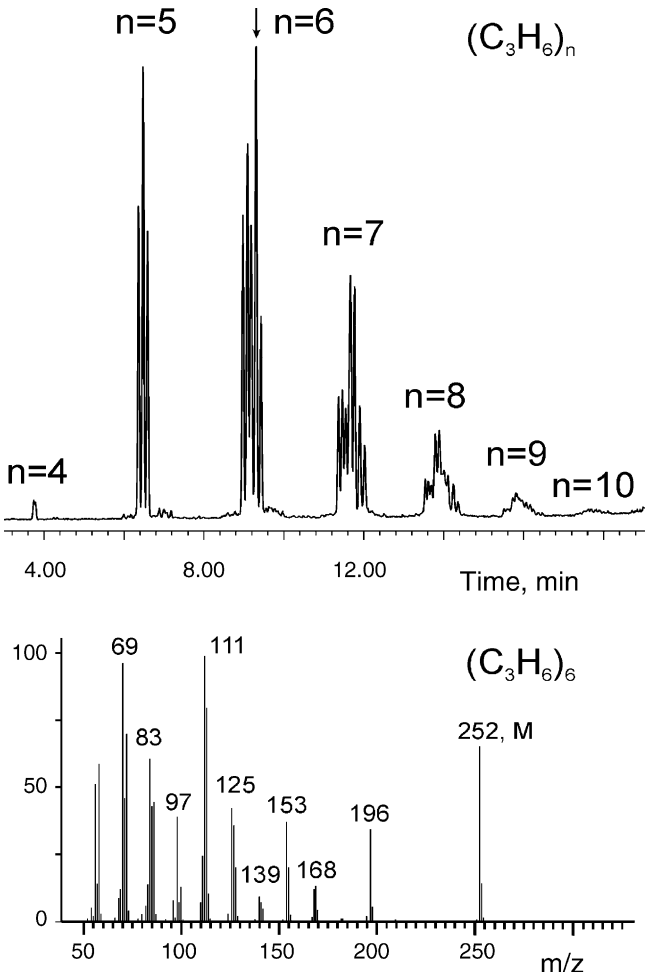


Fig. 9. Supersonic GC–MS analysis of polypropylene oligomers $(C_3H_6)_n$, n = 4–10. The peak multiplicity is due to prevalence of several isomers for each oligomer. A representative cold EI mass spectrum of $(C_3H_6)_6$ is shown at the bottom trace, taken from the isomer that is indicated by the arrow.

mass spectrum of the most abundant product that is shown at the bottom trace. This mass spectrum resembles that of sqalene in the NIST library ($C_{30}H_{50}$) but from synthetic consideration it is probably of another unidentified hydrocarbon with an empirical formula closer to C_nH_n. The mass spectrum of an even bigger hydrocarbon is shown in the upper right insert mass spectrum, which demonstrates the availability of obtaining trustworthy molecular ion for all these compounds. The indicated odd molecular ion at m/z = 533 is due to mass defect of the hydrogen atoms while its nominal molecular ion should be m/z = 532. The mass spectrum at the upper left insert shows additional unexpected information in that the molecular ion depicted is m/z = 242 but the high mass fragment near it has m/z = 199 that is 43 amu below the molecular ion. This type of fragmentation (that was also found in a few other GC peaks) hinted us towards the adverse effect of oxidation of the polyvinyl, hence CH_3CO mass spectral loss. Following these results a further study of these polymers under tight anaerobic conditions is being planned.

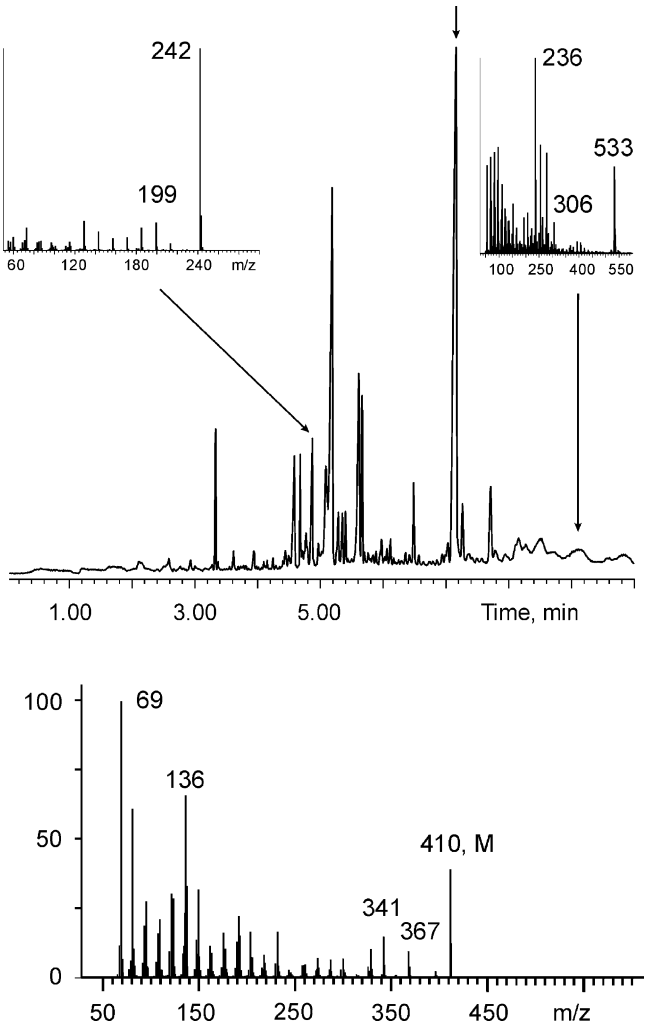


Fig. 10. Supersonic GC–MS analysis of polyvinyl oligomers produced by UV photo polymerization of acetylene. A ChromatoProbe sample introduction device was used with intra injector thermal desorption of the synthetic powder. The upper trace shows the obtained total ion mass chromatogram while the bottom trace is the cold EI of the most intense mass chromatogram peak. The upper cold EI mass spectra (inserts) are of the compounds indicated by arrows.

4. Discussion and conclusions

Several examples were shown of samples that failed to be analyzed by standard GC–MS, in which the Supersonic GC–MS succeeded and provided valuable information that helped synthetic organic chemists in further developing their synthetic methods. The analysis of novel synthetic organic compounds and general service GC–MS clearly benefited from the following features of the Supersonic GC–MS:

1. Availability of enhanced molecular ion with Cold EI, that was almost always available and thus could be trusted. We estimate that while in *standard thermal* 70 eV EI the molecular ion is observed in ∼70% of samples, in *Cold EI* it is observed in ∼98% of the samples. This feature was considered by our "customers" as the single most important advantage of the Supersonic GC–MS.
2. Extended range of thermally labile and low volatility samples that could be analyzed. This feature was of particular importance for the analysis of novel synthetic organic compounds since many of these compounds are thermally labile and some of them are low volatiles as well.
3. Availability of Cluster CI to supplement Cold EI in the rare cases that the molecular ion was absent or weak. Note, that Cluster CI and Cold EI switching could be performed without opening the vacuum system and took only a few seconds thus it was a practical complementary method.
4. Availability of extended structural, isomer and isotope mass spectral information.
5. Availability of ChromatoProbe for direct sampling of solids that cannot be dissolved in standard solvents.
6. Fast analysis that was completed in typically 5 min. After the elution of the suspected peak of interest the data was evaluated while the chromatography continued thus typical turn-around time was 4–10 min until ready for next injection. This feature although initially under appreciated by our "customers" proved to be highly valuable as it enabled on-line analyses while the chemist was in-place for providing his feedback in case further information or a change of the method was needed. It also helped to increase his confidence level in the validity of the results.
7. Since the fast GC–MS analysis time is only a few minutes and it can deal with extended range of thermally labile compounds, GC–MS was preferred over the use of ChromatoProbe (for sample introduction) for most applications. In addition to its simpler operation (in comparison with probe) GC–MS provides further valuable qualitative and quantitative information on the sample purity and identity of other synthetic by-products.

We note that for this particular application sensitivity was not an issue as neat or 1000 ppm sample solutions were provided and quantitation or calibration is also not an important requirement.

In conclusion, the Supersonic GC–MS proved itself in the last 3 years in the analyses of over 50 samples of synthetic organic compounds of four groups in our University, with great success with those samples that failed with standard commercially available GC–MS instrumentation. As a result, we now ask for samples from other labs and universities in Israel to further test and evaluate our capabilities and meet new challenges.

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