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Temperature dependence of ion mobility signals of halogenated compounds

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ABSTRACT

Ion mobility spectrometry (IMS) as handheld and transportable sensor technique permits the sensitive detection of halogenated compounds with importance in environmental monitoring and process control. The negative ion mobility spectra mostly show one product ion peak which can be attributed to $(H_2O)_nX^-$ ions due to dissociative electron attachments. For minimizing memory effects and contaminations, modern ion mobility spectrometers work at elevated temperatures. In this paper, we investigated the influence of temperature on peak position, resolution and relative abundance of ions formed from halogenated substances. Elevated temperatures affect the peak position in different way. For fluorine- and chlorine-containing product ions, changes in hydration and clustering have a considerable influence on peak position, while these processes are of minor importance for bromine- and iodine-containing product ions. In these cases, the drift time differences mainly result from differences in drift behavior due to differences in gas density, the mean free path of ions and different collision rates. The drift time shift with elevated temperatures provides an enhanced peak-to-peak resolution. Improved separation efficiency can therefore be established with increased temperatures for negative product ions of halogenated compounds. Furthermore, an enhanced sensitivity was found for all compounds with increasing temperatures. However, independent on the temperature, the order of sensitivity is mainly determined by the bonding state of halogen atoms within the molecules.

1. Introduction

Halogenated substances belong to the most widespread target compounds in process control and environmental monitoring. Especially volatile and semi-volatile halogenated compounds are among the most important pollutants in the environment. For example, perchloroethylene, trichloroethylene, trichloromethane and dichloroethylene are the most prevalent groundwater contaminations in both, Europe and United States [1].

Ion mobility spectrometry (IMS) has been developed as field-deployable sensor technique for emission monitoring and long-term monitoring of water or groundwater in combination with suitable sample preparation methods, e.g. membrane extraction [2], purge and trap [3] or solid phase microextraction (SPME) [4]. The spectrometers are configured as transportable and handheld units which work with batteries or accumulators. Furthermore, no additional gas supply is necessary and the devices are operated at atmospheric pressure. IMS analyzers exhibit a fast response within few seconds and high sensitivity for numerous chemical substances. In contrast to other field screening techniques, ion mobility measurements provide characteristic spectra for substances investigated and do not provide only a sum signal. Therefore, IMS became an important sensor technique for on-site monitoring. As known from previous investigations, ion mobility based techniques permit the sensitive detection of chlorinated compounds [5].

Determining ion mobilities initially requires the formation of ions from neutral sample molecules. The method of ionization most commonly used in IMS analyzers today is chemical ionization initiated with a radioactive source, typically 100 or 300 MBq of ^{63}Nickel (^{63}Ni) or Tritium (^{3}H). In addition to positive reactant ions, negative ions are also being formed in an ion source principally through the attachment of thermalized electrons to molecular oxygen. The dominant reaction pathway provides $(H_2O)_nO_2^-$ as reactant ions in addition to various adducts such as $(H_2O)_nO_2O_2^-$ or $(H_2O)_n(CO_2)O_2^-$. Negative product ions are mainly formed from neutral sample molecules (MX) due to charge transfer reactions and include dissociative electron attachments (Eq. 1)

$$(MX)+(H_2O)_nO_2^- \rightarrow M+X^-+nH_2O+O_2 \qquad (1)$$

and associative electron attachments according to Eq. (2)

$$(MX)+(H_2O)_nO_2^- \rightarrow (MX)O_2^-+nH_2O \qquad (2)$$

Negative product ions from halogenated compounds are mainly formed via dissociative charge transfer. Halogenated compounds therefore provide well-defined spectra consisting of one major peak which can be attributed to $(H_2O)_nX^-$ product ions [6].

The ions are gated into the drift tube as an ion swarm via an electronic shutter grid which is briefly opened at a given time

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interval of few microseconds. In the drift tube, the ions move as a swarm toward a detector down a voltage gradient through a gas atmosphere provided by a flow of purified air or nitrogen, usually in a direction opposite that of ion motion. The ions traverse the drift region of ~5 to 15 cm in a few milliseconds. The drift time of an ion swarm can be associated with the ions through mass, charge and collision cross-section, which include structural parameters (physical size and shape) and the electronic factors describing the ion-neutral interaction forces. Therefore, ions with different mass and/or structure attain different drift velocities providing a basis for separation of ions in IMS analyzers [7].

Due to improvements in engineering and technology the spectrometers commonly used today are equipped with a heated ionization region and a heated drift tube. The advantage of such a configuration is the minimization of memory effects and of possible contaminations of the spectrometers during the field measurement. On the other hand, elevated temperatures can affect the ion mobility spectra in both, peak position and relative abundance of product ions formed.

Previous investigations of the effect of temperature on ion mobility are restricted to studies of the relationship for drift time (t_d) vs. temperature of positive ions without consideration of quantitative effects [8]. According to ion mobility theory, a linear proportionality of $1/t_d$ to the absolute temperature and the reciprocal pressure can be expected [9]. In contrast to a linear relationship between drift times and pressure, the interrelation between drift times and temperature were found to be non-linear due to differences in hydration and clustering [10]. Higher temperatures are associated with a lower degree of clustering because neutral vapors will detach themselves from the primary ion [11]. In addition to these processes, also the formation of positive fragment ions can be affected by temperature. Depending on the functional groups, the comparison of ion mobility measurements at low and elevated temperatures permits the identification of different chemical classes [12]. Furthermore, elevated temperatures cause an increasing resolving power due to the reduced effect hydration and clustering. Increasing peak-to-peak resolutions were observed for negative product ions of $CHCl_3$, $CHBr_3$ and CH_3I at elevated temperatures [13].

Due to their practical meaning, we systematically investigated the temperature dependence of halogenated compounds under three aspects: (1) the influence of temperature on drift times, (2) the influence of temperature on signal intensities and (3) the influence of temperature on resolution. Additionally, the influence of structural features and the substituents was studied depending on the temperature. In addition to this comprehensive approach, a special facet of our work is the quantitative investigation which has not been described before.

2. Experimental

The chemicals were obtained in 99% or better purity from Sigma-Aldrich (Taufkirchen, Germany), and Merck (Darmstadt, Germany). More than 40 different compounds with relevance in environmental chemistry were investigated within this study.

The sample introduction was realized via permeation tubes as described previously [14]. Briefly, 300 μL of neat samples were sealed in polyethylene permeation tubes which were in a temperature-controlled glass column (permeation vessel). Nitrogen (5.0 quality with a moisture content up to 2 ppm) was passed through the glass column, split, and additionally diluted to provide a range of concentrations. The nitrogen flow through the permeation vessel was held constant for at least 8 h. The concentration of the compounds in the sample gas stream was calculated using the weight loss of the permeation tube over a certain time considering the total gas throughput.

A portion of flow was introduced into the ion mobility spectrometer via an internal sampling pump (40 mL min^{-1}) where additional dilution occurred in the recirculated internal flow of scrubbed air of 400 mL min^{-1}. After equilibration, 15 spectra were acquired for each concentration. Each series of measurement was performed at least five times.

The ion mobility measurements were performed with a commercially available spectrometer from STEP Sensortechnik und Elektronik Pockau GmbH (Pockau, Germany). The device is equipped with a tritium ionization source (50 MBq) and works with a uni-directional flow system. Scrubbed air is used as drift gas which is guided within a closed circuit with approximately 400 mL min^{-1}. The ions formed are gated to the drift tube via a 60 μs impulse which is applied to the ion source. An additional grid with the same potential like the first drift ring is located approximately 1 mm apart from the ion source. The drift tube consists of a coated ceramic tube with a length of 5.6 cm. An electric field of 300 V cm^{-1} is applied. The spectrometer can be operated in a temperature range between 50 and 150 °C. The data acquisition and the analysis of spectra were performed using IMS Control Basic software (STEP Sensortechnik und Elektronik Pockau GmbH, Pockau, Germany).

3. Results and discussion

Halogenated substances show characteristic negative product ions which appear at the same peak position in ion mobility spectrum for all substances depending on the substituent. In our previous studies we investigated the influence of structural features of chlorinated compounds on the sensitivity of ion mobility measurements [15]. The spectra in this study were obtained at 40 °C. Increasing sensitivities in the order chlorobenzenes < vinyl- < allyl- < alkyl compounds < benzylchlorides were established. These differences result from the different bonding states of chlorine and the stability of ions formed due to the dissociative charge transfer reaction. The heterolysis of chlorine from the sp^2 hybridized carbon atom in the case of vinyl compounds and chlorobenzenes is evidently limited. In contrast, alkyl chlorides and benzylchlorides with a C–Cl bond to a sp^3 hybridized carbon atom show excellent sensitivities and limits of detection (LODs). Although allyl compounds have the same bonding state, they are more insensitive detectable in comparison to the afore-mentioned compounds. The chemical properties of halogenated compounds and the trend to the heterolysis of chlorine are determined by the polarizability of carbon–halogen bond. The polarity decrease in the order (with Ar: aryl): $R–CH{=}CH–CH_2–X > Ar–CH_2–X > R–X > Ar–X > R–CH{=}CH–X$. This goes along with decreasing bond lengths and increasing bond energies. With the exception of allyl chlorides, this general order can be reproduced in ion mobility spectra. Furthermore, the constitution of ions formed due to the cleavage of chlorine has an influence of possible heterolysis of carbon–chlorine bond. In this case, the cleavage of chlorine is facilitated for allyl- and benzyl-compounds due to the formation of resonance-stabilized carbenium ions. In contrast, halogenated benzenes and vinyl compounds have a low trend to the heterolysis of chlorine due to the enhanced electronegativity of sp^2 hybridized C atoms and the +M (mesomeric) effect of halogens.

In the present study we extended these investigations to high-temperature measurements and included brominated substances. The results are summarized in Fig. 1. All measurements were performed at 150 °C drift tube temperature and included substances with the above-mentioned structural features. There are two conclusions from these measurements. The order of sensitivity is the same as described above and is therefore independent

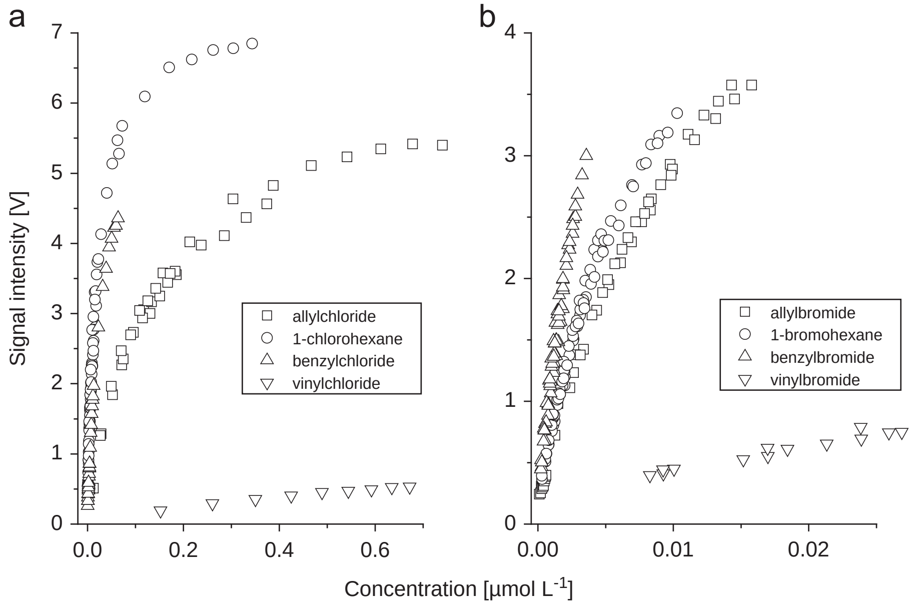

Fig. 1. Calibration graphs of chlorinated (A) and brominated (B) compounds with different structural features. The measurements were performed at 150 °C.

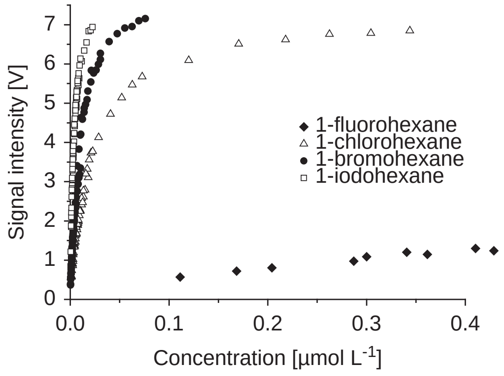

Fig. 2. Different sensitivities of halogenated hexanes depending on the substituent (measured at 150 °C).

on the temperature of the spectrometer. Within the uncertainties of measurements, the order of sensitivity is comparable for chlorinated and brominated compounds. Furthermore, the brominated substances are much more sensitive detectable due to their lower bond energy. Therefore, the structural features can be considered as a main influencing parameter (independent on the temperature) on sensitivity and LODs.

The influence of different substituents is shown in Fig. 2. The calibration curves of 1-fluorohexane, 1-chlorohexane, 1-bromohexane and 1-iodohexane confirm the results described above. The decreasing bond energies in the order F > Cl > Br > I result in different sensitivities. The bond length as inverse indicator for the bond energy of C_6H_{13}-X decreases in the opposite order (X=F: 138 pm; X=Cl: 176 pm; X=Br: 193 pm; X=I: 207 pm). The bond length was calculated on the basis of optimized molecular geometries. Geometry optimization was performed using the semi-empirical AM1 method integrated into the HyperChem 7.5 software (Gainesville, FL, USA).

3.1. *Expected influences of temperature on ion mobility spectra*

There are two general parameters which are influenced by temperature: 1). ion chemistry during the ionization processes at atmospheric pressure and 2). drift behavior within the electric field of drift tube through a gas atmosphere.

The ionization is based on the interaction between the reactant ions and analyte molecules. As known from literature, the nature of these ions considerably depends on temperature. The degree of clustering (n) of $(H_2O)_nO_2^-$ reactant ions and $(H_2O)_nX^-$ product ions varies with changes in temperature. The degree of clustering depending on moisture and temperature can be calculated using known enthalpies (ΔH^o) and entropies (ΔS^o) of hydration. The thermodynamic data are from the Chemistry Webbook (http://webbook.nist.gov/). The free-energy changes (ΔG^o) and equilibrium constants (K) at temperature (T) for each addition of water molecules were then evaluated from the following equations:

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{3}$$

and

$$K = \exp\left(\frac{-\Delta G^o}{RT}\right) \tag{4}$$

where R is the gas constant. The relative concentration of water clusters at a certain temperature and water partial pressure P_w (at a standard pressure P_0) can be calculated according to Eq. (5):

$$K_n = K_0 K_1 \ldots K_n \left(\frac{P_W}{P_0}\right)^n \tag{5}$$

The detailed calculation is described in previous publications [16–19]. Although this procedure permits only a rough approximation due to the variety of available data and their method of determination, the general trend of decreasing clustering with increasing temperatures can be concluded. Table 1 shows the relative abundances of negative reactant ions (RIN). Increasing temperatures cause a lower degree of clustering. Our measurements were performed within a temperature range between 50 and 150 °C where the $(H_2O)_2O_2^-$ reactant ion is the predominant ion. It is noteworthy that the real temperature within the ionization region and drift tube cannot be exactly determined. The recirculated gas flow (which is not integrated in the heated unit due to the low temperature stability of pumps) can affect the real temperature within the drift tube. Furthermore, the temperature is normally recorded on the outside of the drift tube wall. The real temperature inside the drift tube is therefore slightly lower as displayed.

Fig. 3 shows the calculated distribution of clusters depending on the temperature for halide ions and considerable differences can be established. While fluorine and chlorine occur as $(H_2O)_2F^-$ and $(H_2O)Cl^-$ at low temperatures and the degree of clustering decreases with elevated temperatures, Br^- and I^- are the most abundant ions over the whole temperature range. Significant changes in ion chemistry can therefore be expected especially for fluorine and chlorine.

Independent on ion formation, the drift behavior of ions formed through the drift tube is also affected by temperature. These differences result from differences in gas density, the mean free path of ions and different collision rates depending on the temperature. Different simulation programs for predicting the average thermal speed of ions are available. We used the SDS (statistical diffusion simulation) program of the SIMION 8.1 software package (Ringoes, NJ, USA). This method permits the simulation of the motions of charged particles in atmospheric pressure conditions in electrostatic fields. The detailed algorithm is extensively described in Ref. [20]. The input parameters for simulating the drift times are summarized in Table 2. The results are shown in Fig. 4 (dotted lines) for F^-, Cl^-, Br^- and I^-. Due to the uncertainties in ionic radii and the possible occurrence of isomeric forms of $(H_2O)_nX^-$ with $n \geq 2$ [21,22], we included only the non-clustered ions X^- in our calculation.

Table 1
Degree of clustering of reactant ions calculated with a water partial pressure of 1.5×10^{-5} atm (15 ppm).

Temperature [°C]	Relative abundance of $(H_2O)_nO_2^-$ [%]			
	$n=0$	$n=1$	$n=2$	$n=3$
50	0	2	78	21
70	0	5	90	6
90	0	10	88	2
110	1	18	81	0
130	5	28	67	0
150	18	35	47	0
170	43	31	25	0
200	79	15	6	0

Independent on temperature, increasing drift times were calculated with increasing ionic mass ($F^- < Cl^- < Br^- < I^-$). Lower drift times can be expected with elevated temperatures. The calculated drift time differences between 150 °C and 50 °C are 0.76 ms (F^-), 1.08 ms (Cl^-), 1.18 ms (Br^-) and 1.35 ms (I^-). The curves for drift times depending on the temperature differ slightly from a linear slope. A temperature rise from 50 to 150 °C leads to a decrease of drift times of 23.7% related to the calculated drift time at 50 °C for all halide ions.

3.2. *Influence of temperature on drift times*

In addition to the predicted drift times, Fig. 4 shows also the measured drift times depending on the temperature. Considerable differences between calculated and measured values can be established. However, these differences vary for the different halogens investigated. The deviations between simulated and measured drift times become smaller in the order $F^- > Cl^- > Br^- > I^-$. While both curves differ in position and slope for F^-, I^- provides a good

Table 2
Input parameters for simulating the drift times.

	F^-	Cl^-	Br^-	I^-
Ionic mass	18.99	35.45	79.90	126.90
Ionic radius (pm)	266	362	392	440
Charge	−1	−1	−1	−1
Length of drift tube	5.6 cm			
Diameter of drift tube	1.8 cm			
Electric field	300 V cm^{-1}			
Drift gas	Air			
Drift gas flow rate	400 mL min^{-1}			
Pressure	760 Torr			

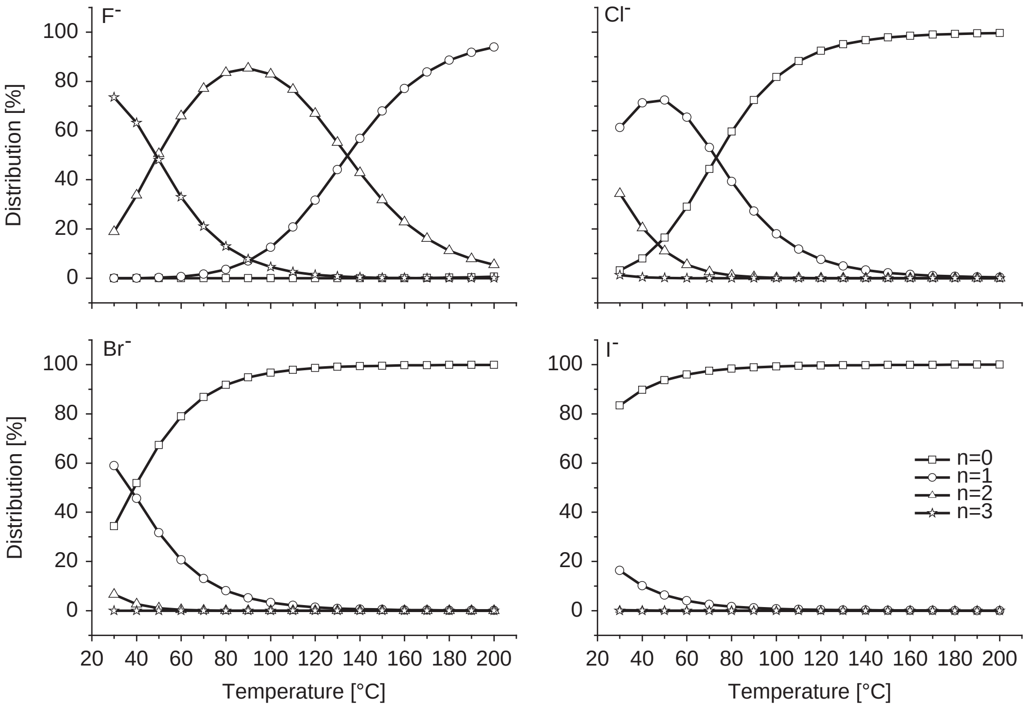

Fig. 3. Calculated degree of clustering for $X^-(H_2O)_n$ depending on the temperature (calculated for 1.5×10^{-5} atm. water partial pressure which corresponds to 15 ppm under the experimental conditions used).

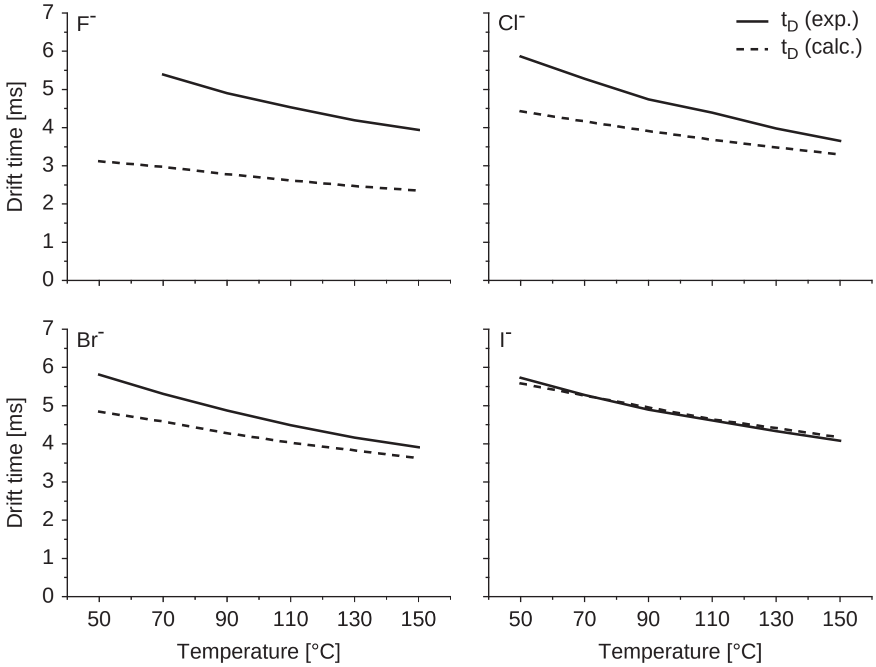

Fig. 4. Predicted drift time (dotted line) depending on temperature without consideration of ion chemistry and electrostatic interactions (calculated with the SDS module of SIMION using ionic mass and ionic radii as substance specific input parameters) and measured drift times of negative product ions formed from halogenated hexanes.

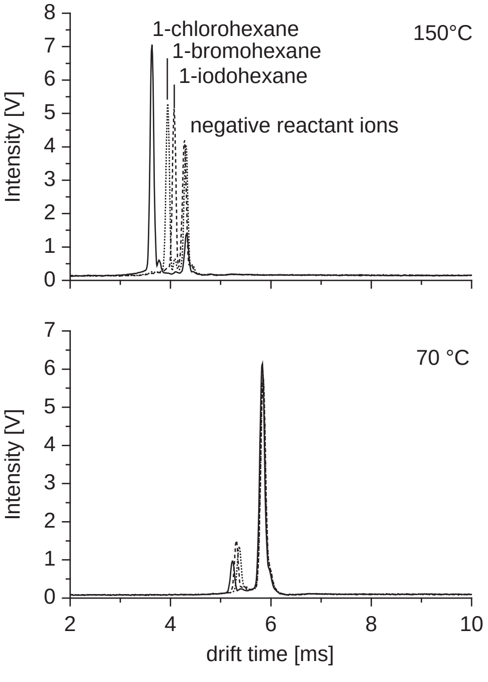

Fig. 5. Ion mobility spectra of 1-halo-hexanes obtained at 70 and 150 °C.

agreement. Cl^- and Br^- product ions show an approximation with increasing temperatures. Generally, F^- is non-detectable at 50 °C for nearly all substances. An evaluable peak can be observed above 70 °C. At this temperature, all product ion peaks appear in a drift time window between 5.28 and 5.39 ms (Fig. 5). Under the experimental conditions used, the product ion peaks of halogenated compounds are not clearly distinguishable from each other. A similar observation was found by Tabrizchi [13] where a better resolution was observed with elevated temperature, which is against the theory. However, it is notable that the length of drift tube has a significant influence on the peak-to-peak resolution and spectrometers with a longer drift tube probably permit the peak separation. A differentiation between the halide product ion peaks is possible at elevated temperatures (see Fig. 5). The order of drift times detected at 150 °C (Cl^-: 3.65 ms; Br^-: 3.91 ms; I^-: 4.08 ms) corresponds with the simulated order. A deviating behavior was established for the product ion peaks formed from fluorinated substances. These peaks appear at drift times close to brominated substances. Generally all product ions show a non-linear dependence on temperature in contrast to simulation where a nearly linear slope was established,

An explanation of these findings obviously results from the possible influence of ion chemistry. As shown in Fig. 3, I^- occurs under our experimental conditions as non-clustered ion and comparable ion chemistry can therefore be expected within the whole temperature range. The agreement between simulated and measured drift times indicates that their temperature-dependence results from different drift behavior and changes in hydration and clustering are of minor importance. In contrast to I^-, the occurrence of F^- cannot be expected. The product ions are $(H_2O)F^-$ and $(H_2O)_2F^-$ which are not comparable with F^- regarding drift behavior and interactions between product ions and drift gas molecules. Other than observed for I^-, the formation of ions with a different degree of clustering depending on the temperature are decisive for the deviating behavior of product ions from fluorinated substances. The product ions of chlorinated and brominated substances can occur as clustered ions at low temperatures while a decreasing degree of clustering can be expected with elevated temperatures. The observed approximation of simulated and measured drift times with elevated temperature suggests a significant influence on ion chemistry at lower temperatures only.

As can be seen, the possible influence of hydration and clustering depends on the physicochemical properties of analytes. A stronger influence of ion chemistry provides a stronger shift in drift time although IMS normally permits a clear separation of ions with a mass difference of 18 amu. However, the hydration and dehydration are equilibrium reactions. Due to the limited residence time in ion source, the formation of ion clusters can also occur within the drift tube and no clear peak separation can be therefore observed [23,24].

3.3. Influence of temperature on signal intensities

For halogenated compounds, increasing temperatures go along with improved sensitivity. Steepening calibration functions enables a better peak evaluation due to the bigger change in peak area with small changes in concentration. This was observed for all substances investigated. Examples are shown in Figs. 6 and 7. As can be seen, the improved sensitivity can be observed for all substituents independent on the structural features. A detailed quantification of the different slopes is not possible due to the nonlinearity of calibration curve and the concentration-dependence of sensitivity.

Comparing the different halogens, chlorine-containing compounds show a stronger temperature-dependence in contrast to Br^- and I^-. With rising temperatures we have observed a more distinct increase of peak areas. This temperature dependence also reflects the influence of ion chemistry. As described above, the degree of hydration of $(H_2O)_nCl^-$ ions decreases at elevated temperatures. Although the ion energetic data are not known, the lower degree of clustering evidently promotes the ionization reaction via dissociative charge transfer at rising temperatures.

It is described in literature that dissociative electron attachments is known to increase with increasing temperatures for many substances. The temperature dependence on signal intensity (at low electron energies) can be described as

$$I(T) = I_0 \exp\left(-\frac{E_A}{kT}\right) \tag{6}$$

where k is the Boltzmann constant and E_A the activation energy [25]. The temperature dependence reflects the thermodynamics of the particular dissociative attachment reaction. An Arrhenius plot (logarithm of detector's response as a function of the inverse temperature) shows a negative slope. This negative slope indicates a dissociative ion fragmentation electron attachment mechanism [26,27]. However, these ionization processes are influenced by ion chemistry depending on the physicochemical properties of ions formed and no clear ionization mechanism can therefore be expected.

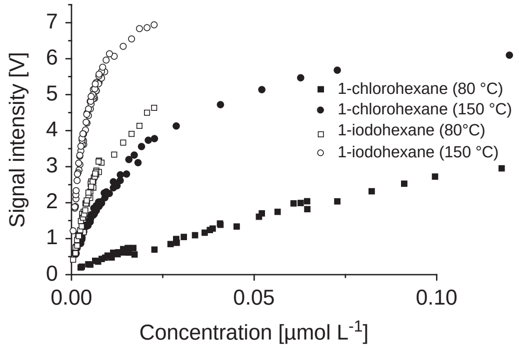

Fig. 6. Temperature-dependences of signal intensities for C_6 alkylhalogenides.

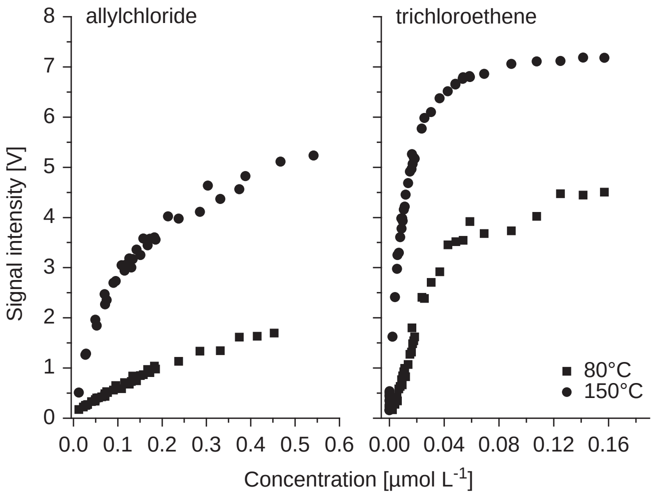

Fig. 7. Calibration curves of trichloroethylene and allylchloride depending on the temperature.

3.4. Influence of temperature on resolution

The separation efficiency in IMS can be described as resolving power (based on a single peak) or peak-to-peak resolution (based on the separation of pairs of peaks) [28]. The formulas for calculating the resolution are shown in Table 3 together with the data determined from our experiments. For comparing the resolving power (R_P), the measurements were performed by adjusting a constant peak height for each temperature. As can be seen from Table 3, the resolving power increases in the order $Cl < Br < I$. The fluorine-containing product ions were not included in this investigation due to their deviating behavior. Generally, increasing R_P values go along with a minimized influence of clustering or hydration. However, differences can be observed depending on the temperature. While RIN and $Cl^-(H_2O)_n$ peaks show comparable R_P values over the temperature range, decreasing values are observed for Br^- and I^- with elevated temperatures. The peak widths at half maximum are very close over the temperature range while decreasing drift times were established. Decreasing R_P values were therefore calculated in contrast to $Cl^-(H_2O)_n$ peaks where a significant decrease of peak widths at half maximum were found.

The concentration has only a minor influence on the resolving power for ions with no significant changes in clustering depending on the temperature. For example, 1-iodohexane was measured in concentrations between 100 ng L^{-1} and 2.2 µg L^{-1}. The R_P values of 51.3 vary ±0.8 within this concentration range.

Table 3 contains also the values of peak-to-peak resolution (R_{PP}) between RIN and product ions. Although the values for 50 °C are slightly different (3.9 (Cl^-), 2.9 (Br^-) and 1.9 (I^-), a differentiation between the product ions is practically not possible (compare with Fig. 5). The R_{PP} value of chlorine containing product ions increases with elevated temperatures due to more distinct changes in drift time while the values for bromine- and iodine-containing ions decrease. Therefore, the application of elevated temperatures permits their separation. These findings are reflected in the peak-to-peak resolution between the product ions. The R_{PP} values between chlorine product ions and iodine product ions increases from 2.9 (50 °C) to 4.7 (150 °C), between bromine product ions and iodine product ions from 0.5 to 1.2 and between chlorine product ions and bromine product ions from 2.5 to 3.1. On the other hand, it can be seen from these values that

Table 3
Resolving power of $(H_2O)_nX^-$ product ion peaks and peak-to-peak resolution between RIN (reactant ion negative) and product ion peaks observed for constant peak height over the whole temperature range.

Temp. [°C]	RIN	$X=Cl^-$		$X=Br^-$		$X=I^-$	
	R_p	R_p	R_{pp}	R_p	R_{pp}	R_p	R_{pp}
50	40.8	32.8	3.9	50.5	2.9	53.6	1.9
70	44.2	37.8	5.3	50.0	2.9	51.6	1.9
90	46.7	41.0	5.6	46.3	2.7	48.8	1.8
110	48.1	38.7	5.9	48.0	2.9	46.2	1.7
130	45.2	36.5	5.8	45.6	2.7	47.9	1.6
150	42.3	38.0	5.5	42.8	2.5	44.7	1.4

Resolving power (R_p)=drift time/ peak width at half height=($t_d/w_{0.5h}$).
Peak-to-peak resolution (R_{pp})=2 × drift time difference of the two peaks/(peak width of peak 1+peak width of peak 2)=$(2\Delta t_d)/(w_{B1}+w_{B2})$.

the present definition of resolution permits only a limited prediction regarding a possible separation of product ion peaks.

4. Conclusion

The quantitative response of halogenated substances strongly depends on the bonding state of halogen atoms within the molecule. The order of sensitivities is the same at different temperatures. However, the temperature itself affects also the relative abundance of product ions formed and the peak position in ion mobility spectrum. With elevated temperature, all compounds investigated here show a significant increase in sensitivity. The shifts in drift times result from both, clustering or hydration and differences in drift behavior depending on the features of ions formed. The shift in drift times has a considerable influence on the separation efficiency between different product ions. While low temperatures do not permit a differentiation of negative product ions formed from halogenated compounds, elevated temperatures provide a clear separation. We have shown that ion chemistry has a significant influence on the resolution in IMS and resolution measurements are therefore only useful for specific operating parameters and certain compounds. Resolution is among the most contentious features of performance to describe and compare to other methods. In comparison with other analytical techniques such as mass spectrometry where resolution is correlated with exacting parameters (mass-to-charge ratios), there is no universally accepted definition of resolution in IMS.

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