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Design and construction of a simple Knudsen Effusion Mass Spectrometer (KEMS) system for vapour pressure measurements of low volatility organics

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Abstract

A design of and initial results from a Knudsen Effusion Mass Spectrometer (KEMS) are presented. The design was adapted from high temperature alloy studies with a view to using it to measure vapour pressures for low volatility organics. The system uses a temperature controlled cell with an effusive orifice. This produces a molecular beam which is sampled by a quadropole mass spectrometer with electron impact ionization calibrated to a known vapour pressure. We have determined P_{298} and ΔH_{sub} of the first 5 unsaturated straight chain dicarboxylic acids: $2.15 \pm 1.19 \times 10^{-2}$ Pa and 75 ± 19 kJ mol⁻¹ respectively for Oxalic acid, $5.15 \pm 0.76 \times 10^{-4}$ Pa and 91 ± 4 kJ mol⁻¹ for Malonic acid, $9.19 \pm 2.26 \times 10^{-5}$ Pa and 93 ± 6 kJ mol⁻¹ for Succinic acid, $4.21 \pm 1.66 \times 10^{-4}$ Pa and 123 ± 22 kJ mol⁻¹ for Glutaric acid and $5.21 \pm 3.84 \times 10^{-6}$ Pa and 125 ± 40 kJ mol⁻¹ for Adipic acid.

1 Introduction

Knowledge of pure component vapour pressures is essential for calculations of gas/particle partitioning of compounds forming atmospheric aerosols. There are many methods of estimating vapour pressures but most of the experimental data collected to date has been for intermediate or high pressure compounds (and often measured at temperatures considerably above ambient) and the proportion of experimental data for low (less than 100 Pa) vapour pressure compounds has been very small. Hence the datasets used for developing the estimation methods have reflected this bias in addition to the fact that components studied tend to have one or two functional groups at the most. The most intensively studied group are hydrocarbons for the oil industry with no functional groups. However, the vapour pressure of simple hydrocarbons are not of interest to the atmospheric community which are often concerned with multi-functional and heavily oxygenated (Johnson et al., 2006). Therefore it is unsurprising that some of the estimation methods can give errors in vapour pressure of several orders of mag-

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nitude for multifunctional compounds at ambient temperatures. The vapour pressure of all aerosol components is necessary to calculate the mass flux of condensing and evaporating compounds. Pure component vapour pressure data are lacking for the majority of multifunctional organic condensable compounds predicted to be formed from gas phase volatile organic carbon (VOC) oxidation (Johnson et al., 2005). Furthermore, the available predictive techniques for vapour pressures are largely unevaluated on multifunctional compounds. It is therefore necessary to evaluate such predictive techniques for selection of those most appropriate for atmospheric application and this requires a reliable method of determining vapour pressures of low volatility compounds at ambient temperatures.

Dicarboxylic acids are present in atmospheric aerosols and have been identified in multiple environments, and concentrations can vary significantly between regions (Bilde et al., 2003). They originate from photo-oxidation of biogenic and anthropogenic compounds but there is speculation about the exact origins and formation mechanisms. They have been previously studied by evaporation rates in Tandem Differential Mobility Analysers (TDMA) (Tao and McMurry, 1989; Bilde et al., 2003; Bilde and Pandis, 2001), Temperature Programmed Desorption (TPD) combined with Proton Transfer Chemical Ionisation Mass Spectrometry (PT-CIMS) (Cappa et al., 2007) and Knudsen mass loss effusion (Silva et al., 2001, 1999) although there are discrepancies between different measurement methods of up to two orders of magnitude for some compounds.

2 Knudsen Effusion Mass Spectrometry

There are a limited number of techniques for measuring the vapour pressures of low volatility components. Knudsen Effusion Mass Spectrometry (KEMS) is an established vapour pressure measurement technique capable of measuring vapour pressures from $10^1 - 10^{-8}$ Pa (e.g. for ceramic solutions and metal alloys at high temperature) (Shilov et al., 1997; Hilpert and Miller, 2004; Hilpert, 2001, 1991; Hastie, 1984). SOA components are likely to have vapour pressures upwards of 10^{-4} Pa, measurable at ambient

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temperature, well inside the range measurable by KEMS. A temperature controlled Knudsen effusion cell, suitable for controlled generation of a molecular beam of the sample organic compounds is coupled to a vacuum chamber, and a quadrupole mass spectrometer allows direct measurement of vapour pressure, analogous to the KEMS systems used to study the vapour pressure of ceramics (Benczk et al., 2006).

2.1 Vacuum system

The KEMS system is constructed primarily from "off-the-shelf" standard conflat UHV components (Hositrade and Caburn), as shown in Fig. 1. A custom cold plate (PSP vacuum) was included to act as a beamstop if hot vapours are used. Copper gaskets are used for most seal except those for sample loading which are Viton. Separate pressure gauges and pumps are used on the upper and lower vacuums shown in Fig. 2.

The two chambers (Figs. 1 and 2) are connected via an all metal gate valve (VAT-valves). Each chamber is separately pumped by 70 l s^{-1} pumping speed V-81-T turbo pumps (Varian) on CF 63 flanges with a SH-110 dry scroll backing pump. Pressure is measured using convector gauges (Varian) for atmospheric pressure down to 10^{-3} mbar, and IMG-100 inverted magnetron ion gauges for $<10^{-4}$ mbar (Varian). Base pressure and pumping speeds are summarised in Table 1.

The mass spectrometer chamber is kept at 10^{-6} mbar or less with the ioniser left on to ensure different samples runs are directly comparable. During sample change the second chamber is isolated via the gate valve and vented to air. A Balzers-Pfeifer quadrupole mass spectrometer was used with a QMS 410 mass analyzer, a QMH 410 RF-box connected to a QMG422 controller. Both faraday cup and secondary electron multiplier detection were used to measure ion intensities. Data collection and processing was performed using a PC running the Quadstar software package.

2.2 Knudsen cell

The Knudsen cell was machined in-house (Fig. 3), and consists of a sample mount rigidly fixed onto a CF63 flange using torr-seal UHV compatible epoxy glue. Heating is provided by a coaxially mounted flexible polyimide heating element (Watlow). Samples are loaded into a removable cell and a lid is fixed onto with a chamfered effusion orifice. Previous workers have found a chamfered effusion orifice ensures that the hole is formed as a "knife edge" helping it act as a 2-D hole rather than a cylinder. Effusion orifices were made with hole sizes of 200 μm , 1 mm, 2 mm and 3 mm. The hole size should be chosen so that the ratio of mean free path to hole size (Knudsen number) is ≥ 10 . Table 2 shows the mean free paths of 3 compounds with the Knudsen numbers using the different hole sizes. Ferrocene, the highest pressure calibration compound, Oxalic acid, the lowest pressure calibration compound and Adipic acid, the lowest pressure compound measured.

2.3 Measurements of calibration compounds

Pressure and thermodynamic data is determined by measuring the total ion signal and comparing this with a sample of known vapour pressure. The Knudsen orifice is small enough that effusive flow occurs from the cell without disturbing the thermodynamic equilibrium. This produces a molecular beam with an intensity proportional to the vapour pressure in the cell above the sample. The system can be used to determine partial pressures of mixed systems. The pressure of the i -th component in the KEMS instrument P_i is given by:

$$P_i = \frac{k I_i T}{\sigma_i} \quad (1)$$

where I_i is the ion intensity measured in the mass spectrometer, σ_i is the ionisation cross section and T is the temperature of the Knudsen cell. And k is the machine constant which incorporates information on the geometry of the system, clausening factor

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of the effusion orifice and any other correction factors, k is determined by using the reference samples. σ_i is calculated by summing the ionisation cross section from each atom in the molecule at the ionisation energy (70 eV) (Hilpert, 2001).

Once the vapour pressure, P , has been determined at a number of different temperatures further thermodynamic data can be obtained using the Clausius-Clapeyron equation (Hilpert, 2001).

$$\ln P = \frac{\Delta H_{\text{sub}}^0}{RT} + \frac{\Delta S_{\text{sub}}^0}{R} \quad (2)$$

where T is the temperature, R is the ideal gas constant and ΔH and ΔS are the enthalpies and entropies of sublimation respectively.

3 Results

Knudsen Effusion Mass Spectrometry has to use a calibration compound in order to determine k and hence provide absolute pressure measurements. Three compounds that had previously been measured by Knudsen mass-loss effusion, an absolute pressure technique, were chosen as reference samples. Ferrocene (Jacobs et al., 1983), Benzophenone (Kruif et al., 1983) and Diphenylethane (Ekeren et al., 1982) each have vapour pressures in the range 1–0.1 Pa at 298 K which is high enough to have reasonable mass-loss data but low enough to provide a calibration for the low volatility compounds the KEMS was constructed for. To check the consistency of the absolute pressure values of the reference samples, each was measured using the other two samples as the calibration compounds. Table 3 shows determinations of the vapour pressures of the each of the 3 reference compounds using the literature values of the other 2.

Spectra were measured at 5 degree temperature increments. The sample was left to equilibrate for 10 min at each temperature step to ensure consistent comparable temperatures were obtained. Ionisation cross sections were calculated by summing up

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the individual electron impact cross sections from each atom in the molecule (Hilpert, 2001) using values from the NIST electron impact database.

We have studied the C_2 - C_6 straight chain saturated dicarboxylic acids: Oxalic, Malonic, Succinic, Glutaric and Adipic acid. Oxalic acid was measured using the 200 μm , 1 mm and 3 mm holes the remainder dicarboxylics had a much lower vapour pressure and were only studied using the 3 mm hole as a result of small signal-to-noise when using the smaller holes in conjunction with the Farady Cup detection. However, when using the secondary electron multiplier there is an enhancement in signal-to-noise by a factor of ≥ 10 which enabled the dicarboxylics vapour pressure to be quantified using the 1 mm hole. Errors were determined by the standard deviation of repeated measurements of oxalic acid using all 3 reference compounds. We have determined a P_{298} of $2.15 \pm 1.19 \times 10^{-2}$ Pa and enthalpies and entropies of sublimation of $75 \pm 19 \text{ kJ mol}^{-1}$ and $213 \pm 55 \text{ J mol}^{-1} \text{ K}^{-1}$ for oxalic acid (Fig. 4), which is comparable to the variation in the calibration compounds.

Oxalic acid was then used as the calibration compound for the remaining dicarboxylics which had much lower volatilities, requiring the 3 mm hole size to be used with the faraday detector. Using the previous calibration compounds with such a large hole would result in too high a pressure in the ionization region of the KEMS, which would result in a risk of the ioniser burning out. The data shown in Table 4 is the average of 2 independent runs using literature (Wit et al., 1982) values for Oxalic acid as the calibration compound with the faraday detector, and 1 run using Malonic acid as the calibration compound with SEM detection.

Figures 5 and 6 shows the results for the vapour pressure and enthalpy of sublimation respectively for the first 5 dicarboxylic acids obtained in this work. Also shown are comparable data from other workers using different vapour pressure techniques, TDMA (Bilde et al., 2003; Tao and McMurry, 1989), PT-CIMS (Cappa et al., 2007), and Knudsen mass loss (Silva et al., 2001). Figure 7 shows a mass spectrometer trace of Malonic acid at 313 K for comparison of the signal to noise for faraday and SEM detection.

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4 Discussions

The agreement between room temperature vapour pressures is reasonably good, the results show the distinct odd-even effect well known in the homologous straight chain dicarboxylics. The data presented in this work tends to give higher values compared to Bilde and Tao and McMurry, especially for Succinic acid, Ravishankara results are at the lower end of reported values. The Enthalpies of sublimation however show considerable differences between the different methods used, this wide variance has also been reported for the higher carbon chain length dicarboxylics. Analogous to the measurement of reaction kinetics the spread of reported experimental values at temperatures other than ambient increases. This probably is as a result of small discrepancies in the $P_{(298 \text{ K})}$ being magnified as the temperature increases affecting the enthalpies.

Bilde and Tao and McMurry both used TDMA to study evaporation rates of aerosol particles of dicarboxylics, rather than bulk samples as in this work. Bilde's and Tao and McMurry's method requires an understanding of the aerosol flow with the TDMA and a model of the evaporation of a particle within the flow tube. The assumptions necessary for this may explain some of the differences between the results obtained in this study. They both state that a major source of errors in their measurement are uncertainties in the theory of mass transfer from transition regime particles, and the presence of unevaporated water within the aerosol particle. Even so the results of this work are in good agreement (within 3σ) for $P_{(298 \text{ K})}$. Da Silva used Knudsen mass loss effusion, similar to the KEMS technique presented in this paper but as a result of the low volatility of the sample and the lack of sensitivity compared to the KEMS technique the data was obtained at much higher temperatures. This was to ensure sufficient sample was sublimed to detect using a balance. Data was extrapolated to obtain results at 298 K. Ravishankara used PT-CIMS to observe the evaporation rates of aerosol samples collected on a cold plate. Their TPD experiments involved a preheating stage to drive off volatile impurities in the sample, however significant fractions of the sample were lost which may inadvertently effect results explaining the lower $P_{(298 \text{ K})}$ compared

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to the $P_{(298\text{K})}$ presented in this work.

Whereas the odd-even effect in vapour pressures is well known, there is no agreement on its existence in enthalpy measurements. Bilde sees an odd-even effect in enthalpy which Ravishankara and Da Silva do not. As a result of the large enthalpy errors for glutaric and adipic it is not possible to say for certain that an odd-even effect in enthalpy is observed in this work. Indeed, if one is observed it is reversed compared to Bilde. However, within experimental error as in the work of Ravishankara we do not observe an odd-even effect in enthalpy.

5 Conclusions

We have presented the design of a Knudsen effusion mass spectrometer for the measurement of the sort of low volatility organics which will partition in the atmosphere into the aerosol phase. We have also measured homologous straight chain dicarboxylics and compared the results with other techniques. KEMS provides a number of advantages over other methods, the use of bulk samples eliminates the needs for simplifying assumptions required when using aerosol based techniques, the only limiting requirement is a sample of known vapour pressure to act as a calibration. The high sensitivity of the mass spec means data can be obtained around room temperature unlike Knudsen mass-loss where temperatures must be significantly elevated for very low volatility samples. The KEMS system presented in this paper can be used to study even lower volatility systems by increasing the orifice size, raising the temperature or improving the sensitivity of the mass spectrometer. Unfortunately water is too volatile for the KEMS system which means we can not study aqueous mixtures such as those that may be present in real atmospheric aerosols, which is a major strength of TDMA type measurements.

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Table 1. Pressures relevant to operation of the Knudsen Effusion Mass Spectrometer.

Pressures (Pa)	Measurement Chamber	Sample Chamber
Base Pressure	10^{-5}	Atm to 10^{-5}
Operating Pressure	10^{-3} – 10^{-5}	10^{-3} – 10^{-5}
Pumping Speed	70 l s^{-1}	70 l s^{-1}
Ion Filament Max Pressure	10^{-2}	n/a
SEM Max Pressure	10^{-3}	n/a

Table 2. Mean free paths and Knudsen numbers (K_n) of 3 compounds; Ferrocene, Oxalic acid and Adipic acid.

Compound	Mean Free Path (mm)	K_n 0.2 mm hole size	K_n 1 mm hole size	K_n 2 mm hole size	K_n 3 mm hole size
Adipic acid	730 000	3 638 000	730 000	364 000	243 000
Oxalic acid	180	910	180	90	60
Ferrocene	3.6	18	3.6	1.8	1.2

Table 3. Vapour pressure (298 K), Enthalpy of sublimation and Entropy of sublimation of the calibration compounds. Literature values ^{1,2,3}(Ekeren et al., 1982; Jacobs et al., 1983; Kruif et al., 1983) are shown. The values determined using the KEMS are also reported to illustrate internal consistency between calibration compounds. The compound in brackets denotes the calibration compound used to determine that value.

Compound	$P_{(298\text{ K})}$ (Pa)	ΔH_{sub} (kJ mol ⁻¹)	ΔS_{sub} (J mol ⁻¹ K ⁻¹)
Benzophenone ¹	0.162	67.6	212
Benzophenone (Ferrocene)	0.135	74.2	232
Benzophenone (Diphenylethane)	0.101	87.3	274
Ferrocene ²	0.760	90.0	300
Ferrocene (Benzophenone)	1.022	76.9	258
Ferrocene (Diphenylethane)	1.226	70.3	238
Diphenylethane ³	0.497	93.7	309
Diphenylethane (Benzophenone)	0.371	106.8	350
Diphenylethane (Ferrocene)	0.598	87.1	288

Table 4. Vapour pressure, Enthalpy of sublimation and Entropy of sublimation of the dicarboxylic acids. The variation for the Oxalic acid is large due to the use of 3 different calibration compounds.

Acid	$P_{(298\text{ K})}$ (Pa)	ΔH_{sub} (kJ mol ⁻¹)
Oxalic	$2.15 \pm 1.19 \times 10^{-2}$	75 ± 19
Malonic	$5.15 \pm 0.76 \times 10^{-4}$	92 ± 4
Succinic	$9.19 \pm 2.26 \times 10^{-5}$	93 ± 6
Glutaric	$4.21 \pm 1.66 \times 10^{-4}$	123 ± 22
Adipic	$5.21 \pm 3.85 \times 10^{-6}$	119 ± 26

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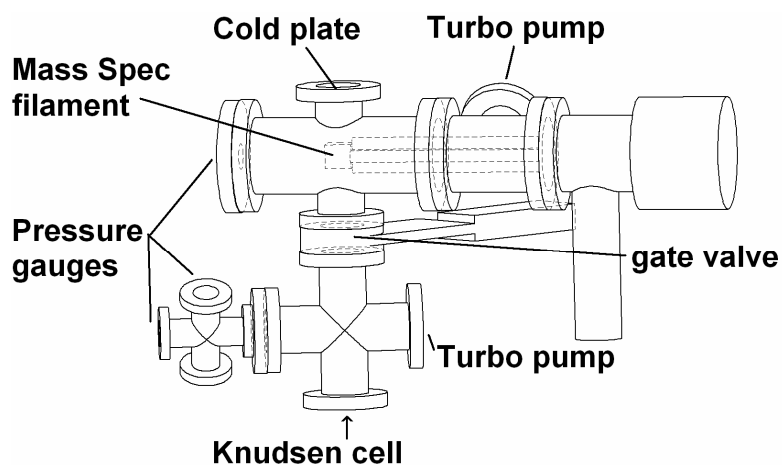


Fig. 1. Vacuum chamber for KEMS system.

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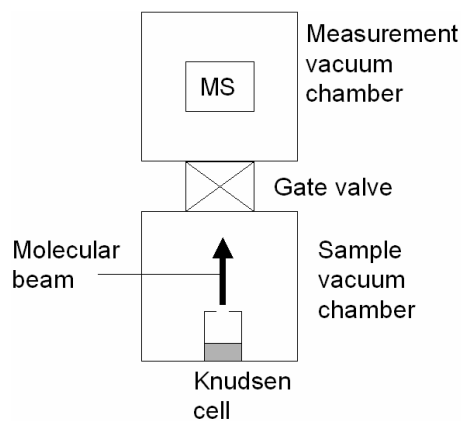


Fig. 2. Schematic of KEMS system.

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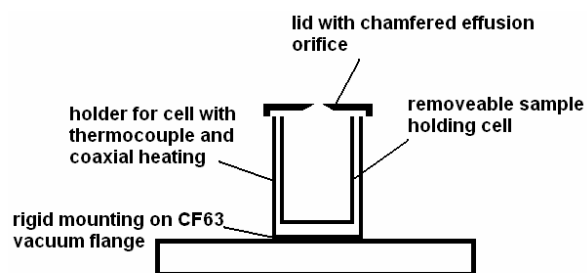


Fig. 3. Schematic of Knudsen cell.

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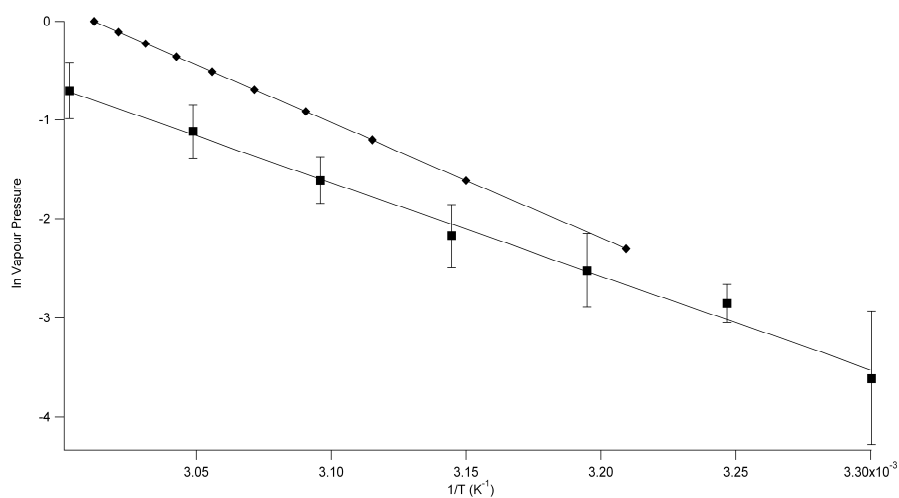


Fig. 4. In vapour pressure against 1/Temperature for Oxalic acid. This work denoted (■) and the overall trend from De Wit (◇).

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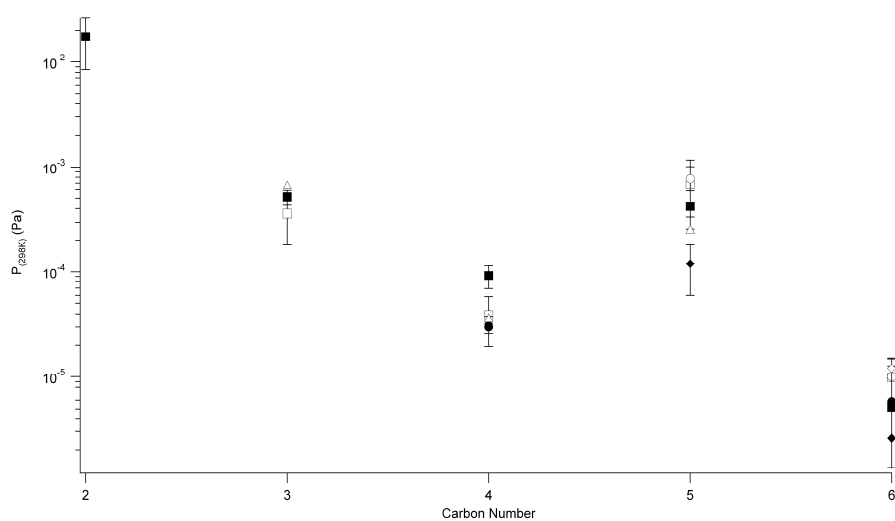


Fig. 5. Vapour pressures at 298 K. This work (■), Bilde (□), Cappa et al., (◆), Chattopadhyay and Ziemann (◇), da Silva (Δ), Davies and Thomas (•) and Tao and McMurry (◊).

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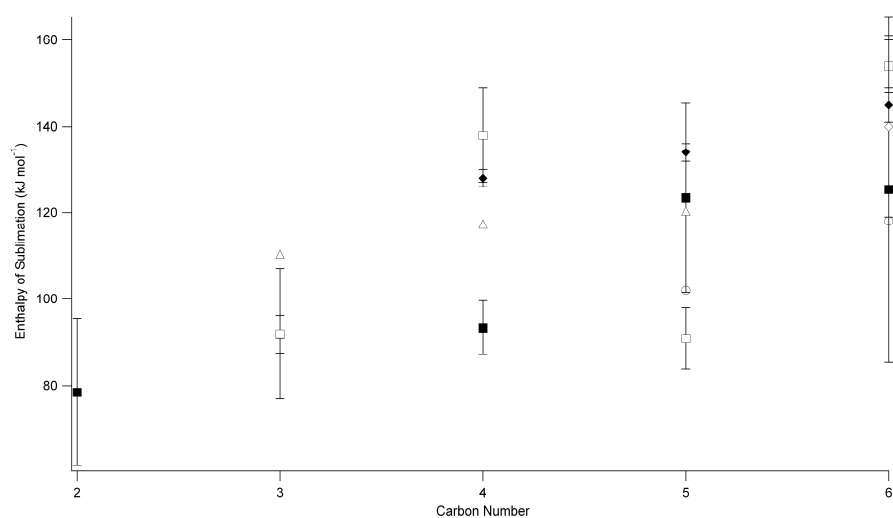


Fig. 6. Enthalpies of sublimation: This work (■), Bilde (□), Cappa et al., (◆) Chattopadhyay and Ziemann (◇), da Silva (Δ) and Tao and McMurry (○).

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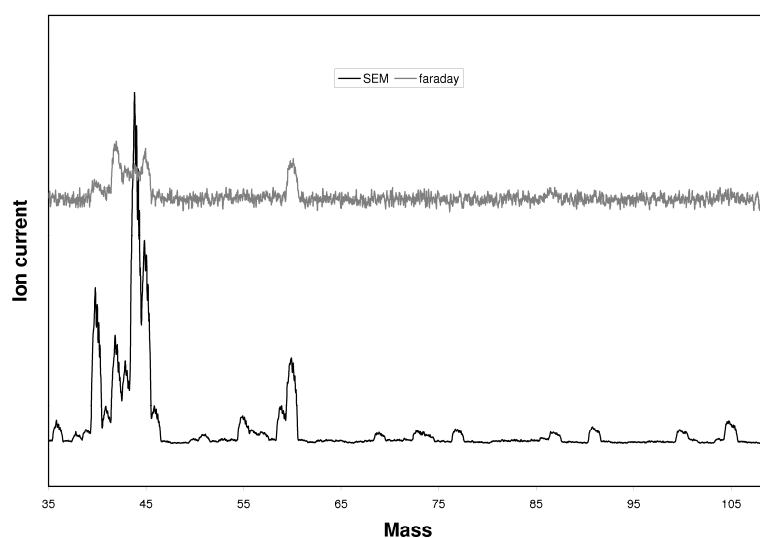


Fig. 7. Mass spectrometer traces for Malonic acid at 313 K using faraday and SEM detection.

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