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Note

Direct coupling of a gas chromatograph to an ion trap detector

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The combination of capillary gas chromatography with mass spectrometry (GC–MS) is a powerful technique in trace analysis of complex samples. The two alternative interfacing methods described in the literature are direct coupling by positioning the GC capillary colum outlet in the evacuated ionization chamber of the mass spectrometer, or the use of a purged jet separator for the transfer of the GC eluate to the inlet capillary of the mass spectrometer[1,2]. In trace analysis the major advantage of the direct inlet system is the unsplit total analyte transfer into the mass spectrometer.

The ion trap detector ITD 700* is generally equipped with an open split interface. In an application note[3], the manufacturer proposed a direct inlet of the GC separation capillary into the analyzer block of the mass spectrometric detector. This construction was based on an early type of transfer line (Fig. 1, version I). To exchange GC capillary columns, the analyzer block of the ITD had to be cooled and the vacuum system was vented, the major disadvantage of most direct couplings in GC–MS equipment[4]. We installed our first direct connection by using the approved commercially available Finnigan transfer line (Fig. 1, version II). Although we have achieved excellent performance with the system, the disadvantages of turning off the instrument, remounting the main transfer line connections at the GC and MS sides and waiting about 24 h for appropriate and stable vacuum conditions to be reestablished were still apparent. With our manipulation of the transfer line (Fig. 1, version III) we tried to overcome this time-wasting procedure. Results obtained and the performance of the new interface are discussed and three applications of the GC-ITD system are presented.

EXPERIMENTAL

Gas chromatography–mass spectrometry

All GC–MS analyses were performed on an Hewlett-Packard Model HP 5890A gas chromatograph directly coupled to a Finnigan ITD 700. For data processing, ITDS software revision 3.0 and the National Bureau of Standards (NBS) mass spectrum library were installed in an IBM AT2 data system. Samples were injected

* ITD 700 is a registered trademark of the Finnigan Corporation (Sunnyvale, CA, U.S.A.).

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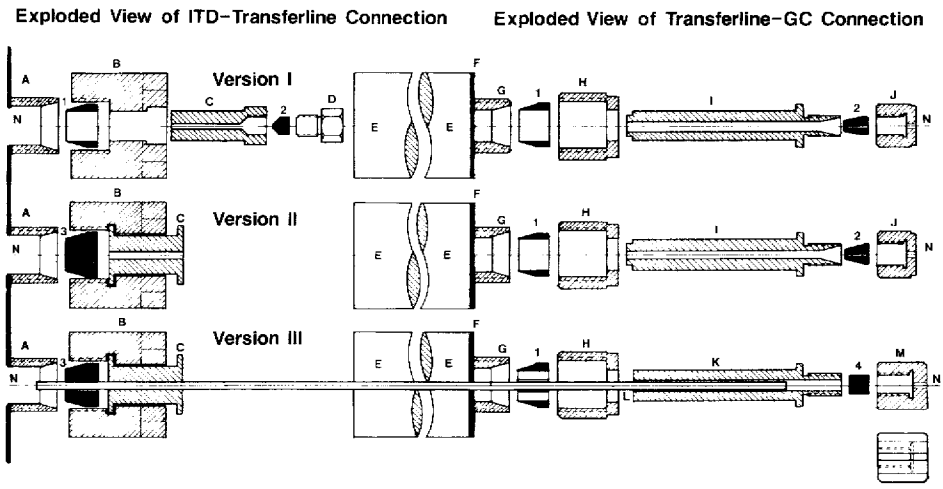


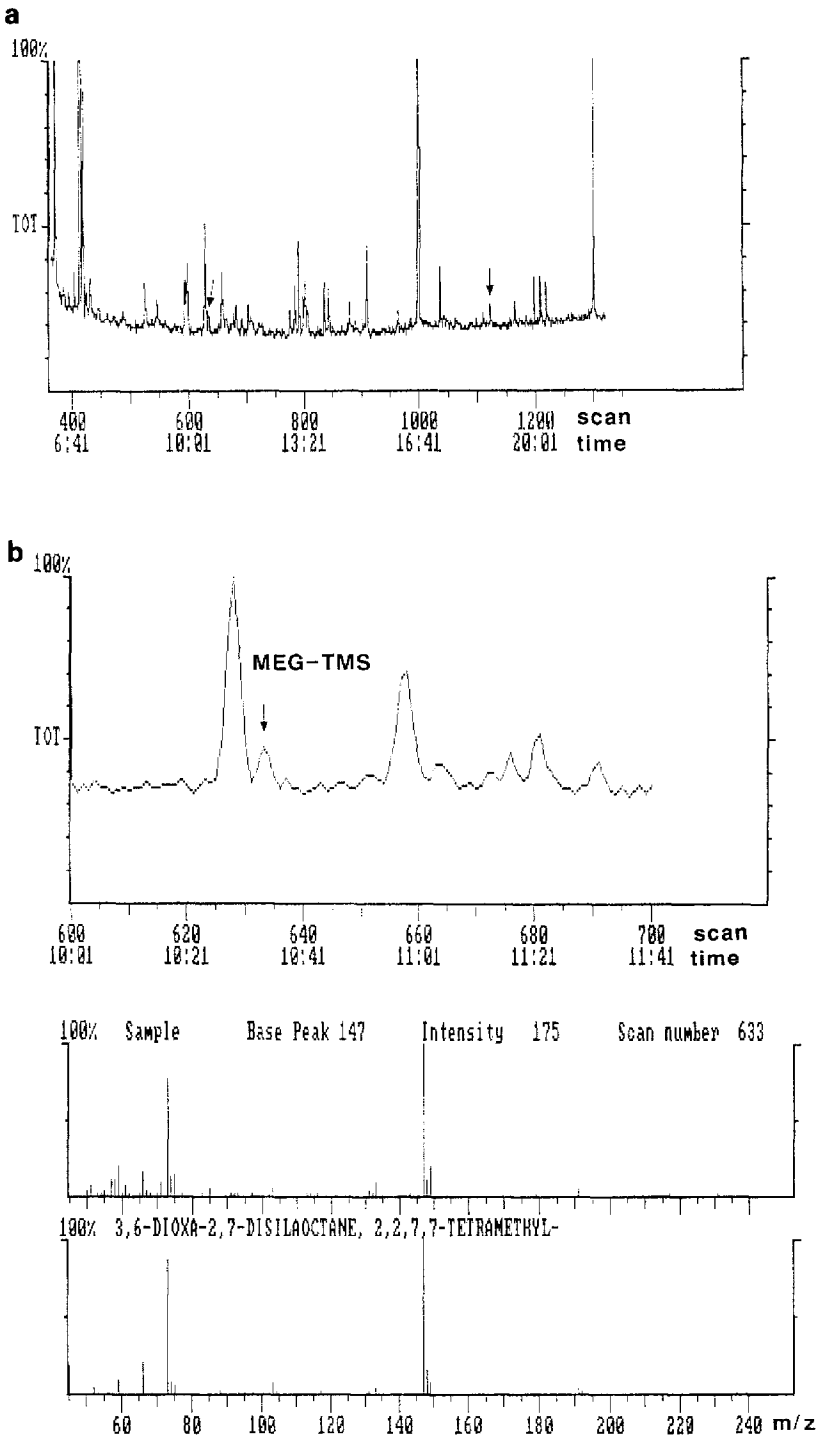
Fig. 1. Cross-sectional view of the GC–transfer line ITD connections. For details see text. A = ITD manifold and Swagelok fitting, B = 7/8-in. nut, C = exit nozzle, D = 3/16- in. nut, E = heated transferline, F = GC oven wall, G = heated open split block, H = 1/2- in. nut, I = GC open split block adapter, J = 3/16-in. Swagelok nut, K = graphpack adapter, L = stainless-steel tubing, I.D. 0.5 mm, O.D. 0.75 mm, silver-soldered to graphpack adapter K, M = slit 7 mm hexnut, N = fused-silica capillary column, 1 = large-ring ferrule, 2 = small ferrule, 3 = large ferrule, 4 = graphpack brass-graphit ferrule.

manually on-column at the GC oven temperature. Retention gaps were installed in some experiments, and injected volumes never exceeded 1.0 μl. The pressure in the ITD analyzer was adjusted by the helium carrier gas flow regulator of the gas chromatograph so that the masses m/z 502 and 503 of the ITD calibrant perfluorotributylamine showed a good separation with a maximum peak height for m/z 502. The optimized flow setting obtained was then used as a pre-set value for all GC capillaries with identical lengths and internal diameters. Our experience has been that the film thickness of the stationary phase has little influence on the performance of the ITD.

Modification of the GC–ITD interface

To modify the GC–ITD coupling, the 7/8-in. nut of the transfer line was disconnected from the ITD manifold. At the GC side, the glass liner was removed from the heatable open split interface block. A 1.3-m section of stainless-steel tubing (0.5 mm I.D., 0.75 mm O.D.) was purged with a stream of pure oxygen and heated at the outside by means of a microburner flame. After cooling to ambient temperature, the tubing was washed with 100 ml each of *n*-hexane, dichloromethane, methanol and acetone. Sonic vibration was applied to support the cleaning effect of the successive washings. One end of the steel capillary was silver-soldered into a Graphpack* adapter. At this connection the inner surface of the tubing was smoothed with a 0.5-mm drilling tool. A 1/2-in. nut and ring ferrule were slid over the tubing onto the Graphpack adapter and the metal tubing was inserted through the transfer line from inside the GC oven. After tightening the nut and ferrule, the large ferrule was positioned

* Graphpack is a registered trademark of Gerstel (Mülheim, F.R.G.).


a
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scan
time
100% Sample Base Peak 147 Intensity 175 Scan number 633
100% 3,6-DIOXA-2,7-DISILAOCTANE, 2,2,7,7-TETRAMETHYL-
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80
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200
220
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m/z

Fig. 2.

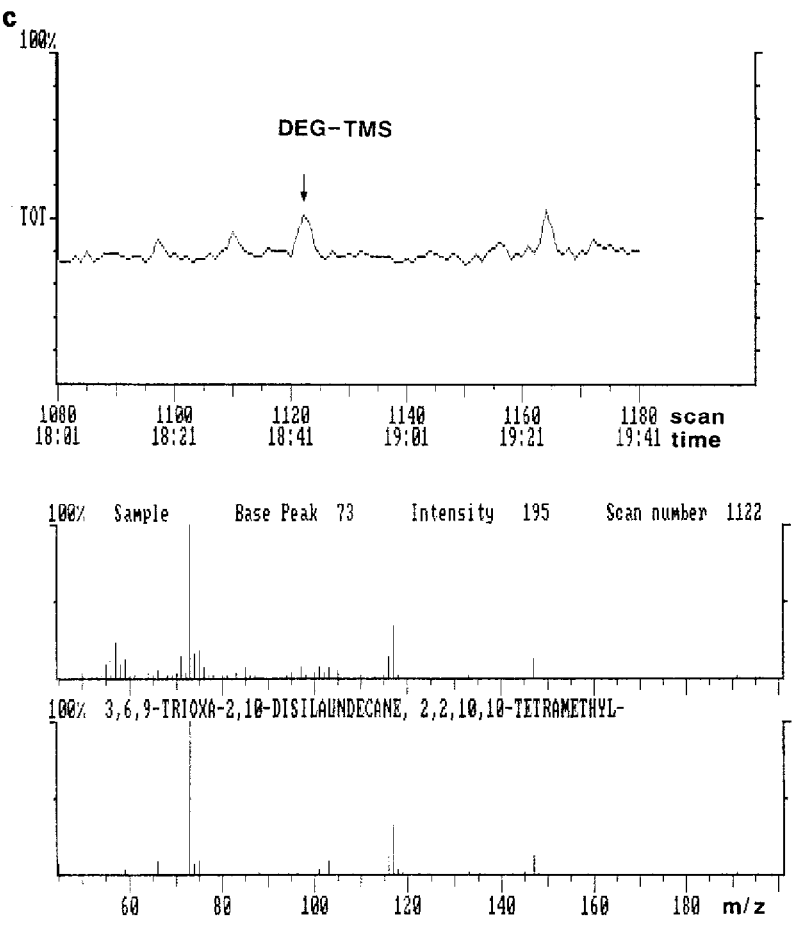

Fig. 2. Directly coupled GC–MS analysis of a diluted calibration standard in *n*-hexane, containing monoethylene glycol-TMS, diethylene glycol-TMS and the internal standards 1,4-butanediol-TMS and *n*-tetradecane. (a) Computer reconstructed total ion current (TIC) chromatogram; (b) TIC section, background-subtracted mass spectrum and NBS library reference spectrum identification for MEG-TMS peak, representing 574 fg monoethylene glycol; (c) TIC section, background-subtracted mass spectrum and NBS library reference spectrum identification for DEG-TMS peak, representing 636 fg diethylene glycol. GC: WCOT fused-silica capillary (60 m × 0.32 mm I.D.), film thickness 0.25 μm; coating SE-54 (SGE); temperature programme 70°C, 10 min; 10°C/min to 140°C, 2 min; 20°C/min to 250°C, 5 min. ITD: electron impact (EI) full scan acquisition, mass range *m/z* 50–250, 1 s per cycle.

onto the free end of the steel tubing in the 7/8-in. nut at the ITD side of the transfer line. The steel capillary should extend 5 mm beyond the large ferrule. This distance was marked with a scoring pencil. After withdrawing the tube from the open split interface block it was cut to the marked length. The exact measure (length of tubing + Graphpack adapter) was noted. After reinstallation, this part was finally sealed vacuum-tight inside the GC oven and at the ITD side. Both connections remained engaged in all further experiments, even during inspection and reassembly of the ion trap. After having fixed the fused-silica separation capillary to the injector, its free

end was marked with an ink pen at the point extending 5 mm beyond the exact length of the steel tubing plus the Graphpack adapter. A Graphpack ferrule was positioned at this mark and the capillary slid through the transfer line. The Graphpack connection was then tightly sealed with the slit hexnut. Replacement of GC capillary columns can now be achieved by simply disconnecting the Graphpack seal inside the GC oven, drawing back the used column and inserting the new one prepared with a Graphpack ferrule attached in the appropriate position as described above. After retightening the Graphpack connection and restabilization of ion trap parameters, the system is ready for GC–MS analysis.

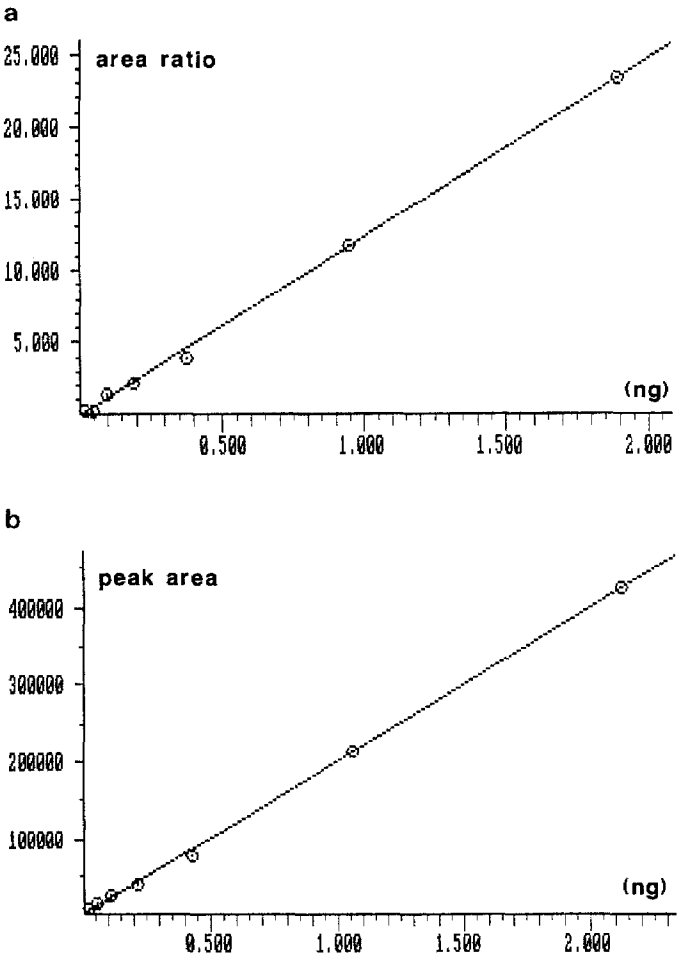

Fig. 3. Calibration plots for monoethylene glycol-TMS and diethylene glycol-TMS. Internal standard: *n*-tetradecane. (a) Peak area of MEG-TMS/peak area of *n*-tetradecane *vs.* corresponding amount of MEG injected (ng). (b) Peak area of DEG-TMS *vs.* corresponding amount of DEG injected (ng). For GC–MS conditions see Fig. 2., except for mass range *m/z* 50–300.

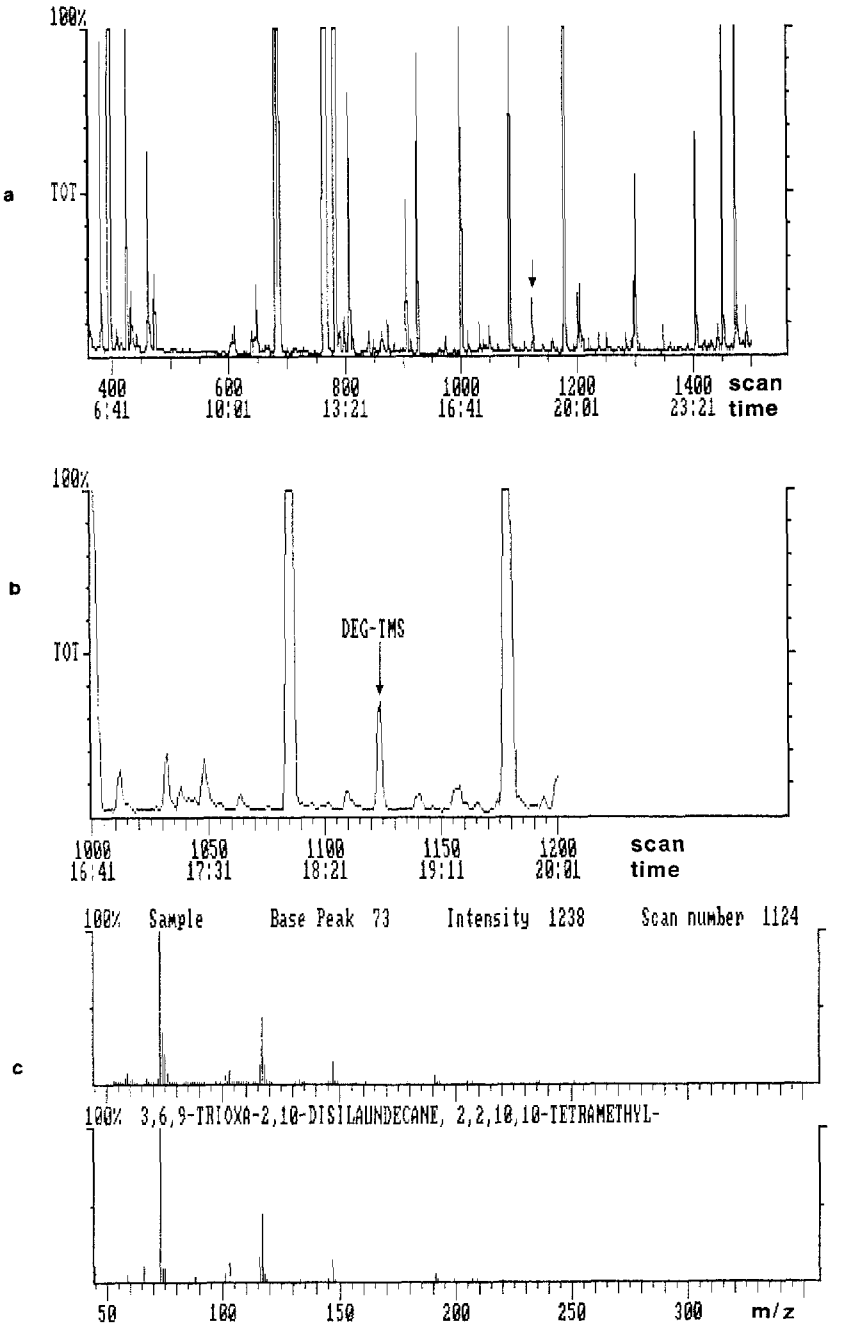

Fig. 4. Directly coupled GC–MS analysis of a white wine sample containing 1.189 mg/l (ppm) diethylene glycol. (a) Computer reconstructed TIC chromatogram of sample extract; (b) TIC section with DEG-TMS peak representing 297 pg diethylene glycol; (c) resulting mass spectrum and NBS library reference spectrum identification of DEG-TMS. For GC–MS conditions see Fig. 2, except for mass range *m/z* 50–300.

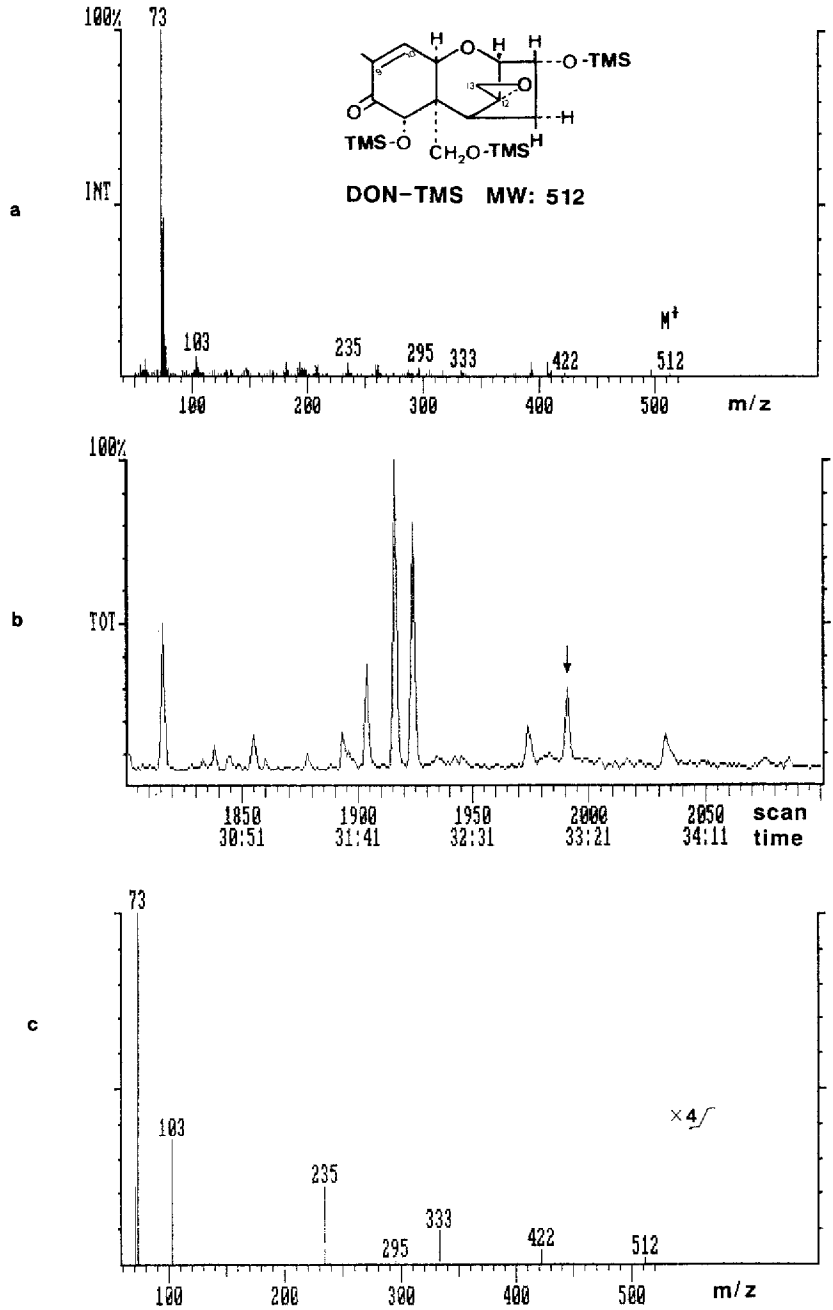

Fig. 5. Directly coupled GC–MS analysis of deoxynivalenol-TMS (DON-TMS). (a) Full scan reference mass spectrum of DON-TMS recorded from 600 pg DON standard. Designated ions are selected for measurements of samples in MID mode: (b) computer reconstructed MID chromatogram of a DON-contaminated wheat sample; (c) MID mass spectrum of DON-TMS peak representing 170 pg deoxynivalenol. GC: WCOT fused-silica capillary (60 m × 0.25 mm I.D.), film thickness 0.10 μm; coating DB-5 (J&W Scientific); 2-m retention gap, fused-silica megabore column, I.D. 0.53 mm (J&W Scientific); temperature-programme 80°C, 5 min; 4°C/min to 140°C, 2 min; 20°C/min to 260°C, 20 min. ITD: (a) EI full scan acquisition, mass range *m/z* 50–550, 1 s per cycle; (b) MID mode, selected ions for DON-TMS *m/z* 73, 103, 235, 295, 333, 422 and 512 (M^+).

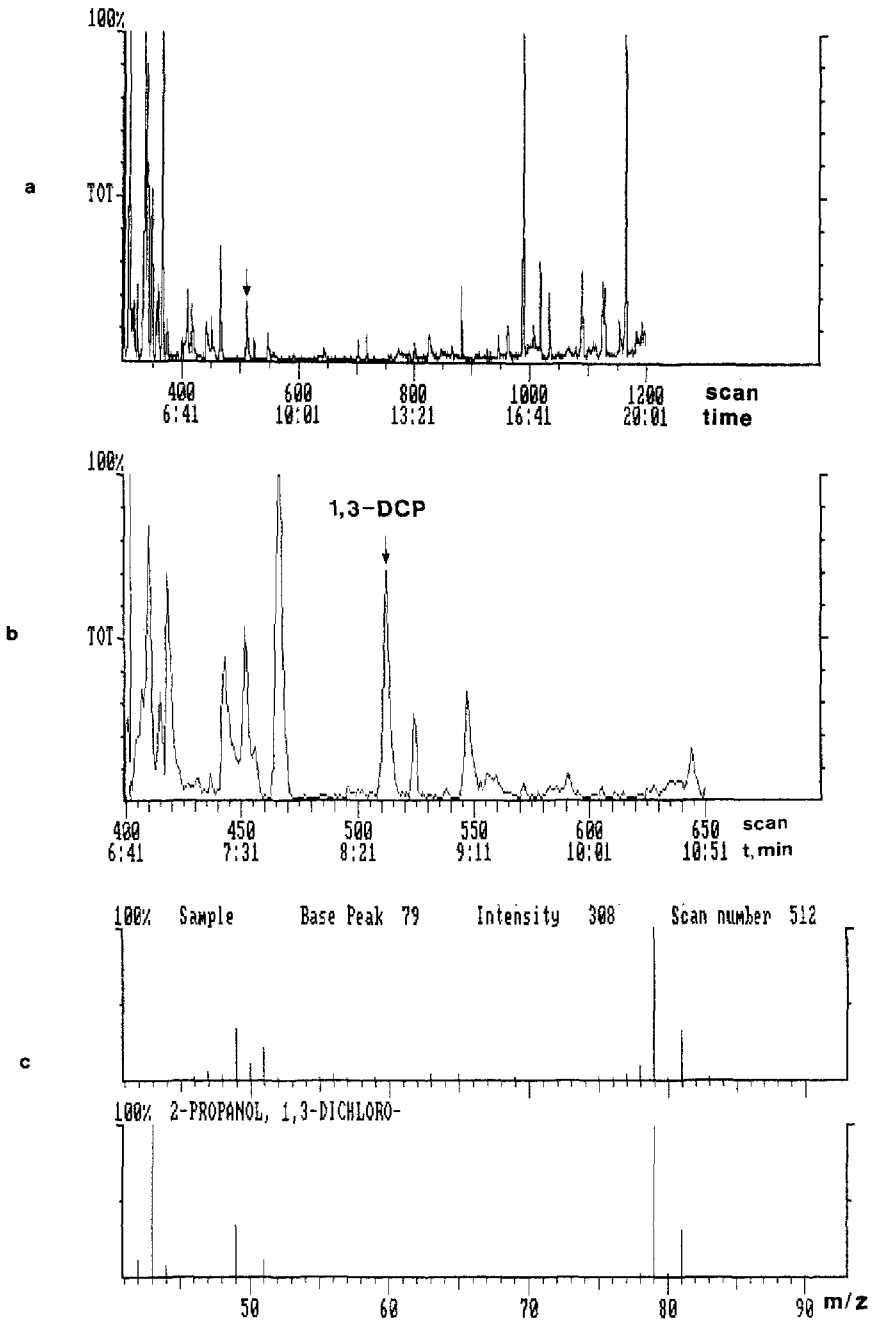

Fig. 6. Directly coupled GC–MS analysis of soy sauce containing 408 μg/kg (ppb) 1,3-dichloro-2-propanol (1,3-DCP). (a) Computer reconstructed TIC chromatogram of sample extract; (b) TIC section with peak representing 75 pg 1,3-DCP; (c) background-subtracted mass spectrum and NBS library reference spectrum identification. GC: WCOT fused-silica capillary (60 m × 0.25 mm I.D.), film thickness 0.25 μm; coating DB-5 (J&W Scientific); 2-m retention gap, fused-silica megabore column, I.D. 0.53 mm (J&W Scientific); temperature-programme 60°C, 8 min: 10°C/min to 200°C, 10 min. ITD: EI full scan acquisition, mass range *m/z* 46–90, 1 s per cycle.

RESULTS AND DISCUSSION

To demonstrate the increased sensitivity of our directly coupled GC–MS system, a calibration standard solution containing trimethylsilyl (TMS) derivatives of monoethylene glycol (MEG) and diethylene glycol (DEG), two compounds of increasing importance in wine control analysis, was diluted. From background-subtracted mass spectra of peaks detected with a signal-to-noise ratio $\geqslant 3/1$, both compounds, MEG–TMS and DEG–TMS, were identified by a full library fit search in rank 1. The amounts of derivatives injected corresponded to 574 fg free monoethylene glycol and 636 fg diethylene-glycol respectively. The total ion current, mass spectra and other information are shown in Fig. 2. In routine laboratory work, linear calibration plots for MEG amounts ranging from 18 pg to 1.89 ng and for DEG amounts from 21 pg to 2.12 ng were used in quantitation (Fig. 3.). The results of the analysis of a contaminated white wine containing 1.19 mg/l (ppm) diethylene glycol are presented in Fig. 4. On two other applications, GC–MS confirmation of GC results was required. In the first case, a wheat flour sample was shown to contain 575 μg/kg deoxynivalenol (DON, vomitoxin), a trichothecene mycotoxin frequently found in cereals[5]. To verify the contamination demonstrated by flame ionization detection (FID), we recorded full scan mass spectra of silylated DON reference material, selected characteristic fragment ions and examined the sample extract using the multiple ion detection (MID) mode. The Finnigan ITD software automatic quantitation procedure identified and calculated the contamination level to be 582 μg/kg (ppb), in excellent agreement with the GC–FID result (Fig. 5).

Another hazardous compound, 1,3-dichloro-2-propanol, in protein hydrolysates treated with hydrochloric acid was analyzed by Velisek *et al.*[6]. Following GC analysis with electron-capture detection (ECD), the contamination of a soy sauce sample was confirmed by using our GC–ITD system, as is demonstrated in Fig. 6. As little as 75 pg of the relatively low-molecular-weight compound (MW 128) were easily detected and identified.

CONCLUSION

Our modification of the Finnigan ion trap detector transfer line allows the rapid replacement of directly coupled fused-silica separation capillaries in GC–MS analysis without venting the vacuum system and time-wasting assembly. We have applied the direct coupling technique for more than 1 year now, and have obtained a remarkable increase in sensitivity of the GC–ITD combination, as is clearly demonstrated by the results described. In our opinion, the device presented could become an attractive alternative for those working in the field of trace analysis with the need to confirm analytical results by GC–MS.

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