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RAPID ANALYSIS OF CHLORINATED DIOXINS IN COMPLEX ORGANIC MIXTURES BY APPLICATION OF A GAS CHROMATOGRAPHY–MASS SPECTOMETRY–CALCULATOR SYSTEM WITH USER-DEVELOPED SOFTWARE

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SUMMARY

A procedure for the rapid analysis of chlorinated dioxins in incinerator fly ash samples by gas chromatography–mass spectrometry (GC–MS) is presented. After Soxhlet extraction of the fly ash with benzene and a 2000-fold sample concentration, the extracted sample is analyzed by GC–MS without further sample treatment. Development of software has permitted ion abundance data to be stored on a single floppy disk for later generation of the total ion abundance plot and as many as six mass chromatograms, in addition to the mass spectra of eluting components. Qualitative and quantitative data for various polychlorinated dibenzo-*p*-dioxins (PCDD) can be obtained from a single GC–MS run. By comparison with the peak height of a 1,2,3,4-tetrachlorodibenzo-*p*-dioxin standard, concentrations of various PCDD isomers were obtained for two different fly ash samples. Estimated sensitivity is 230 pg for the tetrachlorodibenzo-*p*-dioxins.

INTRODUCTION

Many analytical methods concerned with the analysis of toxic organic compounds found in the environment have been reported[1–4]. For such applications, the primary analytical tools employed are gas chromatography (GC) and GC–mass spectrometry (MS). Unfortunately, many of the methods reported involve lengthy extraction procedures followed by complicated sample clean-up steps before GC and GC–MS analyses are carried out. The GC–MS instrumentation is usually a large and expensive computerized system.

Recently, a rapid analytical procedure was reported for the analysis of complex

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organic mixtures associated with atmospheric aerosols which eliminated the sample clean-up steps before analysis and used a relatively simple GC–MS–calculator system[5]. This technique has been applied to the analysis of the organic material extracted from fly ash samples collected from municipal incinerators[6]. Among the many compounds detected were various polychlorinated dibenzo-*p*-dioxin (PCDD) isomers. A modification of this procedure combined with special computer programs specifically for the rapid quantitative analysis of separated PCDD isomers extracted from fly ash samples is presented here.

The procedure consists of Soxhlet extraction of the fly ash with benzene followed by a 2000-fold sample concentration. The condensate is analyzed by GC–MS employing a highly efficient chromatographic packing without further sample treatment. An important aspect of this method is the development of software to control the operation of a GC–MS–calculator system which enabled both qualitative and quantitative analysis of the tetra- (TCDD), penta-, hexa-, hepta- and octachlorodibenzo-*p*-dioxin (OCDD) isomers to be obtained from a single GC–MS run[7]. Analysis can be accomplished even for samples in which dioxin concentrations are very low compared to concentrations of other compounds which co-elute with the various dioxin isomers.

EXPERIMENTAL

Sample collection and storage

Fly ash samples were obtained from a municipal incinerator located in Southern Ontario. Kilogram quantities of grab samples from an electrostatic precipitator were supplied by Dr. A. Foldes of the Ontario Ministry of the Environment. Replicate samples were shipped and stored at ambient temperature in glass containers with metal screw-caps. Drying of the samples before extraction was not necessary.

Sample preparation

Approximately 20-g samples were weighed and placed into medium porosity glass fritted extraction thimbles. Overnight extractions (*ca.* 16 h) were performed in a Soxhlet extraction apparatus using 200 ml of benzene ("distilled-in-glass" grade, Caledon Labs., Georgetown, Canada). Each sample was extracted in replicate, as well as a procedure blank conducted using the assembled Soxhlet apparatus with 200 ml of benzene solvent and without a sample. The sample extract was condensed to about 0.3 ml by rotary evaporation under aspirator vacuum. The condensate was transferred with rinsing to a 1.0-ml graduated Reacti-vial (Pierce, Rockford, Ill., U.S.A.) equipped with screw-cap and PTFE liner. A final volume of 100 μl was achieved by passing a gentle stream of high purity nitrogen (Linde, 99.995%) over the top of the Reacti-vial. Vials were stored in a freezer at −10 to −15°. All glassware was cleaned in an ultrasonic bath containing a 2% aqueous solution of Alconox detergent for 30 min, rinsing with deionized water, then heating in a laboratory oven for 1 h at 300°.

Analysis by GC–MS

A Hewlett-Packard 5992A GC–MS–calculator system equipped with single floppy disk, *x–y* plotter and 2 m × 2 mm I.D. glass column was used for GC–MS analysis. The chromatographic column was packed with a high-performance material

called Aue packing[8]. Chromatographic conditions were: initial temperature, 90°; program rate, 4°/min; final temperature, 250° held for 15 min or less; injection port temperature, 250°; helium carrier flow, 40 ml/min. The quadrupole mass spectrometer was repetitively scanned from 500 a.m.u. to 40 a.m.u. at 330 a.m.u./sec. Mass spectra taken at the top of eluting GC peaks were saved on floppy disk, as were mass spectra taken at the lowest valley between two peaks for later background subtraction. A 1,2,3,4-TCDD standard was run to provide quantitation. The mass spectrometer operating conditions were optimized each day using the manufacturer-supplied program AUTOTUNE. A silicone rubber membrane separator was employed as the GC–MS interface.

Generation of mass chromatograms

The manufacturer supplied GC–MS software did not permit storage of mass chromatogram and total ion current (TIC) data as well as the mass spectra. To conduct these analyses it was necessary to create a program, called Dual-Mode, capable of storing mass spectra, TIC ion data and mass chromatogram ion data in real-time on a single floppy disk[7]. Ion abundances for as many as six ions are extracted from each mass scan, stored on floppy disk and plotted later as mass chromatograms. This differs from the selected ion monitoring (SIM) technique, in which the mass spectrometer is consecutively tuned only to each of the ions selected by the user. Although the SIM technique offers greater sensitivity, no mass spectra can be generated. A separate program was written to plot results on the *x–y* plotter after completion of the run. Details of this software are available from the authors.

RESULTS AND DISCUSSION

By proper choice of the ions to be monitored, the technique of mass chromatography can be used to selectively detect specific compounds or compound classes. For this study, mass chromatograms were generated by Dual-Mode for the characteristic ions at *m/e* 321.9, 355.9, 389.8, 425.8 and 459.7; which permit detection of groups of isomers of the tetra-, penta-, hexa-, hepta- and octachlorodibenzo-*p*-dioxins, respectively.

Fig. 1 shows the TIC for the analysis of a fly ash sample along with the associated mass chromatograms for various chlorinated dioxin isomers. A procedure blank which was run immediately prior to this sample gave straight line plots for the mass chromatograms of the dioxin isomers, indicating that no detectable background compounds were present which possessed interfering ions for this analysis.

The five groups of peaks seen in the mass chromatogram plots of Fig. 1 increase in retention time by fairly constant increments from the *m/e* 321.9 ion, which is characteristic of TCDD, to the *m/e* 459.7 ion, which is characteristic of OCDD. This retention behavior is consistent with a series of compounds having similar structures but differing in one chlorine atom from one group of isomers to the next. Also it is important to note that only two distinct peaks are observed for *m/e* 425.8 ion, characteristic of heptachlorodibenzo-*p*-dioxins, which have only two isomers; and one peak is observed for *m/e* 459.7 ion characteristic of OCDD which has no isomers. The retention time of the 1,2,3,4-TCDD standard coincided with the retention time observed for a sample peak of 22.5 min detected in the mass chromatogram of the *m/e*

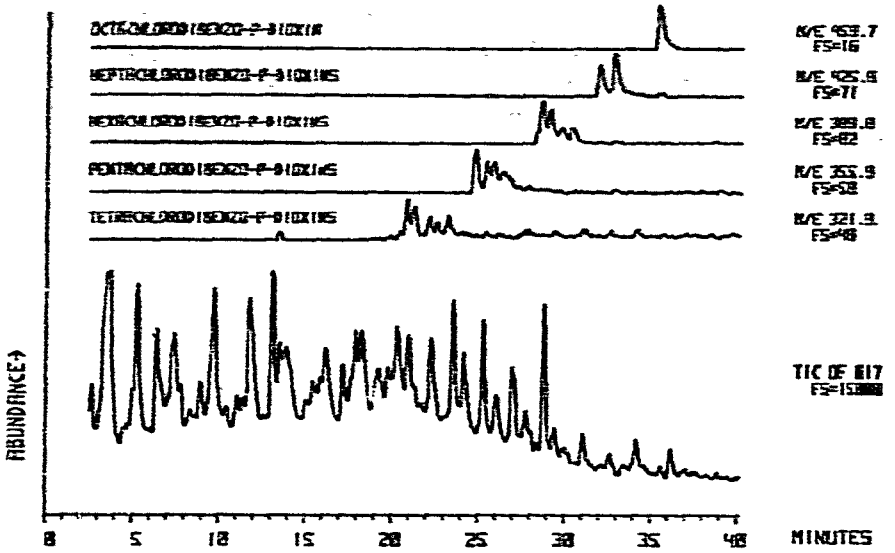

Fig. 1. Plot of TIC and five mass chromatograms from a Dual-Mode analysis of a fly ash sample. Injection volume was 3.1 μl. The mass chromatograms are identified by a particular *m/e* value which corresponds to one set of PCDD isomers.

321.9 ion, characteristic of TCDD isomers. This is shown in Fig. 2, which is a comparison plot of the 1,2,3,4-TCDD standard and the mass chromatogram from Fig. 1 of the *m/e* 321.9 ion.

Fig. 1 shows that the various chlorinated dioxin isomers can be detected even in the presence of large amounts of other compounds which elute at the same or similar retention times. PCDD concentrations are low compared to many of the other

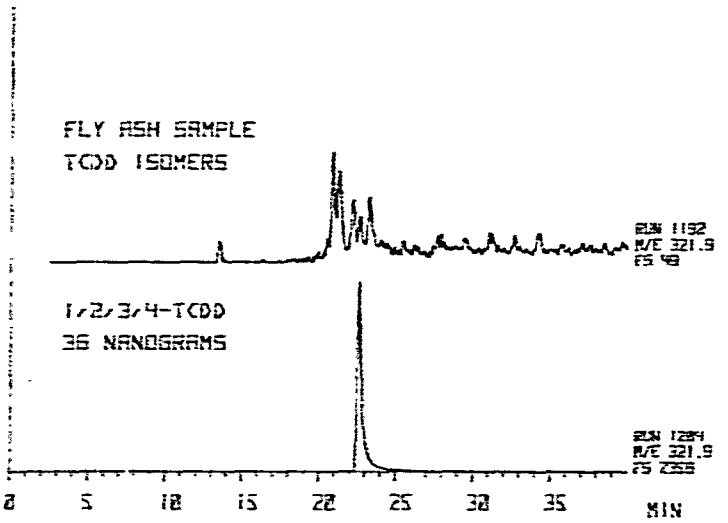

Fig. 2. Comparison between the mass chromatograms for *m/e* 321.9 from Fig. 1 and from a 1,2,3,4-TCDD standard run under identical conditions.

components shown in the TIC, however they are easily detected, since the ions which were chosen for the generation of mass chromatograms are free of interferences for this sample. The resolution observed for the isomers, in particular for isomers of TCDD, demonstrates the separation performance of the chromatographic column employed.

Fig. 3 presents the TIC and mass chromatograms of the dioxins for a second fly ash sample. Even though the total organic compounds detected are at very low levels compared to those in Fig. 1, it is still possible to detect selectively the various PCDD isomers. The relative patterns of the various isomers are almost identical to the patterns seen in Fig. 1.

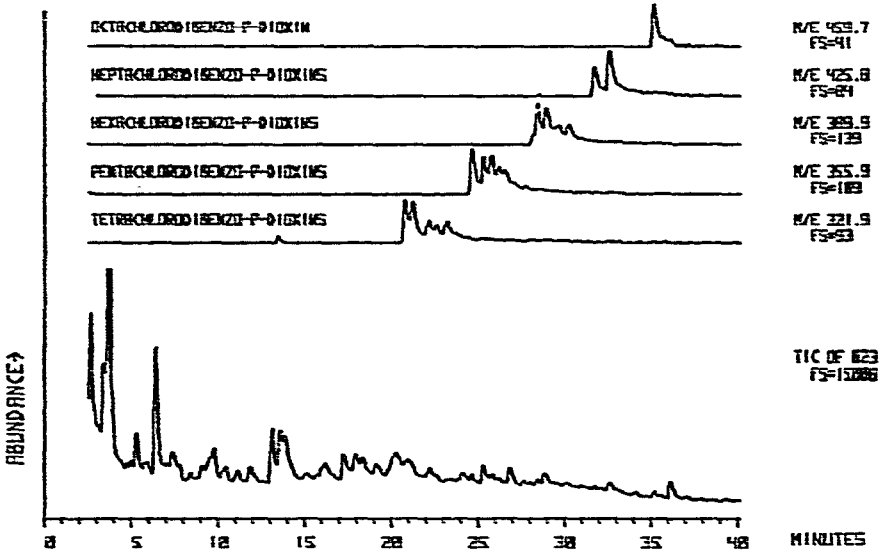

Fig. 3. Plot of TIC and five mass chromatograms for a second fly ash sample. Injection volume was 1.2 μl. Various PCDD isomers are detected even though the total organic loading is much less than for the sample shown in Fig. 1.

Relative concentrations of PCDD may be determined by comparing the full-scale abundance values produced during the Dual-Mode run. By comparing these values given in Fig. 1, it is observed that the hexachlorinated isomers are of greater abundance than the other PCDD isomers for this sample, followed by the hepta-, penta-, tetra- and octachlorinated species. In Fig. 3 a different pattern of concentrations is observed as the hexachlorinated species are the most abundant, followed by the penta-, tetra-, hepta- and octachlorinated dioxins. Each set of PCDD isomers is of greater abundance for the sample shown in Fig. 3 than for the sample in Fig. 1.

By comparing peak heights from Figs. 1 and 3 to that of the 1,2,3,4-TCDD standard (Fig. 2), quantitation of the various PCDD isomers was calculated assuming the same response factor for all isomers. These estimates are presented in Table I.

Since there may exist other compounds which possess ions in their mass spectra having *m/e* values that correspond to the *m/e* values chosen as indicating the presence of the various PCDD compounds, it is necessary to have the complete mass spectrum

TABLE I

ESTIMATED CONCENTRATIONS OF PCDD ISOMERIC GROUPS IN FLY ASH SAMPLES

Based on peak height comparison of individual PCDD peaks from the mass chromatograms of Figs. 1 and 3 with the 1,2,3,4-TCDD standard in Fig. 2 run under the same conditions. A relative response factor of 1 is assumed for all isomers.

Isomeric group	*Total concentration of isomer groups (ng/g)*	
	Sample 1 (Fig. 1)	*Sample 2 (Fig. 3)*
Tetrachlorinated dioxins	4.2	19
Pentachlorinated dioxins	4.9	27
Hexachlorinated dioxins	5.1	24
Heptachlorinated dioxins	3.2	8.8
Octachlorodibenzo-*p*-dioxin	0.42	2.7

of each compound for positive identification. The advantage of the Dual-Mode run over the more sensitive SIM technique is that mass spectra of the detected components can be retrieved from disk and compared to mass spectra of standard compounds. Specific identification of individual isomers can then be made by matching retention times as in Fig. 2.

Fig. 4 shows the mass spectra of five PCDD compounds ranging from the tetrachlorinated to the octachlorinated species which were all obtained during a single

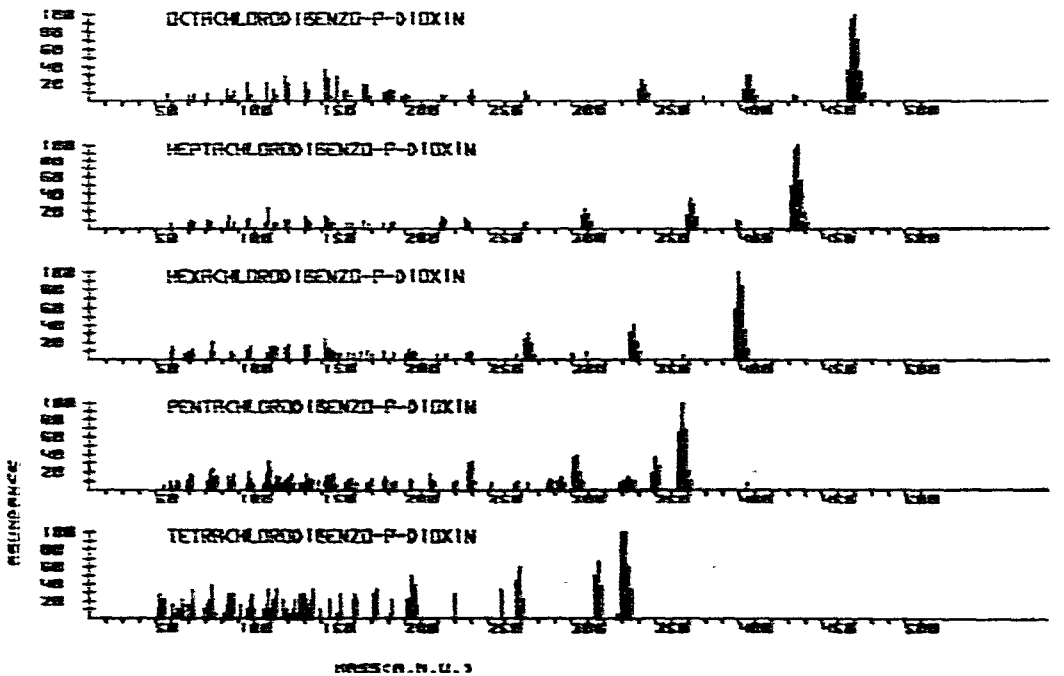

Fig. 4. Mass spectra of tetra-, penta-, hexa- and octachlorinated dibenzo-*p*-dioxins obtained from a single Dual-Mode run of a fly ash sample.

Dual-Mode run of a fly ash sample. The TCDD spectrum was obtained from a very low abundance peak, however the characteristic isotope pattern is still observable. Isotope ratios are not ideal due to the low abundance of the TCDD peak.

Limits of detection can be obtained from data given in Fig. 2. By choosing a noise threshold of 15 counts (full scale), the standard run corresponds to a detection limit of 230 picograms for 1,2,3,4-TCDD. The choice of 15 counts full scale as a noise limit is based on the background response seen in Fig. 2 beginning at a retention time of about 25 min. Lower detection limits can be obtained for some of the other PCDD isomers which have lower levels of background contamination.

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