

Vapour Pressure Determination for Dibenzo-*p*-dioxin, Dibenzofuran, Octachlorodibenzo-*p*-dioxin and Octachlorodibenzofuran Using a Knudsen Effusion Method

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A new apparatus with Knudsen effusion method especially designed for the vapour pressure measurements of dioxin congeners and other POPs is described. Crystalline benzoic acid and anthracene were first used to test the new designed apparatus. The vapour pressure and enthalpy results of the two reference compounds were found in good agreement with accepted literature data. The vapour pressure and enthalpy results of crystalline DD, DF, OCDD and OCDF determined with the new apparatus are presented, and compared with the literature data measured with other methods.

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Keywords: vapour pressure, Knudsen effusion method, enthalpy of sublimation, entropy of sublimation, benzoic acid, anthracene, dibenzo-*p*-dioxin (DD), dibenzofuran (DF), octachlorodibenzo-*p*-dioxin (OCDD), octachlorodibenzofuran (OCDF), Polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs)

1. Introduction

Polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) are worldwide encountered toxic substances known as persistent pollutants. PCDD/Fs are mainly trace by-products of industrial processes. A variety of thermal and metallurgical processes, such as incinerators for municipal waste, metal scrap smelting, sintering plant of iron and steel industry, facilities of non-ferrous metal industry, cement kilns and power plant *etc.*, have been identified as point sources of dioxins. Due to dramatic reduced emission from waste incinerators, the other industrial processes became significant sources of PCDD/Fs. Therefore, it is essential necessary to turn attention to the dioxins emission from those processes.

Vapour pressure is an important physicochemical parameter to predict the behaviours of PCDD/Fs in the environment. It is a significant factor for predicting atmospheric concentrations and modelling incineration behaviours. However, PCDD/Fs are extremely low volatile substances, *e.g.* the vapour pressure of 2,3,7,8-TeCDD is in the range of 10^{-7} to 10^{-8} Pa at 298 K.¹⁾ It is difficult to obtain precise data for such low vapour pressure, and the values cited in the literature sometimes show a difference of 2 to 3 orders of magnitude among different researchers.^{2,3)}

A low vapour pressure can be measured by the gas saturation method, the Knudsen effusion method and the vapour pressure balance method. In fact, such measurements are rare for PCDD/Fs, because of the low volatility, high toxicity and cost. Rordorf, however, has measured some PCDD/Fs vapour pressures by the gas saturation method.⁴⁻⁷⁾

Knudsen effusion method is one of the most accurate techniques for measuring the vapour pressure of a low-volatility substance, and has long been employed for this. There are numerous references using this method, and many researchers have used it to determine the low vapour pressures of organic compounds,⁸⁻¹¹⁾ although it has still not been applied

for PCDD/Fs.

To obtain precise vapour pressure data and assess the available information, the present study employed the Knudsen effusion method to determine the vapour pressures and enthalpies of sublimation of dibenzo-*p*-dioxin (DD), dibenzofuran (DF), octachlorodibenzo-*p*-dioxin (OCDD) and octachlorodibenzofuran (OCDF).

2. Experimental

2.1 Samples

Benzoic acid (Aldrich Chem. Co., mass fraction 0.99+) and anthracene (Aldrich Chem. Co., mass fraction 0.99+) were used as reference compounds to test the apparatus. Samples of the four PCDD/Fs used for this study were dibenzo-*p*-dioxin (DD) (Wako Pure Chemical Industries, Ltd., mass fraction 0.97), dibenzofuran (DF) (Wako, mass fraction 0.98), octachlorodibenzo-*p*-dioxin (OCDD) (Radian Corporation, mass fraction 0.99), and octachlorodibenzofuran (OCDF) (Radian, mass fraction 0.98). All the samples are crystalline solid.

2.2 Apparatus and procedure

The vapour pressures were measured by Knudsen effusion method using the apparatus shown in Fig. 1. The apparatus is especially designed for vapour pressure measurements of dioxin congeners and other persistent organic pollutants (POPs). Due to high toxicity and high cost, the sample amount used in each experiment has to be as small as possible, so that size of Knudsen effusion cell should also be as small as feasible.

The sample container known as a Knudsen cell is shown in Fig. 2 in detail. Vapour effusion through the small orifice at the lid of the cell gives a molecular beam that spreads out in an evacuated space.

Knudsen effusion cells, made of aluminium, are 4.4 mm in internal diameter (*D*), 4.6 mm in depth (*H*) and 0.1 mm in

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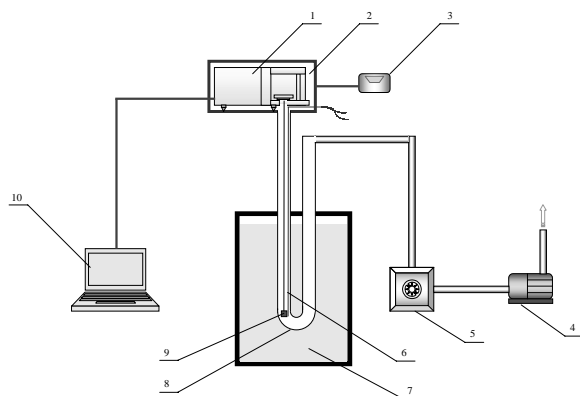


Fig. 1 Apparatus schematic for vapour pressure measurement. 1. METTLER TOLEDO MX5 Microbalance, 2. High Vacuum Chamber, 3. ULVAC Ionisation Vacuum Gauge Control, 4. Rotary Pump, 5. Turbo Molecular Pump, 6. Platinum Resistance Thermometer, 7. THERMO OH-16 Oil Bath, TAITEC Co., Ltd., 8. U-Pyrex Tube, 9. Knudsen Effusion Cell, 10. Data System.

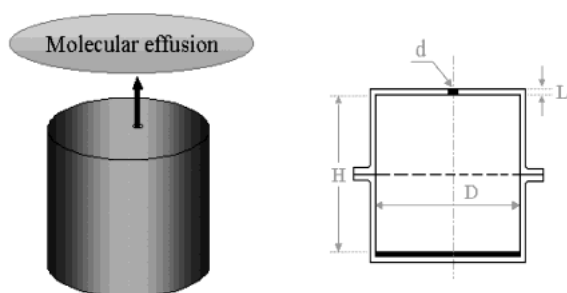


Fig. 2 Scheme of Knudsen effusion cell.

wall thickness (L). There is an effusion hole coaxially located at the lid of the cell. Four types of orifice diameter (d) were used in the trial: (0.05, 0.10, 0.15, and 0.20) mm.

The sample was first ground into powder, and then charged and compressed in a thin layer on the bottom of the effusion cell, so as to get a flat surface and good heat transfer. After charging the sample, the Knudsen cell (9 in Fig. 1) was hermetically sealed by a special presser, and was hung on the hook of a calibrated microbalance 1 (METTLER TOLEDO MX5 Microbalance) by a long chain at the centre of the Pyrex tube 8. The Pyrex tube 8 is 600 mm long and has an internal diameter of 14 mm. Precision of the calibrated microbalance 1 is one microgram. A high vacuum (less than 10^{-2} Pa) of the system was established by a rotary pump 4 (DUO 2.5A, Balzers) and a turbo molecular pump 5 (TCP Balzers). Mass loss of the samples was continuously collected by the data system 10 on line, and an ionisation vacuum gauge 3 connected to the high vacuum chamber 2 measured the vacuum of the system.

The high accuracy oil bath 7 (THERMO OH-16, TAITEC Co., Ltd, Japan) can maintain a constant temperature with an accuracy of ± 0.03 K to ± 0.1 K in the temperature range of 298 to 523 K. Accuracy of the effusion cell temperature is of vital importance, so the temperature at the cell hanging position was measured by a calibrated platinum resistance thermometer 6.

2.3 Treatment of results

The measurement of the mass loss Δm (kg) of the samples in a specified period of time t (s) at a constant temperature

T (K) enables us to evaluate the vapour pressure using the effusion eq. (1).^{12,13)}

$$P_K = \{\Delta m / (A_o \cdot K_C \cdot t)\} \cdot (2 \cdot \pi \cdot R \cdot T / M)^{1/2} \quad (1)$$

where P_K (Pa) is the vapour pressure near the orifice, K_C is the Clausing factor, A_o (m^2) is the area of the orifice, M ($\text{kg} \cdot \text{mol}^{-1}$) is the molecular mass of the effusing vapour, and R ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) is the gas constant. Accurate K_C is cited in the literature.¹²⁾

The Knudsen cell, because of the continuous loss of vapour through the orifice, is not really an equilibrium system. The vapour pressure P_K calculated from rate of effusion may thus be less than the equilibrium pressure P_{eq} that a substance would exhibit in a completely closed system. Using different approaches, Whitman¹⁴⁾ and Motzfeldt¹⁵⁾ both arrived at the conclusion that the measured pressure P_K is related to the equilibrium vapor pressure P_{eq} by

$$P_{eq} = P_K \left[1 + \frac{K_C A_o}{A_S} \left(\frac{1}{\alpha} + \frac{1}{W'} - 2 \right) \right] \quad (2)$$

where A_S is evaporating sample area, α is vaporisation coefficient, the factor W' is the Clausing coefficient for the cell itself, and $W' = D/2H$.

For a cylindrical Knudsen cell in which height equals diameter, that is, $W' = 0.5$, the Whitman-Motzfeldt equation can be rewritten as

$$P_{eq} = P_K [1 + K_C \cdot A_o / (\alpha \cdot A_S)] \quad (3)$$

For typical Knudsen cell dimensions, A_o/A_S is less than 0.01. If $\alpha \approx 1$, $A_o/(\alpha \cdot A_S) \ll 1$, and therefore $P_{eq} \approx P_K$. The experimental error is great enough to mask the difference between P_{eq} and P_K . This study thereby employed eq. (1) to evaluate vapor pressure of samples.

The sublimation enthalpy of the sample can be obtained using the Clausius-Clapeyron eq. (4).

$$\ln p = -(\Delta_{\text{sub}} H / R) / T + \Delta_{\text{sub}} S / R \quad (4)$$

The experimental results were plotted into a natural logarithm of vapour pressure ($\ln p$) vs. $1/T$, the slope of the straight line was $\Delta_{\text{sub}} H / R$, and the intercept was $\Delta_{\text{sub}} S / R$. The enthalpy and entropy of sublimation obtained by this method referred to the mean values in the experimental temperature range.

3. Results and Discussion

This study employed benzoic acid and anthracene to test the performance of the apparatus described above. Both ben-

Table 1 Vapour pressure results of benzoic acid and anthracene.

Benzoic acid		Anthracene	
T/K	p/Pa	T/K	p/Pa
299.15	0.13	348.15	0.29
303.25	0.22	353.15	0.49
308.15	0.38	358.15	0.81
313.15	0.66	363.15	1.29
318.15	1.13	368.15	1.96
323.15	1.86		

Table 2 Sublimation enthalpies of benzoic acid and anthracene.

Compound	Reference	Temperature range (T/K)	$\ln(p/\text{Pa}) = a - b \cdot 10^3 \cdot (K/T)$		$\Delta_{\text{sub}} H(T)$ (kJ·mol ⁻¹)
			<i>a</i>	<i>b</i>	
Benzoic acid	This study	299–323	34.031 ± 0.300	10.790 ± 0.093	89.71 ± 0.77
	C. G. De Kruif and J. G. Blok, 1982 ¹⁸⁾	316–391	34.038	10.803	89.45 ± 0.10
	M. Colomina <i>et al.</i> , 1982 ¹⁹⁾	293–313	34.231	10.867	90.35 ± 0.13
	M. A. V. Ribeiro da Silva <i>et al.</i> , 1995 ²⁰⁾	307–314	33.601 ± 0.330	10.669 ± 0.102	88.70 ± 0.85
	M. A. V. Ribeiro da Silva <i>et al.</i> , 1995 ²⁰⁾	304–317	34.320 ± 0.302	10.886 ± 0.100	90.51 ± 0.83
	R. Sabbah <i>et al.</i> , 1999 ¹⁶⁾	298.15			89.700 ± 1.000*
Anthracene	This study	348–368	34.199 ± 0.641	12.332 ± 0.229	102.53 ± 1.90
	C. G. De Kruif, 1980 ⁸⁾	337–361	33.457	12.075	100.4 ± 1
	B. F. Rordorf, 1985 ⁵⁾	318–373	33.002	11.877	98.74
	P. C. Hansen and C. A. Eckert, 1986 ¹⁷⁾	313–363	34.261	12.339	102.60 ± 2.6
	V. Oja and E. M. Suuberg, 1998 ¹⁰⁾	318–363	33.281	12.024 ± 0.337	100.0 ± 2.8
	R. Sabbah <i>et al.</i> , 1999 ¹⁶⁾	298.15			103.360 ± 2.670*

*The value at 298.15 K, $\Delta_{\text{sub}} H$ (298.15 K)

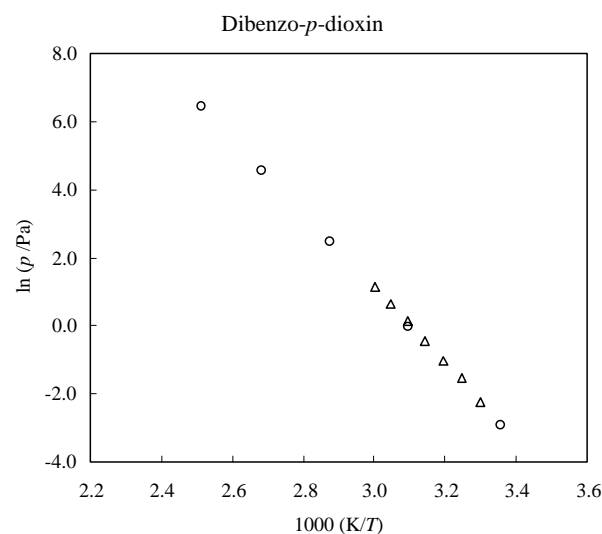
Table 3 Experimental vapour pressure results of four PCDD/Fs.

DD		DF		OCDD		OCDF	
<i>T</i> /K	<i>p</i> /Pa	<i>T</i> /K	<i>p</i> /Pa	<i>T</i> /K	<i>p</i> /Pa	<i>T</i> /K	<i>p</i> /Pa
303.15	0.107	295.35	0.284	448.15	0.0912	438.15	0.107
308.15	0.215	298.35	0.398	453.15	0.141	443.15	0.160
313.15	0.358	303.15	0.665	458.15	0.204	448.15	0.252
318.15	0.628	308.15	1.22	463.15	0.291	453.15	0.395
323.15	1.14	313.15	1.94	468.15	0.416	458.15	0.598
328.15	1.90	318.15	3.04	473.15	0.607	463.15	0.882
333.15	3.08			478.15	0.838	468.15	1.24
				483.15	1.20		
				488.15	1.67		
				493.15	2.32		

zoic acid and anthracene are recommended as reference materials for the measurements of low vapour pressure and sublimation enthalpy.¹⁶⁾ The use of benzoic acid as a reference material has been questioned because of the possibility of association of the acid in the gas phase. However, it continues to be used as a reference materials and all available experimental evidence suggests that it is a suitable reference material. Murata *et al.*²¹⁾ have reported that the degree of dissociation of the dimer in the saturated vapour to be higher than 0.997 at 298.15 K, it means that the fraction of benzoic acid molecules (as monomers) which form the dimer in the saturated vapour at 298.15 K is smaller than 0.3%. Unfortunately there is no report on the dimer fraction in the saturation PCDD/Fs vapor. However, the structure of benzoic acid is coplanar, similarly PCDD/Fs are coplanar structure, and the experimental temperatures are much higher than 298.15 K, therefore the fraction of dimer in the saturation PCDD/Fs vapour was believed to be neglectable.

Vapour pressure Measurements of benzoic acid and anthracene with the present apparatus were made in the temperature range of 299 to 323 K and 348 to 368 K, respectively. The experimental results of vapour pressure are listed in Table 1.

The vapour pressures and sublimation enthalpies of benzoic acid and anthracene have been measured by a variety of

Fig. 3 Vapour pressures for Dibenzo-*p*-dioxin. ○ Rordorf 1989;³⁾ Δ This study.

different techniques and investigators. The vapour pressure and sublimation enthalpy results compared with the recent reports are listed in Table 2. Table 2 shows that the vapour pressure and sublimation enthalpy results of benzoic acid and anthracene measured with the present apparatus are in good agreement with accepted literature data.

The testing results of the compounds give us confidence in the present apparatus, which has the advantages of accurate online mass loss determination, vapour pressure measurements at different temperature within an experiment, and much smaller sample amount and shorter experimental time than other such studies.

The experimental results of the vapour pressures for DD, DF, OCDD and OCDF are summarised in Table 3. For comparison, the data reported in the literatures are plotted together in Figs. 3, 4, 5 and 6, respectively, although not many are available.^{2,3,7,17)}

Figure 3 shows that vapour pressures at low temperature (303 to 333 K) of DD obtained in this study are in good agreement with the data measured with gas saturation

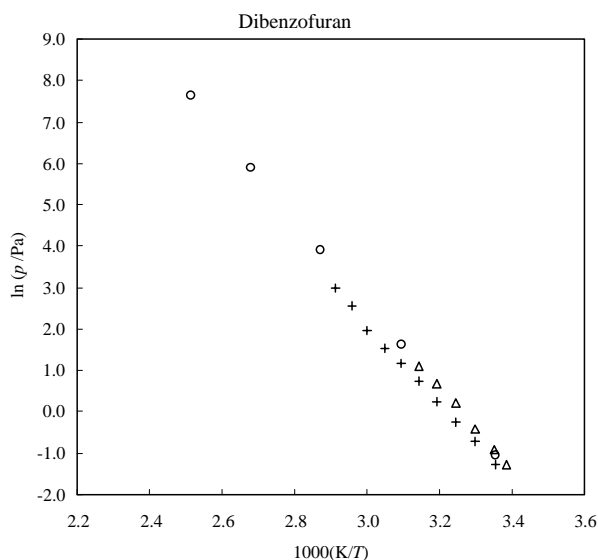


Fig. 4 Vapour pressures for Dibenzofuran. \circ Rordorf 1989;³⁾ + Hansen & Eckert 1986;¹⁷⁾ Δ This study.

method by Rordorf.³⁾ By fitting the experimental results to the Clausius-Clapeyron eq. (4), sublimation enthalpy of DD calculated from the vapor pressure results is (93.61 ± 1.17) $\text{kJ} \cdot \text{mol}^{-1}$. This value is comparable to $92.25 \text{ kJ} \cdot \text{mol}^{-1}$ obtained by Rordorf.³⁾

For DF vapour pressure, the results at low temperature measured by this study are also in good agreement with the data by Rordorf.³⁾ The values measured with gas saturation method by Hansen and Eckert¹⁷⁾ are much lower than the two studies as shown in Fig. 4. The sublimation enthalpy of DF obtained by this study is $(82.15 \pm 1.46) \text{ kJ} \cdot \text{mol}^{-1}$, this value is slightly lower than that by Rordorf and higher than that by Hansen and Eckert as shown in Table 4.

Figure 5(a) compares the results of this study and the data of Rordorf.³⁾ Using the regression method of vapour pressure and GC retention indexes, Eitzer and Hites²⁾ obtained the vapour pressure value of $2.75 \times 10^{-6} \text{ Pa}$ for supercooled liquid state OCDD at 298 K, this value is also shown in Fig. 5.

As shown in Fig. 5(b), in the experimental temperature range, vapour pressure values of OCDD obtained in the present study are not so different from the data by Rordorf,⁷⁾ (both studies have the same vapour pressure value of OCDD at 458 K), but the enthalpy result is much different. The enthalpy of sublimation for OCDD obtained here is $(131.14 \pm 0.60) \text{ kJ} \cdot \text{mol}^{-1}$ in the experimental temperature range, much lower than $151.13 \text{ kJ} \cdot \text{mol}^{-1}$ proposed by Rordorf.

For OCDF vapour pressure, Fig. 6 shows that the results of this study are in reasonable agreement with the data measured by Rordorf.³⁾ The enthalpy of sublimation obtained in this study is $(141.72 \pm 1.85) \text{ kJ} \cdot \text{mol}^{-1}$ in the experimental temperature range, slightly lower than that by Rordorf (Table 4).

4. Conclusions

The experimental results of vapour pressure and enthalpy for DD, DF, OCDD and OCDF can be summarised with the following quantities:

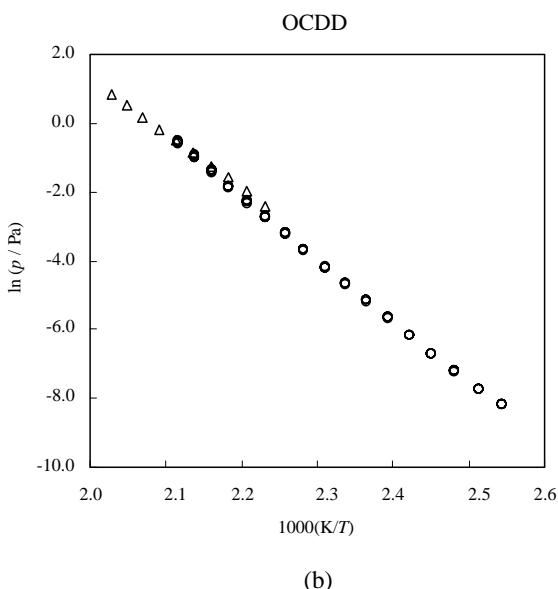
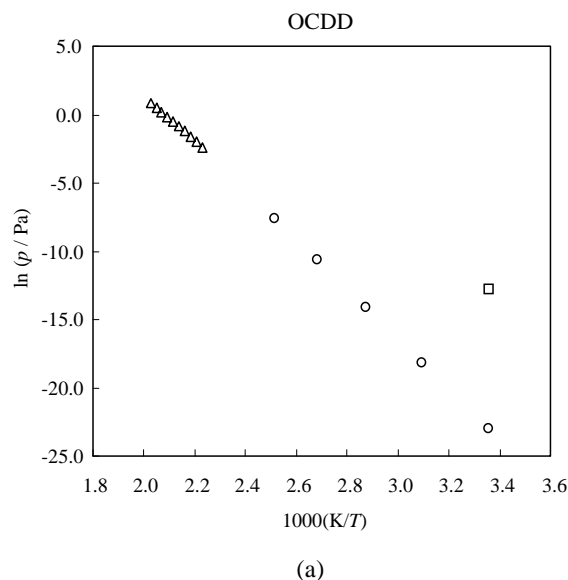


Fig. 5 Vapour pressures for OCDD. (a) \circ Rordorf 1989;³⁾ \square Eitzer & Hites 1998;²⁾ Δ This study. (b) \circ Rordorf 1990;⁷⁾ Δ This study.

DD,

$$\ln(p/\text{Pa}) = (34.944 \pm 0.444) - (11259 \pm 141) \cdot (K/T),$$

$$\Delta_{\text{sub}}H(T) = (93.61 \pm 1.17) \text{ kJ} \cdot \text{mol}^{-1} (303 \text{ to } 333 \text{ K})$$

DF,

$$\ln(p/\text{Pa}) = (32.203 \pm 0.576) - (9880.4 \pm 176.0) \cdot (K/T),$$

$$\Delta_{\text{sub}}H(T) = (82.15 \pm 1.46) \text{ kJ} \cdot \text{mol}^{-1} (295 \text{ to } 318 \text{ K})$$

OCDD,

$$\ln(p/\text{Pa}) = (32.825 \pm 0.153) - (15773 \pm 72) \cdot (K/T),$$

$$\Delta_{\text{sub}}H(T) = (131.14 \pm 0.60) \text{ kJ} \cdot \text{mol}^{-1} (448 \text{ to } 493 \text{ K})$$

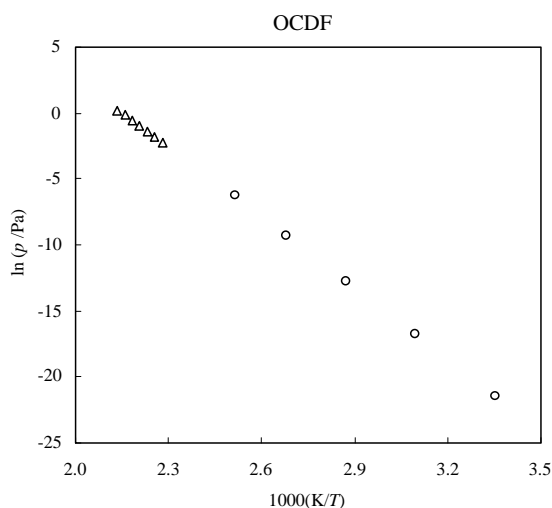
OCDF,

$$\ln(p/\text{Pa}) = (36.664 \pm 0.485) - (17046 \pm 220) \cdot (K/T),$$

$$\Delta_{\text{sub}}H(T) = (141.72 \pm 1.83) \text{ kJ} \cdot \text{mol}^{-1} (438 \text{ to } 473 \text{ K})$$

Table 4 Enthalpies of sublimation of four PCDD/Fs.

Compound	Reference	Method	Temperature range K	$\ln(p/\text{Pa}) = a - b \cdot 10^3 \cdot (K/T)$		$\Delta_{\text{sub}} S(T)$ J·K ⁻¹ ·mol ⁻¹	$\Delta_{\text{sub}} H(T)$ kJ·mol ⁻¹
				<i>a</i>	<i>b</i>		
DD	Rordorf 1989 ³⁾	Gas saturation	298–398	34.319	11.095	285.29	92.25
DD	This study	Knudsen effusion	303–333	34.944 ± 0.444	11.259 ± 0.141	290.52	93.61 ± 1.17
DF	Rordorf 1989 ³⁾	Gas saturation	298–398	33.54	10.313	278.49	85.63
DF	Hansen & Eckert 1986 ¹⁷⁾	Gas saturation	303–343	30.641	9.5183	254.76	79.14
DF	This study	Knudsen effusion	295–318	32.203 ± 0.576	9.8804 ± 0.1760	267.73	82.15 ± 1.46
OCDD	Rordorf 1989 ³⁾	Gas saturation	298–398	38.156	18.207	316.48	151.13
OCDD	This study	Knudsen effusion	448–493	32.825 ± 0.153	15.773 ± 0.072	272.91	131.14 ± 0.60
OCDF	Rordorf 1989 ³⁾	Gas saturation	298–398	38.889	17.980	323.03	149.43
OCDF	This study	Knudsen effusion	438–473	36.664 ± 0.485	17.046 ± 0.220	304.82	141.72 ± 1.83

Fig. 6 Vapour pressures for OCDF. ○ Rordorf 1989;³⁾ △ This study.

The vapour pressure and enthalpy results for DD, DF and OCDF determined by Knudsen effusion method in the present study are in reasonable agreement with the values measured by gas saturation method in the studies by Rordorf. The sublimation enthalpy result of OCDD obtained by the present study are much lower than the value measured by Rordorf, although the vapour pressure values of OCDD in the experimental temperature range are comparable with the data by Rordorf.

It was confirmed that the present apparatus using the Knudsen method is suitable for the measurements of vapour pressure of dioxin congeners and other POPs. A reliable thermodynamic data set can be evaluated for major dioxin congeners and other POPs using this apparatus.

Acknowledgements

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