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DISTRIBUTION OF ORGANIC COMPOUNDS ADSORBED ON SIZE-FRACTIONATED MUNICIPAL INCINERATOR FLY-ASH PARTICLES

R. E. CLEMENT and F. W. KARASEK*

Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1 (Canada)

SUMMARY

Two different samples of fly-ash have been separated into different size fractions by manual sieving using standard screens. Both samples showed the same trends of relative distribution of organic compounds on fractions. Average particle sizes for the various fractions were: 30 μm, 80 μm, 125 μm, 200 μm, 550 μm and particles > 850 μm. Each fraction was extracted with benzene by ultrasonic agitation, and the concentrated extracts analyzed by gas chromatography and gas chromatography–mass spectrometry for total organic compounds, *n*-alkanes, phthalates, selected polynuclear aromatic hydrocarbons and polychlorinated dibenzo-*p*-dioxins. The largest concentrations of tetra- and pentachlorodibenzo-*p*-dioxins occurred on the larger (550 μm) particles while the 30-μm particles had greater relative concentrations of octachlorodibenzo-*p*-dioxin. The largest (> 850 μm) sized fraction consisted of two distinctly different types of particles. One of these types was light, black-ash particles such as are obtained from the combustion of newsprint. These light ash particles had high concentrations of total organic compounds and tetrachlorinated dioxins, relative to the other size fractions. Printed words could still be discerned on some of these ash particles, indicating that these particles escaped complete combustion.

INTRODUCTION

The disposal of municipal refuse by incineration is widely practised. Since it is possible to generate large amounts of usable energy from the incineration process, its use and importance will increase. However, it has been shown that the electrostatically precipitated fly-ash residue formed during incineration contains hazardous organic compounds such as the polynuclear aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-*p*-dioxins (PCCDs)[1–4]. The high toxicity of the PCDDs has prompted interest in analysis of the organic compounds found in incinerator fly-ash at trace levels. Of particular interest is the distribution of various compounds on different particle size fractions, since particles of less than 3-μm diameter are respirable by humans and therefore present a special health hazard. In addition it has

been reported that the fly-ash particles contained in the stack gases contain about ten times the PCDD concentration of the precipitated fly-ash[5,6]. It has been proposed that these particles are the smaller ones with higher surface area to account for this observation. No data are available on their size distrubiton.

Work on the size distribution of pollutants on fly-ash has been for the determination of various trace and ultra-trace elements in fly-ash sampled from coal-burning steam plants[7-10]. Recent work on atmospheric particulate matter has shown that the highest concentrations of PAHs are found on the respirable size fraction of the collected particulate matter[11-14]. One study has reported similar results for PAHs on different size fractions of particulate matter from a coke oven emission source[15].

These previous studies examined particles that were collected and fractionated by cascade impactor devices. None of the studies has investigated bulk samples that contain a broad range of particle sizes, from the respirable size fraction to those in excess of 800 μm diameter. Knowledge of the size distribution of the bulk fly-ash will be helpful in the study of the routes of distribution into the environment of organics sorbed onto these particles. In particular, we wanted to develop data that would indicate the relative concentration of PCDDs on large *versus* small particles to test the hypothesis that small particles contain greater concentrations of organics. In this study a large fly-ash sample is separated into different size fractions by hand-sieving. Organic compounds are extracted by benzene using ultrasonic agitation and the extracts analyzed for organic compounds, including selected PAHs and the various PCDD isomers, by gas chromatography (GC) and combined GC–mass spectrometry (MS).

EXPERIMENTAL

Sample collection and storage

A large (324 g) grab-sample of fly-ash was taken from a southern Ontario municipal incinerator by Ontario Ministry of Environment personnel. The incinerator operating temperature was *ca.* 900°C and electrostatic precipitation was used. The sample was stored in a plastic bag in the dark at room temperature. After extraction, sample extracts were stored in a freezer at *ca.* −15°C. A second sample was obtained by compositing two smaller samples collected from the same incinerator on different days.

Fractionation of fly-ash

Six size fractions of fly-ash were obtained by using five Tyler sieves (W.S. Tyler, St. Catherines, Canada). The brass sieves had metal screens with openings of 850 μm, 250 μm, 150 μm, 106 μm and 63 μm. All sieves, including the top and bottom collector, were cleaned by ultrasnonic agitation with an aqueous solution of Alconox detergent for *ca.* 15 min. This was followed by rinsing with tap water, deionized water and methanol, and then air drying. Hand-sieving was performed and all fractions were stored in polypropylene containers equipped with polypropylene screw-caps that had first been rinsed with small portions of benzene, then air-dried. After sieving of the fly-ash, it was observed that the largest particle fraction (> 850 μm) consisted of two distinctly different types of particles. These two components of the large size fraction were partially separated by hand and were analyzed individually. Hand

separation of these larger particles was difficult and incomplete. However, each portion is estimated to have no more than 10% contamination from the other. One component of this fraction consisted of light, black ash particles. The other component was large agglomerate particles.

Sample extraction and concentration

In a previous study, fly-ash samples were extracted overnight by Soxhlet extraction apparatus[4]. However, fine particle fractions do not allow free solvent flow through the extraction thimble, therefore all extractions were performed using ultrasonic agitation[19]. Samples (10 g) were added to individual flasks with 100 ml of benzene and agitated in an ultrasonic bath for 1 h. Enough water was added to the bath to cover the portion of the flask that contained the fly-ash and benzene. The glass stoppers that were used to cap flasks during the extraction were occasionally loosened to prevent excessive pressure from developing. After 1 h of agitation, the fly ash was allowed to settle and the benzene was decanted into fresh flasks through porous glass frits. This procedure was repeated twice more, for 30 min each time, with 100 ml of fresh benzene added each time. After the third extraction cycle, the fly-ash was transferred to the glass frit and rinsed three times with 10-ml portions of fresh benzene. During each of the three extraction cycles, the water bath temperature increased from ca. 30 to 50°C.

The benzene from the three extraction cycles and rinsings was condensed to 2–3 ml by rotary evaporation under aspirator vacuum. This extract was transferred with three benzene rinsings to a 10-ml pear-shaped flask. After rotary evaporation to between 50 and 100 μl, concentrated extracts were transferred with three rinsings to a 1.0-ml reacti-vial equipped with screw-cap and PTFE liner. A final volume of 100 μl was achieved by blowing a stream of helium gas across the top of the vial. All glassware, including reacti-vials and transfer pipets, was cleaned by ultrasonic agitation for 30 min with Alconox detergent. After thorough rinsing with tap water and deionized water, the glassware was then placed in an oven at 300°C for a least 1 h. All equipment was allowed to cool to ambient temperature before use. Solvents were "distilled-in-glass" grade (Caledon Labs., Georgetown, Canada). Benzene solvent (300 ml) was carried through the entire process as a procedure blank.

Gas chromatographic analysis

A Hewlett-Packard 5830 GC with flame ionization detector (FID) was equipped with a 6 ft. × 2 mm I.D. glass column, packed with Aue packing[16]. A temperature program of 90°C initial temperature to 250°C final temperature at 4°C/min was employed for all sample extracts. Injection temperature was 250°C, detector temperature 275°C, and the helium carrier gas flow-rate 37 ml/min, measured at 90°C. A slope sensitivity of 0.1 mV/min was used for peak detection.

For calculation of retention index, a normal hydrocarbon standard mixture was analyzed periodically. Peak areas and retention times were punched onto computer cards, and retention indices were calculated by the Fortran program RICALC[17]. These retention index and peak area values were displayed as bar-graph plots using a Calcomp plotter by the program GCPLOT[17].

GC–MS analysis

Normal hydrocarbons, phthalate esters, selected PAHs and various PCDD isomers were analyzed by a Hewlett-Packard 5992 GC–MS–Calculator using the selected ion monitoring (SIM) technique. In this mode of operation. the quadrupole mass spectrometer was selectively tuned to each of six pre-selected ions for 166 msec dwell time on each ion. The ions monitored for the tetra- through octachlorinated dibenzo-*p*-dioxins were 321.9. 355.9. 389.8, and 459.7. respectively. Chromatographic conditions were as described previously. A 1,2,3,4-tetrachlorodibenzo-*p*-dioxin standard (1.2.3.4-TCDD) was used to quantitate the various tetrachlorinated dioxin isomers, assuming a relative response factor of unity. An octachlorodibenzo-*p*-dioxin (OCDD) standard was used to quantitate this compound. A third standard consisting of selected *n*-hydrocarbons. phthalates and PAHs was also analyzed for the quantitation of these compounds. The PAHs in this standard were biphenyl. fluorene. fluoranthene and benzo[*a*]pyrene.

The GC–MS system was also operated in the scanning mode employing user-developed software[18]. Spectra were scanned from 500 to 40 a.m.u. at 330 a.m.u./sec. A high mass peak threshold was used so that low-level background peaks would be rejected. Spectra taken at the lowest point of the valleys between consecutive peaks were saved for later background subtraction.

RESULTS AND DISCUSSION

Gas chromatographic results

Two samples of fly-ash from the same incinerator but taken on different days were size-fractionated and the organic compounds extracted as described in the Experimental section. The ranges of particle sizes for the different fractions. together with the percentage of total sample weight contained in each fraction, are presented in Table I. Relative concentrations of organic compounds were estimated from GC–FID data. The two fractionated fly-ash samples are referred to as sample A or B. Sample A is the single large sample and sample B is a composite of two smaller

TABLE I

FLY-ASH FRACTIONS OBTAINED BY MANUAL SIEVING

Particle size range μm	Average particle size (μm	Percentage of total sample weight		Relative concentration of organic compounds	
		A	B	A	B
<63	30	37.5	42.7	100	14
63 106	80	26.9	16.8	66	2
106 150	125	9.5	11.9	24	5
150 250	200	8.2	11.5	24	4
250 850	550	14.3	12.1	57	35
Light ash (>850)	—	1.6	2.0	78	100
Agglomerate particles (>850)	—	2.1	3.0	3	17

samples. For both A and B, *ca.* 60% of the total sample weight consisted of particles smaller than 106 μm. Fig. 1 is a photographic display of the various sized fractions from sample A. For comparison, a sample of fly-ash before size fractionation and a sample of bottom ash from the incinerator furnace grates are also shown. Bottom ash is the residue that remains at the bottom of the furnace grates and is only indirectly related to particles collected by the electrostatic precipitator. The clear lumps of material in the bottom ash are pieces of glass.
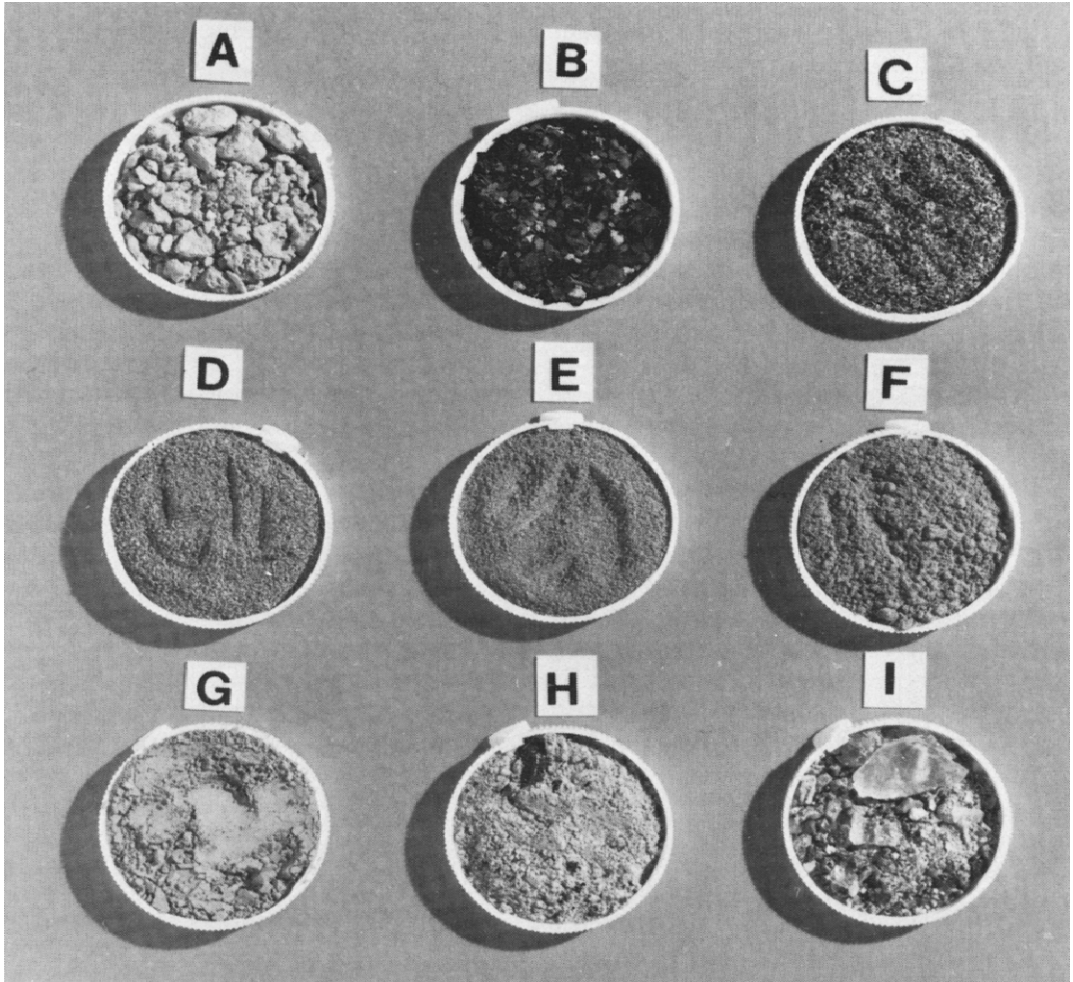

Fig. 1. Size fractions obtained from manual sieving of Ontario fly-ash. A, Agglomerate particles >850 μm; B, black ash >850 μm; C, 550 μm particles; D, 200 μm particles; E, 125 μm particles; F, 80 μm particles; G, 30 μm particles; H, original fly-ash; I, residue from bottom of furnace grates (not from electrostatic precipitator).

In the separated fly-ash fractions of sample A, the large, light, black ash particles have the appearance of the ash formed from the combustion of newsprint. Printed words could still be observed on some of these light ash particles, which indicates that they have spent most of their residence time in the cool parts of the

combustion process. The other large particle fraction (agglomerates) consisted of roughly spherical agglomerate particles, which were much heavier than the light ash particles. These could easily be broken into smaller particles, However, this was not done until just prior to extraction.

GC–FID results obtained for the various size fractions of sample A are displayed by the program GCPLOT in Fig. 2. Peak areas were corrected for extraction weights and injection volumes before plotting. Results for the largest size fraction were not included in this plot since particle size boundaries for this fraction are not defined. For convenience, each size fraction other than the largest (particles > 850 μm) is referred to by its average particle size, which is estimated as the approximate
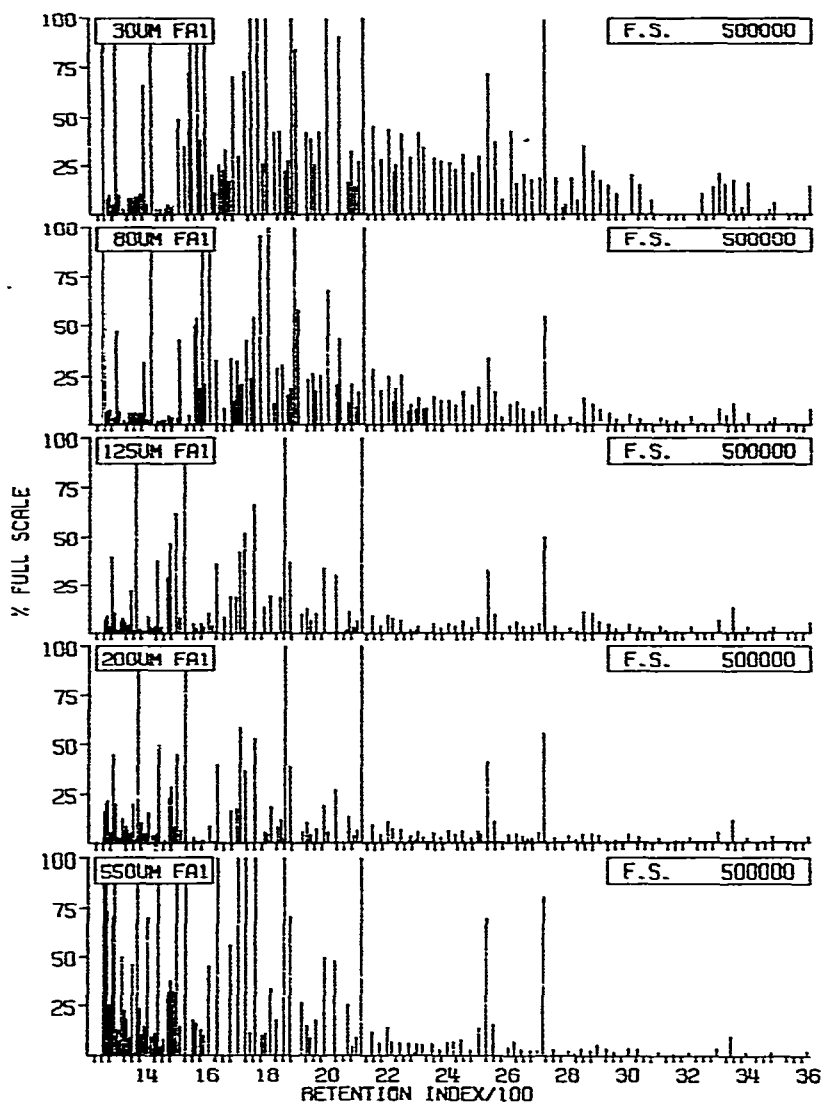

Fig. 2. Comparison of GC–FID data of size fraction extract condensates.

middle value between boundary screen sizes. In the largest size fraction the black ash particles have a high concentration of total organic compounds relative to the other size fractions for both samples. In Fig. 2 it can be seen that many of the major peaks are common to all of the fractions, although large concentration differences are evident GC data primarily show that large differences in the concentrations of individual components and total amount of organic compounds exist between the fractions of different particle size.

GC–MS analysis

The major components of the various extracts of different size fractions identified by GC–MS analysis for both samples are *n*-alkanes, phthalates, and chlorinated benzenes; many other compounds were present, but at relatively low concentrations. However, no differences were observed in the types of compound that were detected in the various size fractions.

Results of SIM analysis of extracts of the various size fractions for phthalates, *n*-hydrocarbons, and selected PAHs are given in Table II for sample A. These analyses were not performed for sample B. Dibutyl phthalate was the largest single component in all the size fractions analyzed. However, its concentration could only be estimated because the abundance of this compound was great anough to cause the mass spectrometer to go into a standby state during SIM analysis. This indicates that the concentration of dibutyl phthalate in each sample must be greater than the highest reported concentration of 3200 ng/g fly-ash for diethyl phthalate in Table II.

TABLE II

CONCENTRATIONS (ng/g) OF PHTHALATES. *n*-HYDROCARBONS AND PAHs EXTRACTED FROM DIFFERENT SIZE FRACTIONS OF SAMPLE A

	Average particle size (µm)					Light ash (>850)	Agglomerate particles (>850)	Totals (ng/g)
	30	80	125	200	550			
Diethyl phthalate	240	95	150	650	1200	3200	750	6300
Dioctyl phthalate	690	510	510	680	910	2800	330	6400
Biphenyl	43	35	33	160	240	700	55	1300
Fluorene	24	3.8	3.5	—	69	—	—	100
Anthracene*	16	4.0	2.9	2.9	—	—	—	26
fluoranthene	76	51	68	97	120	150	7.9	570
Pyrene	44	16	13	18	9.1	—	—	100
Normal alkanes	14,000	7900	5200	5400	11,000	5500	900	50,000
Totals	15,000	8600	5900	7000	14,000	12,000	2000	65,000

* Concentrations based on fluoranthene response with relative response factor of unity.

The largest concentrations of the various compounds that were determined were not always associated with the small size fraction as was expected. Comparing results for the 30–550-µm particles, it is observed that the 550-µm particles have the greatest concentration of diethyl phthalate, biphenyl, fluorene, and fluoranthene. The

30-μm particles have the largest concentration of anthracene and pyrene. Dioctyl phthalate and total n-hydrocarbons are distributed almost equally among all size fractions. There is some evidence in Table II that the smallest particles contain a greater concentration of higher-molecular-weight PAHs, while the large particles have a greater concentration of the low molecular weight PAHs.

Table III gives for the different size fractions the concentrations of various PCDDs determined by GC–MS–SIM. The first sample (A) presented in Table III is the same one for which earlier reported PAH results apply. Concentrations are reported in terms of nanograms per gram of each particular size fraction. To obtain the amount of PCDDs that would be obtained in a gram of non-size-fractionated fly-ash, each value in Table III must be multiplied by the appropriate weight fraction. Only the 1,2,3,4-TCDD and OCDD standards were available during this study. Values for the penta-, hexa-, and heptachlorinated dioxins were based on the response for 1,2,3,4-TCDD, with a relative response factor of unity. Although the actual response factors of these other dioxins were not measured, the relative amounts in the different size fractions of a particular group of isomers are as represented in Table III. No clear trend is apparent in the concentrations of penta- and hexachlorinated dioxins with respect to particle size, except that the 200-μm and 550-μm particles have about three times more of these dioxins than do the smaller particles (30-μm and 80-μm fractions). Heptachlorinated dioxins concentrations are more nearly uniform throughout all size fractions.

TABLE III

DIOXIN ISOMER DISTRIBUTION IN FLY-ASH SIZE FRACTIONS

Average particle size (µm)	Weight fraction	Concentration of dioxin isomers (ng/g)*					Total
		Tetra	Penta	Hexa	Hepta	Octa	
Sample A							
30	0.37	2.2	3	3	3	9.5	20
80	0.27	2.0	2	3	3	4.5	10
125	0.09	3.9	4	6	4	6.9	30
200	0.08	7.0	8	10	6	8.2	40
550	0.14	12	10	8	3	3.1	40
>850 (light ash)	0.02	8.4	5	2	0.3	0.2	20
>850	0.02	2.0	2	2	2	8.2	20
Sample B							
30	0.43	2.9	3	3	2	5.0	20
80	0.17	4.3	5	4	1	2.9	20
125	0.12	7.5	9	6	2	4.8	30
200	0.11	8.2	8	5	1	2.0	20
550	0.12	15	10	4	1	0.7	30
>850 (light ash)	0.02	7.3	4	1	0.1	0.2	10
>850 (agglomerate particles)	0.03	4.3	6	5	3	11	30

* Concentrations of penta-, hexa-, and heptachlorinated dibenzo-p-dioxins are based on 1,2,3,4-TCDD standard with relative response factor of unity.

Fig. 3 shows the determined concentrations of OCDD and total TCDD with respect to each of the size fractions for both samples. For both samples, the highest concentration of TCDD was found on the larger (550 μm) particles. Conversely, a much lower TCDD concentration was found on the smallest (30 μm) size fraction. There is an almost uniform decrease in TCDD level with respect to particle size, which can be observed in Fig. 3. This trend is observed with both samples. A clear trend is not as evident in the concentration of OCDD, which was detected on each of the size fractions. However, the smallest concentration for OCDD in the well-defined size fractions was detected on the larger (550 μm) particles, while the largest concentration was in the smallest (30 μm) particles. These trends are observed for both replicate sample, though the samples were collected several months apart.
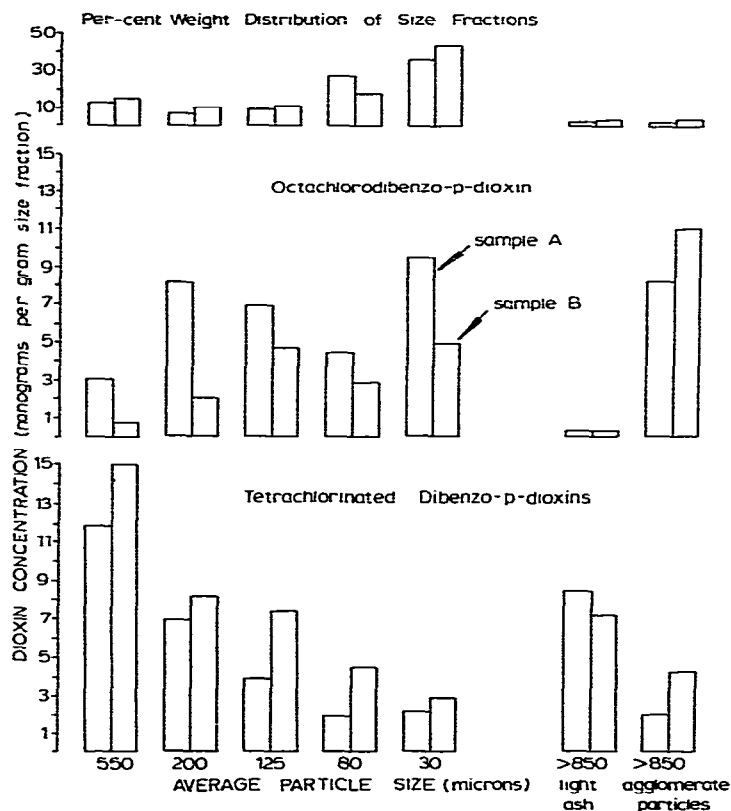

Fig. 3. Comparison of tetra- and octa chlorinated dioxin concentrations in different size fractions.

The largest (> 850 μm) particles, which were sub-divided into black ash particles and large agglomerate particles, also showed some definite trends. Very low levels of OCDD were detected on the black ash particles. However, large concentrations of OCDD were found on the large agglomerate particles, relative to the other size fractions. By contrast, the TCDD concentrations were greater in the ash particles than the agglomerate particles. Both samples studied showed the same trends. The black ash particles were the type of ash residue that remains after combustion of

books and newsprint. Because printed words could still be observed on some of these particles, a definite fraction of the fly-ash consists of particles that have escaped complete combustion. However, as can be seen from Fig. 3, the light ash particles represent a very low proportion by weight of the total fly-ash sample.

It has been reported by Stalling and co-workers[20,21] that recovery of 2,3,7,8-TCDD adsorbed on granular charcoal surfaces is difficult. The carbonaceous surfaces of the light ash particles analyzed in this study are not granular in nature as were the particles in Stalling's work. The ash particles were thin flakes having smooth surfaces; thus extraction of organics from these particles is more efficient than for extraction of organics from irregular granular particles with larger surface areas. Also, an exhaustive ultrasonic extraction was performed using three portions of fresh benzene for a total extraction time of 2 h. Furthermore, the 550-μm particles contained a much larger proportion of the light ash particles than did the 30-μm particles, yet the concentration of total TCDD was much greater for the larger particles than for the smaller particles. Extraction efficiencies for TCDD and OCDD should not vary greatly for different size fractions under the extraction methods employed in this study. Therefore, the very large concentration difference between total TCDD and OCDD on the light ash particles compared with the much smaller differences observed for any of the other fractions indicates that the ash particles were those that experienced very different incinerator conditions from the remainder of the fly-ash particles. This may also explain why the concentration of TCDD is much greater than that of OCDD on the 550-μm particles, since this fraction contained a larger proportion of the light ash than the other size fractions.

Although both samples that were size-fractionated showed the same trends with respect to the relative distributions of organic compounds, the validity of the results was checked further by re-analyzing the extracts of the size fractions of sample
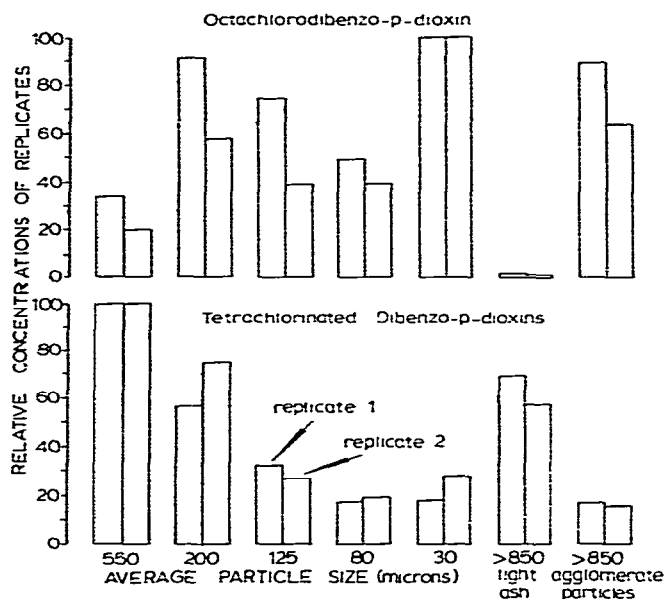

Fig. 4. Results of duplicate determinations of TCDD and OCDD.

A for PCDD by GC–MS, using the same conditions as reported previously. Fig. 4 shows the results of duplicate determinations of each size fraction of sample A for total TCDD and OCDD. Results are normalized to the largest concentration = 100 % for TCDD and OCDD. Relative concentrations of TCDD and OCDD for the different size fractions are the same for duplicate determinations, although variations in the results for OCDD are larger than results for TCDD. The possibility of a trend towards enrichment of some compounds on the larger particles does not contradict findings of studies that show a higher concentration of organics on the respirable (< 10 μm) particles, since it is not known in this study what proportion of such particles are present in the 30-μm fraction. Also, other studies have not reported distributions of organics in the very large particles that were examined here. Although the finding of PCDDs in municipal incinerator fly-ash has now been well documented, the results of this study show that there is still much work to be performed in the analysis of this material and in correlating results to incinerator operating conditions.

REFERENCES

1 K. Olie, P. L. Vermeulen and O. Hutzinger, *Chemosphere*, 8 (1977) 455.
2 H. R. Buser, H. P. Bosshardt and C. Rappe, *Chemosphere*, 9 (1978) 165.
3 M. D. Erickson and E. D. Pellizzari, *Bull. Environ. Contam. Toxicol.*, 22 (1979) 688.
4 G. A. Eiceman, R. E. Clement and F. W. Karasek, *Anal. Chem.*, 51 (1979) 2343.
5 O. Hutzinger, in R. Bekher, M. Grasserbauer and H. Malissa (Editors), personal communication.
6 R. Liberti, *Nature, Aim and Methods of Microchemistry. Proceedings of the 8th International Microchemical Symposium, Graz, Austria, August 25–30, 1980*, Springer, New York, 1981.
7 J. M. Ondov, R. C. Ragaini and A. H. Biermann, *Environ Sci. Technol.* 13 (1979) 946.
8 D. G. Coles, R. C. Ragaini, J. M. Ondov, G. L. Fisher, D. Silberman and B. A. Prentice, *Environ Sci. Technol.*, 13 (1979) 455.
9 R. D. Smith, J. A. Campbell and K. K. Nielson, *Environ. Sci. Technol.* 13 (1979) 553.
10 J. A. Campbell, J. C. Laul, K. K. Nielson and R. D. Smith, *Anal. Chem.*, 50 (1978) 1032.
11 L. van Vaeck and K. van Cauwenberghe, *Atmos. Environ.*, 12 (1978) 2229.
12 L. van Vaeck, G. Broddin and K. van Cauwenberghe, *Environ. Sci. Technol.*, 13 (1979) 1494.
13 R. C. Pierce and M. Katz, *Environ. Sci. Technol.*, 9 (1975) 347.
14 A. H. Miguel and S. K. Friedlander, *Atmos. Environ.*, 12 (1978) 2407.
15 G. Broddin, L. van Vaeck and K. van Cauwenberghe, *Atmos. Environ.*, 11 (1977) 1601.
16 W. A. Aue, C. R. Hastings and S. Kapila, *J. Chromatogr.*, 77 (1973) 299.
17 R. E. Clement, *Application of Computer Techniques to the Collection and Analysis of Analytical Data, M. Sc. Thesis.*, University of Waterloo, Waterloo, 1976.
18 L. C. Dickson, R. E. Clement, K. R. Betty and F. W. Karasek, *J. Chromatogr.*, 190 (1980) 311. ·
19 G. A. Eiceman, A. C. Viau and F. W. Karasek, *Anal. Chem.*, 52 (1980) 1492.
20 J. N. Huckins, D. L. Stalling and W. A. Smith, *J. Ass. Offic. Anal. Chem.*, 61 (1978) 32.
21 D. L. Stalling, J. L. Johnson and J. N. Huckins, *Environmental Quality and Safety, Supplement. Vol. 3*, George Thieme, Stuttgart, 1975, pp. 12–18.