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DETERMINATION OF DIBENZOTHIOPHENE IN OILS BY LIQUID CHROMATOGRAPHY–TANDEM MASS SPECTROMETRY

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SUMMARY

Quantitative trace analysis for organic compounds in complex matrices such as oils often requires time-consuming sample pretreatment. Two examples are shown of the use of a highly selective tandem mass spectrometer as a liquid chromatographic detector for the quantification of dibenzothiophene in a crude petroleum oil and in an alternate fuel oil. No sample preparation except an appropriate dilution was required. A preconcentrating liquid chromatography–mass spectrometry interface was used, allowing detection limits of *ca.* 20 ng to be attained.

INTRODUCTION

Quantiative trace analysis for organic compounds in complex matrices such as oils often requires time-consuming and laborious sample preparation. Techniques such as extraction, preparative scale liquid chromatography (LC), and conventional column chromatography are often employed. These manipulations, in addition to being time consuming, can lead to the introduction of systematic errors.

The combination of LC with a mass spectrometric detector (LC–MS) has been used to perform some analyses of this sort without sample pretreatment[1,2]. In other analyses, however, interferences arise which cannot be resolved either by the LC separation or by the selectivity of a single mass spectrometer.

The technique of tandem mass spectrometry (MS–MS) with collision-induced dissociation offers another degree of selectivity. This is accomplished by separating all ions of the mass corresponding to the ion of interest and subjecting them to collision with N_2. Fragment ions specific to the ion of interest can then be separated by a second mass analyzer.

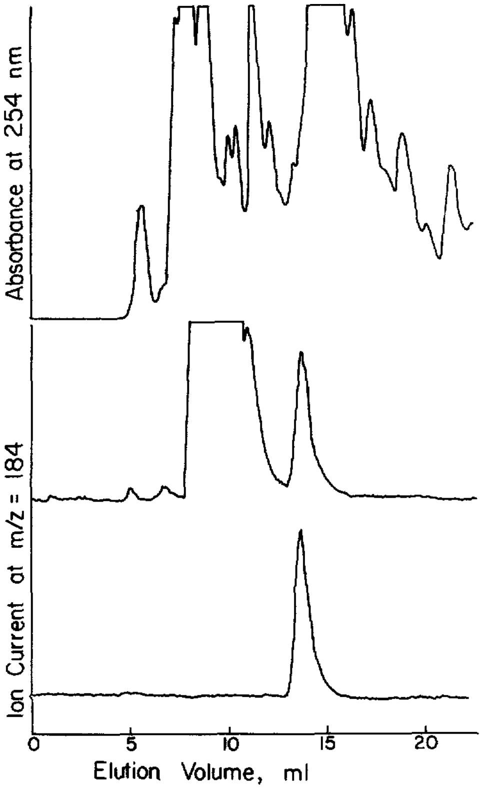
The present paper discusses the use of a triple quadrupole mass spectrometer as an LC detector for the determination of dibenzothiophene in a petroleum crude oil (SRM 1582) and a solvent-refined coal liquid (SRC-II).

EXPERIMENTAL

A triple quadrupole mass spectrometer was used in the single-ion monitoring mode for both of the filtering quadrupoles, the first being set for *m/z* 184 (corresponding to M^+ for dibenzothiophene) and the second for *m/z* 152 [corresponding to $(M - 32)^+$]. The pressure of the nitrogen collision gas and the collision energy were adjusted to give maximum yield of daughter ions. The values were *ca.* $5 \cdot 10^{-4}$ torr and 25 eV.

A conventional liquid chromatograph was used in the normal-phase mode. The column was a proprietary polar (amino-cyano) column protected with a precolumn containing a pellicular packing of similar characteristics. The solvent was hexane containing 1.5% dichloromethane for the LC–MS and 2% dichloromethane for the LC–MS–MS runs, and the flow-rate was 1.5 ml/min. The oil samples were diluted 1:5 or 1:20 and the injected volume was 20 µl.

The interface between the liquid chromatograph and mass spectrometer was a preconcentrating interface of our own design and construction[1]. For the analysis of the SRC-II, the concentrator current was adjusted so that the concentration enhancement was *ca.* fifteen-fold. For the analysis of the SRM 1582, maximum sensi-



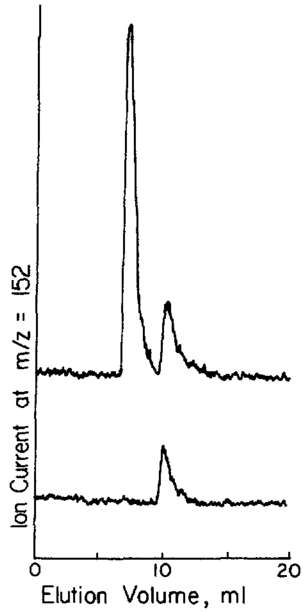


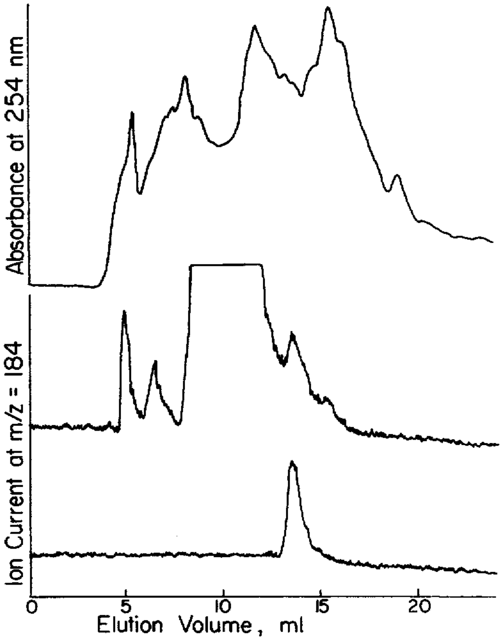
Fig. 1. Chromatographic traces from LC–MS analysis for dibenzothiophene in SRC-II. Upper trace, UV absorbance at 254 nm; center trace, single-ion monitoring at *m/z* 184 for SRC-II; lower trace, single-ion monitoring at *m/z* 184 for standard solution.

Fig. 2. Chromatographic traces from LC–MS–MS analysis for dibenzothiophene in SRC-II. Upper trace, single-ion monitoring of daughter ion *m/z* 152 from parent ion *m/z* 184 for SRC-II; lower trace, single-ion monitoring of daughter ion *m/z* 152 from parent ion *m/z* 184 for standard solution.

tivity was required. Accordingly, the concentrator was adjusted so that virtually all the chromatographic effluent entered the mass spectrometer. This proved to be about a forty-fold concentration enhancement. In this latter case, the concentrator was only turned on when the compound of interest was about to elute from the column. This prevented the introduction of large amounts of other compounds from the oil into the mass spectrometer.

RESULTS

The first analysis undertaken was one which had already been accomplished with LC–MS, namely the determination of dibenzothiophene in SRC-II. The LC–



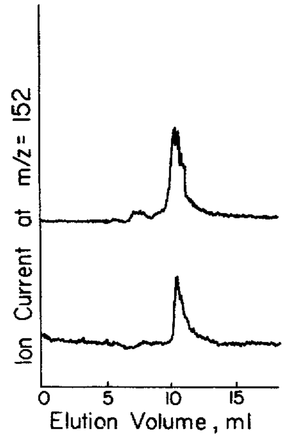


Fig. 3. Chromatographic traces from LC–MS analysis for dibenzothiophene in SRM 1582. Upper trace, UV absorbance at 254 nm; center trace, single ion monitoring at m/z 184 for SRM 1582; lower trace, single ion monitoring at m/z 184 for standard solution.

Fig. 4. Chromatographic traces from LC–MS–MS analysis for dibenzothiophene in SRM 1582. Upper trace, single-ion monitoring of daughter ion m/z 152 from parent ion m/z 184 for SRM 1582; lower trace, single-ion monitoring of daughter ion m/z 152 from parent ion m/z 184 for standard solution.

TABLE I

DETERMINATION OF DIBENZOTHIOPHENE

Standard deviations and number of measurements are shown.

Sample	*Dibenzothiophene concentration (μg/ml)*		
	LC–MS	*LC–MS–MS*	*Other NBS methods*
SRC-II	933 ± 57 (n = 5)	1017 ± 78 (n = 11)	1020 ± 70
SRM 1582	–	41.3 ± 6.7 (n = 12)	33 ± 2

MS results are given in Table I and a chromatogram is shown in Fig. 1. The LC–MS–MS results are also given in Table I and a chromatogram is shown in Fig. 2. Concentrations of dibenzothiophene in these oils found at the National Bureau of Standards by other methods[3,4] are also provided in Table I. As can be seen in Table I, the LC–MS results for SRC-II are somewhat lower than the results from LC–MS–MS and other methods. While the uncertainties overlap, this suggests that the LC–MS–MS results may be more reliable.

The chromatograms shown in Fig. 3 are the result of an attempt, using LC–MS, to quantify dibenzothiophene in SRM 1582, a petroleum crude oil sample. It can be seen that the dibenzothiophene peak appears only as a small shoulder which is not suitable for quantification. Fig. 4 shows a chromatogram made in the LC–MS–MS mode. In this case, the dibenzothiophene is completely resolved from the other components of the mixture. The results are given in Table I.

Quantification in all cases was by comparing peak heights with those resulting from prior and/or subsequent injections of standard solutions of dibenzothiophene. The lower precision and accuracy in the SRM 1582 measurements arises because the amount of dibenzothiophene present is only several times the detection limit.

CONCLUSION

We have demonstrated a very rapid and fairly sensitive method for the analysis of dibenzothiophene in oil samples. Time per run is reduced to *ca.* 7 min, and the detection limit is less than 20 ng. It is interesting to note that the extremely high selectivity of the tandem mass spectrometer almost obviates the need for a chromatographic separation.

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