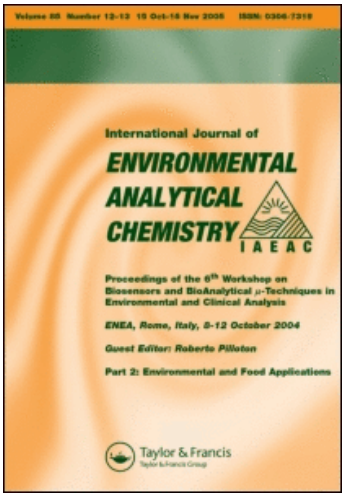


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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**To cite this Article** Pettit, K. , Brown, R. S. and Jones, P. W.(1990) 'Quantification of 2,3,7,8-TCDD by GCMS', International Journal of Environmental Analytical Chemistry, 38: 2, 135 — 141
**To link to this Article: DOI:** 10.1080/03067319008026922
**URL:** http://dx.doi.org/10.1080/03067319008026922

*Intern. J. Environ. Anal. Chem.*, Vol. 38, pp. 135–141
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# QUANTIFICATION OF 2,3,7,8-TCDD BY GCMS

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The quantitative analysis of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is extremely important due to its high toxicity and association with many synthetic and chlorinated chemicals.[1] Problems are often encountered with the separation of this analyte and the specificity and sensitivity of the analytical equipment. The accurate quantification of 2,3,7,8-TCDD is dependent upon three major factors; the maximum sensitivity of the instrumentation, the separation of the 2,3,7,8-TCDD isomer from the other closely eluting isomers and the reduction or complete elimination of interferences. The maximum sensitivity was obtained by operating the mass spectrometer at 30eV and 500$\mu$A trap current. High resolution chromatographic separation was achieved using DB17 capillary column producing base-line resolution for the separation of the 2,3,7,8-TCDD isomer. Highly selective analysis was achieved using selective decomposition monitoring which proved useful in the analysis of heavily contaminated samples that still presented a problem with high resolution mass spectrometry.

KEY WORDS: Tetrachlorodibenzo-p-dioxin, mass spectrometry, capillary chromatography, selected decomposition monitoring.



## INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are two series of tricyclic aromatic compounds that exhibit very similar physical and chemical properties. The extreme toxicity of some of these congeners have been the subject of much concern in many countries.[2–8] In general, PCDDs and PCDFs and non-ortho PCBs are classified as highly toxic substances[9] the degree of toxicity being dependent on the number and position of the chlorine substituents.[10] The single most toxic isomer being the 2,3,7,8-TCDD.[9–11] Due to the large variations in toxicity between closely related congeners, highly selective, specific and sensitive analytical techniques are required for their measurement. The most specific has been high resolution GCMS.[12,13] Gas chromatography-mass spectrometry has been widely used for the detection and quantification of mixtures of environmental origin.[14,15] In the case of complex environmental samples it is generally found that the chromatographic separation of an individual component is incomplete causing difficulty in identification. In this case specific detection and identification may be achieved by selected ion monitoring (SIM). The specificity may be enhanced by the use of high resolution SIM.[16]

The quantification of 2,3,7,8-TCDD by GCMS is dependent upon its complete

separation from the other closely eluting TCDD isomers. Several fused silica columns are well documented as being capable of separating 2,3,7,8-TCDD from the other closely eluting TCDD isomers as defined by the USEPA column performance mixtures[13,14,16–18] and recently the use of a novel column, Crystaline Polysiloxane, has been reported.[19] However these columns either have long retention times or are degradable.[20]

We have recently adopted an alternative technique, selected decomposition monitoring, for highly selective quantitative analysis of PCDDs and PCDFs by GCMS. The monitoring of a specific fragmentative process may be achieved by the detection of the metastable ion corresponding to the decomposition of the respective ions in the first field free region of a double focussing mass spectrometer.[21]

A similar study has been performed using HRGC/MS/MS/SRM methodology[22] showing the capability of selected decomposition monitoring to be effective in the analysis of heavily contaminated samples. However, unlike our study, this relied upon a third sector being used as a gas collision cell.



## EXPERIMENTAL

The instrument used for this investigation was a HP5890 gas chromatograph coupled to a VG70S/11-250J double focussing mass spectrometer. For selected ion monitoring of TCDD at high resolution (M/ΔM 10,000; 10% valley) ions of m/z 219.8965, 321.8936, 331.9368 and 333.9339 were monitored.

The dioxin congeners were obtained from Prochem, St Albans, Hertfordshire.

The gas chromatography capillary columns investigated were supplied by J & W Scientific.

| | | | |
|---|---|---|---|
| 30 m | DB1 | 0.25 mm id | 0.25 μm df |
| 60 m | DB5 | 0.32 mm id | 0.25 μm df |
| 30 m | DB17 | 0.25 mm id | 0.25 μm df |
| 30 m | DB225 | 0.32 mm id | 0.25 μm df |

| *Column* | *Init Temp °C* | *Time m* | *Rate 1 °C/s* | *Temp 1 °C* | *Time 1 m* | *Rate 2 °C/s* | *Temp 2 °C* | *Time 2 m* |
|---|---|---|---|---|---|---|---|---|
| DB5 | 130 | 2 | 65 | 240 | 20 | 5 | 290 | 20 |
| DB17 | 130 | 2 | 50 | 240 | 15 | 50 | 275 | 60 |
| DB225 | 130 | 2 | 20 | 220 | 10 | — | — | — |

## RESULTS AND DISCUSSION

Signal-to-noise evaluation studies of electron voltage and trap current settings on the VG 70S dedicated electron impact source with a helium flow of 1–2 ml/min demonstrate that TCDD is most efficiently ionized at 30 eV and 500 μA trap current. The ionization efficiency was reduced considerably when the source was operated outside a very narrow energy window ranging from 28 eV to 35 eV. The

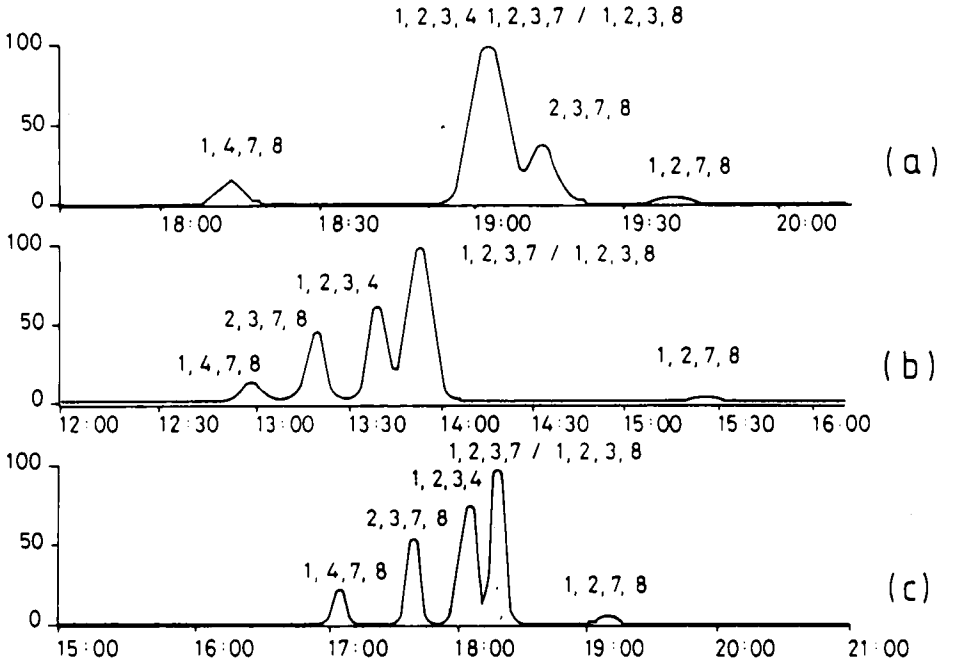


**Figure 1** Separation of 2,3,7,8-TCDD from other closely eluting isomers using (a) a DB5 capillary column, (b) a DB225 capillary column, (c) a DB17 capillary column. Chromatic conditions are as previously described. The mass spectrometer was operated in High Resolution SIM mode monitoring ions of mass 321.8936 and 333.9339 with total cycle time of 0.5 seconds. The mix was spiked with $^{13}C$ 2,3,7,8-TCDD to ascertain the retention time of 2,3,7,8-TCDD.



ion source, when operated at 1000 $\mu$A produced a much lower signal-to-noise ratio but with a wider ionization window. The filament emission was unstable when operated below 35 eV.

Elevated source temperatures can influence the fragmentation when the compound is ionized. Source temperatures between 220 °C and 300 °C were investigated (lower temperatures were impossible to maintain due to thermal diffusion from the high re-entrant temperature required to ensure that TCDD is eluted from the capillary column). It was found that no significant increase in signal-to-noise ratio was observed with change in source temperature. At source temperatures below 270 °C, frequent baking of the ion source was required to maintain maximum sensitivity.

The accurate quantification of 2,3,7,8-TCDD is only possible if it can be chromatographically separated from the other 21 TCDD isomers. The USEPA TCDD capillary column performance mixture contains the five TCDD isomers which elute very close to the 2,3,7,8-TCDD isomer and is used to assess a capillary column's performance.[20]

The most widely used capillary column (DB5–60 m) for dioxin analysis cannot resolve the 2,3,7,8-TCDD isomer from the other closely eluting isomers—Figure 1a. The DB1–30 m capillary column as expected is also incapable of aiding the

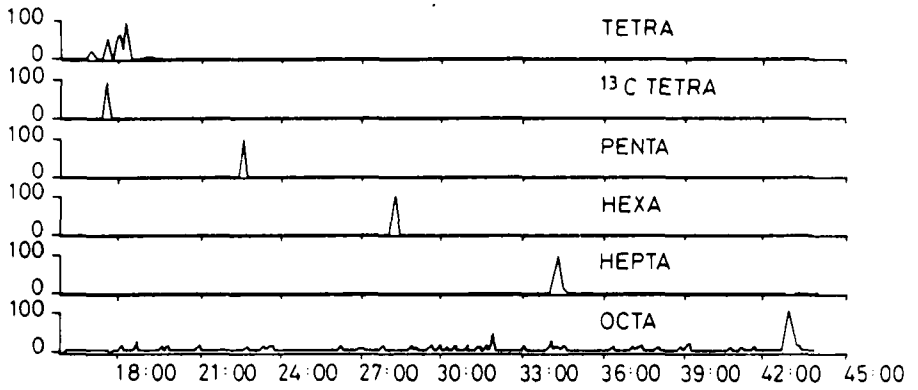


**Figure 2** Total PCDD analysis using a DB17 capillary column. The USEPA TCDD mixture was spiked with a $^{13}C$ isomer for each congener group. The ions monitored were 321.8936, 333.9339, 369.8919, 403.8530, 437.8140, 471.7750 in High Resolution SIM mode with a total cycle time of 1 second.



quantification of 2,3,7,8-TCDD but can be used for total TCDD analysis. Figure 1b demonstrates the resolution obtained for the separation of the 2,3,7,8-TCDD isomer using a DB225–30 m capillary column. Although capable of resolving the 2,3,7,8-TCDD isomer from the other TCDD isomers it is unsuitable for total tetra through octa dioxin analysis as the more polar congeners are retained. The BD17–30 m capillary column has achieved base-line resolution for the 2,3,7,8-TCDD isomer—Figure 1c, whilst Figure 2 demonstrates that the DB17 capillary column is suitable for total tetra through octa dioxin analysis.

The use of alternative acquisition techniques for the quantification of 2,3,7,8-TCDD can have a dramatic influence on the interpretation of the results. Figure 3a shows the ion current traces at low resolution for SIM analysis of TCDD on a DB5–60 m capillary column; 2,3,7,8-TCDD is difficult to quantify due to the interferences present in the sample.

The specificity of high resolution SIM (10 000 RP) facilitated accurate quantification of 2,3,7,8-TCDD by selectively removing inteferences of the same nominal mass present in low resolution SIM—Figure 3b.

Selective decomposition monitoring (SDM) is a selective technique which is an alternative to high resolution SIM. The mass spectrometer is operated at low resolution and the accelerating voltage and electrostatic analyser are unlinked. In this way, it is possible to monitor an ion of mass $M_2$ formed from a parent ion of mass $M_1$ in the first field free region (FFR) of a magnetic mass spectrometer. The formation of the daughter ion is enhanced by the admission of a collision gas into the FFR.

For dioxin analysis the decomposition in the FFR is the loss of COCl from the parent ion.

$$C_{12}H_4O_2Cl_4^+ \rightarrow C_{11}H_4OCl_3^+ + COCl.$$

The selectivity of SDM is demonstrated by Figure 4. When compared against

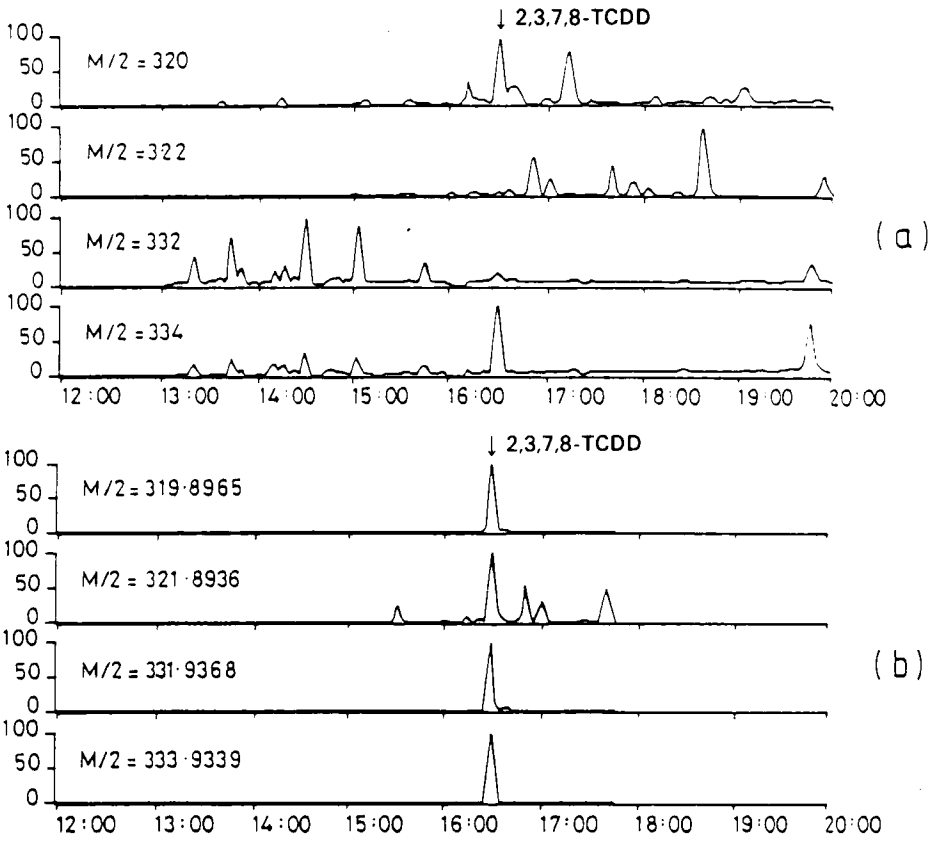


**Figure 3** Analysis of heavily contaminated environmental sample by (a) low resolution SIM, (b) high resolution SIM. Chromatographic conditions are as previously described. An environmental sample was spiked with $^{12}C$ 2,3,7,8-TCDD and $^{13}C$ 2,3,7,8,-TCDD. In each case the two most abundant ions in the tetra elutes window were monitored (as indicated above) with a total cycle time of 1 second in High Resolution SIM mode with PFK was used as a lock mass.

the low resolution SIM ion traces of the same sample—Figure 3 it is evident that interferences are removed and accurate quantification possible. TCDD identification under USEPA guidelines states that the ration between the two most abundant molecular ion peaks much between 0.65–0.90. When TCDD is quantified by SDM these ratios are no longer valid as the loss of COCl is being monitored, the theoretical isotope ratio for three chlorines being 0.9–1.3. SDM has proved useful in quantification analysis of heavily contaminated samples. The signal-to-noise ratio of TCDD is almost comparable to high resolution SIM but the specificity seems to be greater. For accurate quantification of 2,3,7,8-TCDD in heavily contaminated samples the selectivity of SDM has to be weighed against the sensitivity of high resolution SIM.

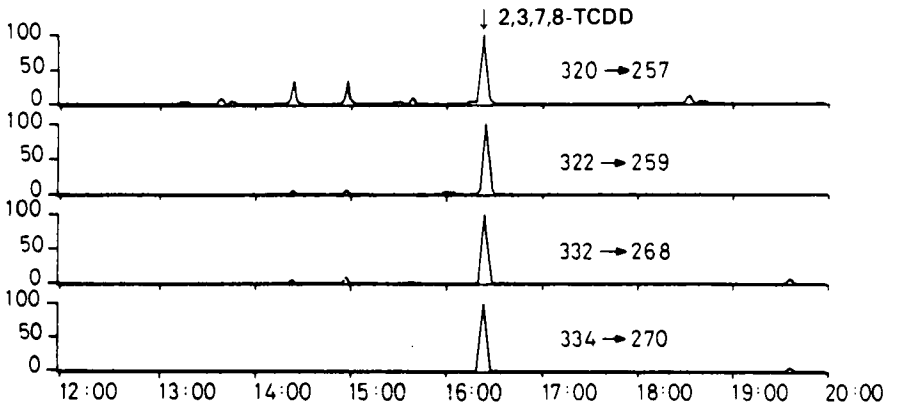


**Figure 4** Analysis of heavily contaminated sample by selected decomposition monitoring. Chromatographic conditions were as previously described. The sample is as described in Figure 3. The mass spectrometer was operated at 1000 RP with an air leak into the 1st field free region to obtain a 10% drop in transition. The transitions monitored are as indicated with no lock mass.



## CONCLUSIONS

The determination of part-per-trillion levels of PCDDs and PCDFs can be performed by many laboratories but in some cases, especially when the sample matrix size is small, the analytical instrumentation can dramatically improve the detection limits for the determination of PCDDs and PCDFs. The VG 70S electron impact source shows a definite improvement in sensitivity for the analysis of PCDD and PCDF when operated at 30 eV and 500 $\mu$A trap current under GC conditions. The extremely narrow ionization window indicates that the electron voltage was critical but may be filament dependent. We did not investigate this but will do so in the future. The extensive work that has been put, by numerous laboratories, into the chromatographic separation of 2,3,7,8-TCDD from the other TCDD isomers indicates the current concern on its accurate quantification. Although many suitable capillary columns have been cited, it is felt they have extremely long retention times and the separations achieved do not give unambiguous quantifications of 2,3,7,8-TCDD. The DB17 capillary column has shown base-line resolutions for the separation of 2,3,7,8-TCDD from the other TCDD isomers with a retention time of 18 minutes. It will not replace the 60 m DB5 capillary column for routine analysis due to congener window overlap, but it is felt that total analysis may be performed in two analyses with no retention of any congener by the capillary column.

The presence of high levels of potential interferences in environmental samples indicates that low resolution SIM is not specific enough for the identification and accurate quantification of PCDDs and PCDFs. The use of high resolution SIM does improve the detection and identification of the congeners that are still susceptible to interference with heavily contaminated samples. Although high resolutions are obtainable with most magnetic mass spectrometer (in excess of 20 000) its use is impracticable due to the inherent loss of sensitivity. In this case, the use of selected decomposition monitoring may aid the identification of the

PCDD and PCDF congeners. In our opinion, this alternative technique will not replace high resolution SIM for routine analysis but may be used as a complementary technique for those samples that require a higher selectivity than can be achieved by conventional HRGCMS.

It is our intention to investigate the advantages of selected decomposition monitoring and to investigate methods for improving sensitivity so that its use for routine dioxin analysis can be properly assessed.

*Acknowledgements*

Mrs J. Ford and Mrs A. May for typographical presentation.

*References*

1. C. Rappe *et al.*, *Health Effects of Halogenated Aromatic Hydrocarbons* (Nicholson and Moore, NYAS, 1979), Chap. 1, pp. 1–19.
2. C. Rappe *et al.*, *Nature* **292** (1981).
3. C. Rappe *et al.*, *Public Health Risks of Dioxins* (Lawrence W. Kaufman, 1984), pp. 57–61.
4. M. L. Grose, *Environmental Res.* **33,** 261 (1984).
5. M. Graham *et al.*, *Chemosphere* **14,** 925 (1985).
6. S. Focchetti *et al.*, *Adv. Mass Spec.* **8,** 1405 (1980).
7. P. H. Chen *et al.*, *Chemosphere* **12,** 1507 (1983).
8. C. Rappe *et al.*, Conference on Toxic Substances (1984).
9. E. McConnel, in: *Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products*, R. Kimbrough, ed. (Elsevier/North-Holland, New York, 1980), pp. 109–150.
10. J. Goldstein, in: *Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products*, R. Kimbrough, ed. (Elsevier/North-Holland, New York, 1980), pp. 151–190.
11. M. P. Esposito *et al.*, *Dioxins* (USEPA Report no. EPA-600/2-80-197, Nov. 1980).
12. W. B. Crummett, *Chemosphere* **12,** 429 (1983).
13. C. Rappe, *Environmental Sci. Technol.* **18,** 78 (1984).
14. L. M. Smith *et al. Anal. Chem.* **56,** 1830 (1984).
15. C. Rappe *et al.*, in: *Application of New Mass Spectrometry Technique in Pesticide Chemistry*, J. Rosen, ed. (J. Urley and Sons, 1985).
16. R. Boughman and M. Meselson, *Advances in Chemistry Ser. 120* (Blair 1973).
17. H. Buser and C. Rappe, *Anal. Chem.* **56,** 442 (1984).
18. Mazer *et al.*, *Anal. Chem.* **104** (1983).
19. D. O. Duebelbeis *et al.*, *Proceedings of Dioxin '87.*
20. J. R. Donnelly *et al.*, *Chlorinated Dioxins and Dibenzofurans in Perspective* (Rappe, Choudhary and Keith, 1986), pp. 381–398.
21. J. R. Chapman, *Practical Organic Mass Spectrometry* (J. Wiley & Sons, 1985).
22. Y. Tondeur *et al.*, *Biomed. Environ. Mass Spectrom.* **14,** 449 (1987).