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Thermal Ionization Ion Mobility Spectrometry of Alkali Salts

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Positive and negative thermal ionization ion mobility spectra (TI-IMS) of some sodium and potassium halides are reported here. The data provide the first measurement of the thermal ionization ion mobility spectrometry of inorganic compounds. A thin Nichrome filament was used as a thermionic ionization source. Sample was directly deposited on the filament, where it was heated and ionized. Each salt produced a different ion mobility pattern, but all sodium salts spectra were common in their first peak. This peak differs from the common peak observed in the spectra of potassium salts. The drift time of the second peak in all spectra was found to be linearly dependent on the size of the counteranion of the salt. Negative thermal ionization ion mobility spectra of alkali halides were also observed. An alkali halide salt (MX), in general, produced its own anion as well as some heavier ions that are thought to be hydrated $X^-(MX)_n$ species. The capability of the method in quantitative analysis was demonstrated by measuring potassium impurity in sodium bromide. A detection limit of 0.01% K^+ in NaBr and a linear range of 3 orders of magnitude were obtained. The results from this study suggest that TI-IMS has potential as a field technique for the detection of some elements in samples.

Ion mobility spectrometry (IMS) has been known to be an excellent tool for detection of organic substances since it was introduced in 1970 by Karasek and Cohen.¹ Its high sensitivity, simplicity, and short response time contribute to its wide use in portable gas monitors to detect toxic gases, chemical warfare agents, and drugs of abuse.² It has also been used in detection of biomolecules,³ such as cytochrome c, peptides,⁴ and proteins, by employing an electrospray ionization source. In addition, surface ionization has been employed in IMS to selectively monitor nitrogen-containing base molecules.^{5,6} Despite the wide use of IMS, its application has mainly been limited to volatile organic

compounds. As with any analytical technique, the ability of IMS to detect inorganic substances is of considerable interest. In this connection, Hill has recently reported electrospray ionization ion mobility spectrometry of nonvolatile compounds such as cationic species. In his work, metal salts of nitrate, chloride, and acetate anions were examined and the elements Al, As, Cr, K, La, Mn, Ni, Pb, Sr, U, and Zn were detected at low ppm levels.⁷ Dion et al. performed electrospray IMS to separate inorganic cations in aqueous solutions.⁸ They observed a single response ion in the spectra produced from aluminum sulfate, lanthanum chloride, strontium chloride, uranyl acetate, and zinc sulfate.

Thermal ionization (TI) is a well-known technique, based on surface ionization phenomenon. This technique is widely used in mass spectrometry, particularly for isotope ratio determination.⁹ Thermal ionization is generally used for elemental analysis. In summary, an inorganic sample is deposited on a metal ribbon, such as Pt or Re, in microgram to nanogram quantities. The sample may be in the form of a solution of any chemical compound containing the element in question. An electric current heats the ribbon to a high temperature. The heating of such a thermoanode results in the thermal decomposition of the sample, with subsequent evaporation (particularly in the form of ions) and diffusion into the surface layer of the anode.¹⁰ The source is then capable of prolonged operation, which is sustained by the diffusion of the element to be analyzed to the surface.

The use of thermal ionization in IMS can be traced back to Wohltjen's¹¹ work in developing an alkali bead emissive source for selective ionization of organophosphorus compounds. A glass or ceramic bead, including an alkali metal compound on its surface, was immersed in a mixture of air and hydrogen and heated by a filament to a temperature of 200–1000 °C. When the sample gas came into contact with the alkali bead, phosphorus- and nitrogen-containing molecules were selectively ionized. Furthermore, a selective ionization source, using inorganic salts (doped solid electrolyte) that react with sample molecules was developed.¹² In the reaction region of IMS, an alkali salt was heated to provide a chemical reaction between the alkali cations or

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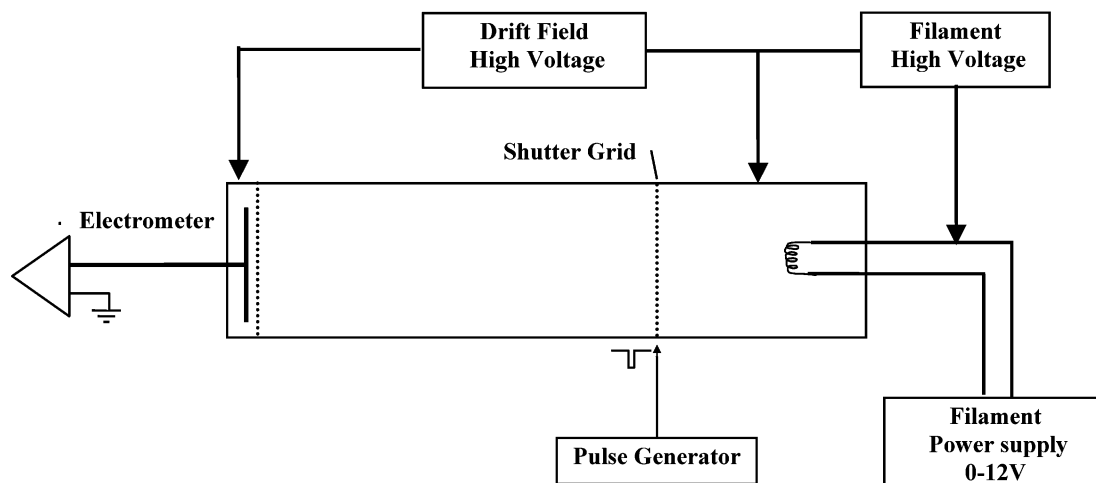


Figure 1. Electrical setup for the thermal ionization ion mobility spectrometer.

complement anions with the sample to form product ions. This source may, in some cases, operate without the need for hydrogen gas. Roehl et al. developed a variety of alkali cation emitters, including salt-coated and solid electrolytes, for the ionization source of IMS.¹³ All alkali salts used in that work, including LiCl, KF, NaCl, CsBr, and Rb₂SO₄, produced a major reactant ion at approximately the same drift time. IMS-mass spectrometric studies showed that the reactant ions were of the form $(\text{H}_2\text{O})_n(\text{N}_2)_m\cdot\text{alk}^+$, where alk^+ is the alkali cation.¹³ Organic samples were ionized via a cation attachment reaction, which produced complex ions of the kind $(\text{H}_2\text{O})_n(\text{N}_2)_m\text{M}\cdot\text{alk}^+$. The development was largely directed toward military applications.

In the present work, thermal ionization was used as the ionization source for IMS, in a way very similar to that used in mass spectrometry. The technique was employed in both positive and negative polarities to detect and characterize inorganic substances, particularly some sodium and potassium salts. The results provide the first measurement of thermal ionization ion mobility spectra of inorganic compounds.

EXPERIMENTAL SECTION

The ion mobility spectrometer used in this study is very similar to that described previously,¹⁴ except for the ionization source, which was replaced by a thermionic emitter. A thin Nichrome filament, heated by a variable-power supply, was used as the ionization source. Heater power supply was isolated from ground by a transformer. An isolated high-voltage power supply was employed to adjust the potential of the filament with respect to the first guard ring. The electrical setup is shown in Figure 1. The application of the second high-voltage power supply enabled the instrument to operate in two modes of ionization; either corona discharge or thermal ionization. When corona discharge spectrum was recorded, the filament heater was switched off but its potential was set to ~ 4 kV. For thermal ionization spectra, the filament heater was switched on and its potential was set to ~ 50 – 200 V with respect to the first guard ring.

To prevent contamination and memory effect, a separate filament was used for each substance. The filament was degassed by strongly heating it for 15 min prior to loading the sample. Then the filament was contacted with dilute solutions ($\sim 1\%$) of the alkali salt and heated to dryness before inserting to the ionization region of the IMS tube. The alkali salts used in this work were extrapure grade and were purchased from Fluka. Pure nitrogen with a flow rate of ~ 500 mL/min was used as the drift gas. No carrier gas was used in this work. The drift tube temperature was 100°C , and a drift field of 350 V/cm was used. Reduced mobilities, in positive mode, were determined with respect to the reactant ion peak ($K_0 = 2.40$ cm² V⁻¹ s⁻¹ at 100°C) of the corona discharge. For the negative polarity, the reduced mobilities were determined with respect to Cl⁻ ion peak ($K_0 = 3.05$ cm² V⁻¹ s⁻¹ at 100°C).

RESULTS AND DISCUSSION

(a) Positive Thermal Ionization. Two closely separated peaks were observed when a blank filament was heated to red, as shown in Figure 2. The intensities of the two peaks increased with the filament temperature, but they were not very sensitive to the filament potential. The observed peaks could not be due to corona discharge since the filament potential was held at 50 V (with respect to the first guard ring), which is much below the onset of the corona discharge. Due to low ionization potential, sodium and potassium are easily ionized in thermal ionization sources. Therefore, the ions produced by filament are likely to be alkali ions. Mass spectrometric studies revealed that all the elements used as filament materials show strong Na⁺ and K⁺ ion emission when heated in an ion source.⁹ Roehl and Spangler also reported $(\text{H}_2\text{O})_n(\text{N}_2)_m\text{Na}^+$ and $(\text{H}_2\text{O})_n(\text{N}_2)_m\text{K}^+$ ions in their work on alkali emissive sources.¹³ The two peaks were identified by adding a small amount of sodium or potassium salt to the filament. The sodium peak was the one that appeared in longer drift times.

Corona discharge usually started at a potential of ~ 4 kV when the filament was cold. However, when the filament was heated, increasing the filament potential above 1.5 kV started the corona discharge. In fact, the onset of the corona discharge was considerably decreased for the heated filament. It was possible to have both thermal and corona discharge ionizations at the same time. This provided the possibility of calculating the reduced

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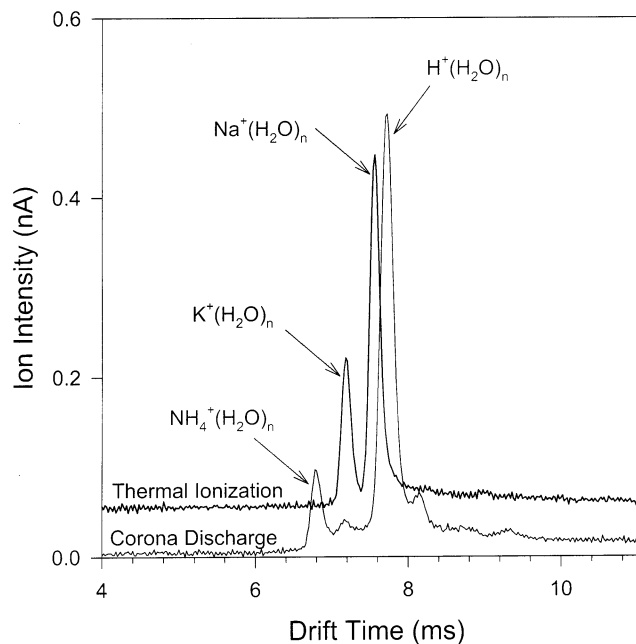


Figure 2. Ion mobility spectrum of blank filament in comparison with the spectrum recorded with corona discharge ionization source.

mobilities for the filament peaks with respect to the reactant ion peak (RIP) produced by the corona discharge. The peaks produced from the hot filament lay between the two major reactant ions of corona discharge. It is well known that the major reactant ions produced in corona discharge are protonated water clusters.¹⁵ Trace impurity of ammonium in the ionization region also gives rise to production of hydrated NH_4^+ . The reduced mobilities obtained for the hydrated ions NH_4^+ , K^+ , Na^+ , and H^+ were 2.73, 2.58, 2.45, and 2.40 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. In fact, the ions appeared on the mobility scale in the order of $\text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{H}^+$, which is opposite to their size order. The reason is that small ions give rise to stronger electric fields than large ones, so small ions are more extensively hydrated or clustered than big ions. This is also true in solution. The ionic mobilities of NH_4^+ , K^+ , Na^+ , and H^+ in water are 7.63×10^{-8} , 7.62×10^{-8} , 5.19×10^{-8} , and $36.23 \times 10^{-8} \text{ m}^2 \text{s}^{-1} \text{V}^{-1}$, respectively.¹⁶ H^+ in solution is an exception since it is easily exchanged between water molecules.

The peak intensities arising from the filament gradually decayed and reached zero after ~ 15 min under intense heating. Contaminating the filament with potassium or sodium salts restored the peak. In addition, some other peaks were also observed for each sample. Each substance showed a different ion mobility pattern as demonstrated in Figure 3 for the case of NaCl . The relative ratios of the peaks were dependent on the applied voltage, the filament temperature, and the amount of sample loaded on the filament. At room temperature, no difference was observed between the drift times of the sodium and potassium peaks. However, at elevated temperatures, the sodium and potassium peaks were well resolved.

Thermal ionization ion mobility spectra of sodium and potassium halides at 100 °C are shown in Figure 4. Spectra of sodium

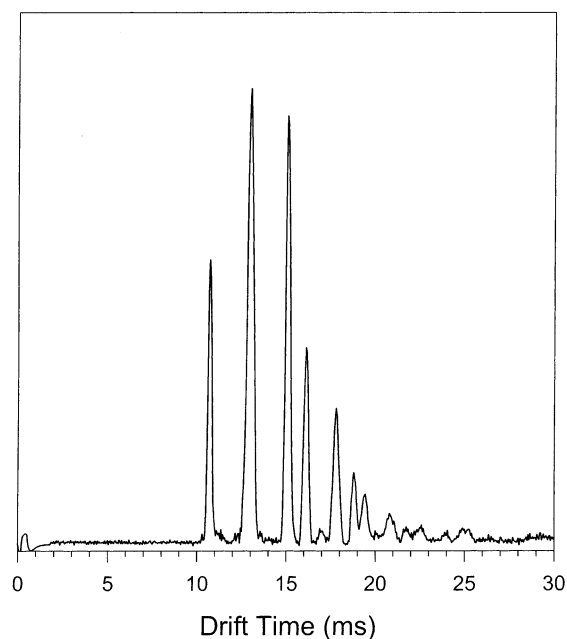


Figure 3. Thermal ionization ion mobility spectrometry of sodium chloride at 25 °C.

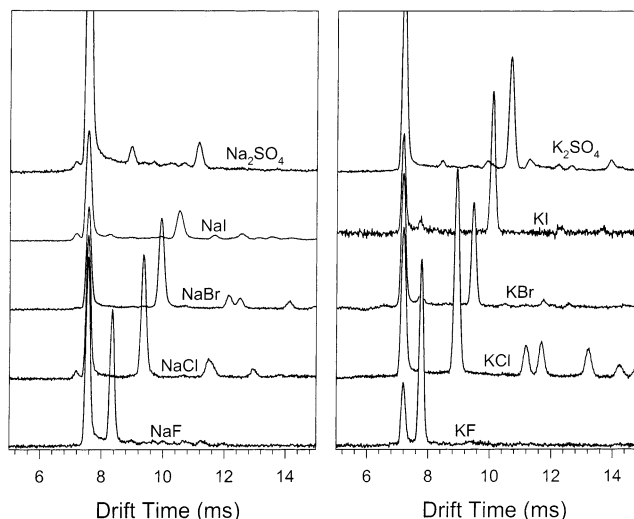


Figure 4. Thermal ionization ion mobility spectra of some sodium and potassium salts at 100 °C.

salts show a common peak, which differs from that of potassium salts. The drift time of the second peak increases with the size of the counteranion of the salt. A mass spectrometer is required to precisely identify the ions. However, in the absence of a mass spectrometer, one may speculate on the identity of the ions. Mass spectrometric analysis of the desorbed ions has shown that only M^+ ions are desorbed in the ionization of the MX salts.¹⁰ Bencsath and Field reported that thermal ionization mass spectra consist solely of the alkali cations.¹⁷ Roehl and Spangler also reported only $(\text{H}_2\text{O})_n(\text{N}_2)_m\text{Na}^+$ and $(\text{H}_2\text{O})_n(\text{N}_2)_m\text{K}^+$ reactant ions in their work on alkali emissive sources.¹³ However, Butman et al. observed K^+ , K_2^+ , K_2Cl^+ , and K_3Cl_2^+ in positive thermal ionization mass spectrometry of KCl , and Hayden and Lewis observed Na^+ and NaCl^+ (the later with less intensity) in thermal ionization of NaCl from a single tungsten filament ion source.¹⁸ Therefore,

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positive thermal ionization of an alkali halide (MX) may in general produce M^+ , M_2^+ , MX^+ , and $M^+(MX)_n$ ions. The relative intensities depend on the filament temperature, the filament potential, and the surface coverage as well as the temperature and pressure of the reaction region. Fujii et al.¹⁹ have studied the mechanism of surface ionization of alkali halides. They pointed out that the ionization at lower temperatures is governed by the dissociative ionization process and at higher temperatures it is governed by neutral dissociation and ionization process. As in this work a Nichrome filament was used as the ionizing filament, the temperature could not be increased as high as a tungsten filament in a vacuum. Therefore, it is expected that the dissociative ionization process is the dominant process and consequently M^+ ions are mainly formed. On the other hand, neutral molecules (MX) are also desorbed from the hot filament. The neutral molecules may be attached to the emitted ions to form $M^+(MX)_n$. Unlike mass spectrometry, the IMS cell is not evacuated. Thus, the partial pressure of the neutral molecules may reach an appreciable level so that clusters of the form $M^+(MX)_n$ are observed. This is very similar to formation of protonated monomer (AH^+) and dimer (A_2H^+) in conventional IMS. At elevated drift tube temperatures, the intensity of the dimer peak is reduced in favor of the monomer peak. This behavior was also observed in the case of TI-IMS. Comparison of the NaCl spectrum at 25 °C (Figure 3) and at 100 °C (Figure 4) reveals that at elevated temperatures the first two peaks survived (although shifted toward the shorter drift times) but the rest of the peaks were reduced considerably. This behavior was observed for all selected alkali salts, thus supporting the assumption of formation of $M^+(MX)_n$ clusters.

If the common peak is assigned to hydrated M^+ , then the next peak cannot be M_2^+ , otherwise a second common peak must be observed in all sodium salts or all potassium salts spectra. The next peak definitely contains the corresponding halogen of the sample since its drift time increases with the size of the anion. The observed drift times of the second peak are plotted in Figure 5 against the ionic radii of the counteranion of the salts. For both potassium and sodium salts, the drift times changes quite linearly ($r^2 > 0.998$) with the size of the counteranion. This confirms the assumption that the second peak corresponds to an ion containing the counteranion. If the drift times of potassium and sodium salts are divided by the drift time of their own common peak, the two plots interestingly superimpose and the relative drift times can be expressed as: $t_2/t_1 = 0.771 + 4.69 \times 10^{-3}R_{(X)}$, where t_2 and t_1 are the drift times of the common and the next peak for MX salt, respectively, and $R_{(X)}$ is the ionic radius of the corresponding halide (in pm). Because the second peak contains the halogen, it is either MX^+ or $M^+(MX)_n$. To identify the second peak, an experiment was performed with a mixture of KBr and NaBr. If the second peak for potassium bromide and sodium bromide is assumed to be $K^+(KBr)$ and $Na^+(NaBr)$, then the thermal ionization of a mixture of KBr and NaBr should give rise to formation of $K^+(NaBr)$ or $Na^+(KBr)$, which are practically the same. The mobility of such ion would lie between those of $Na^+(NaBr)$ and $K^+(KBr)$. This is similar to formation of asymmetric proton-bound dimers in conventional IMS. When a binary mixture of M and N is introduced into an IMS, in addition to the symmetric

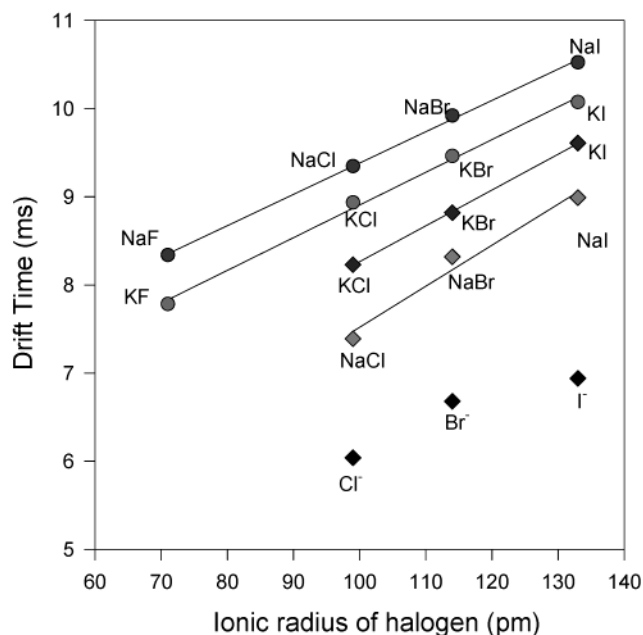


Figure 5. Observed drift time for the second major peak against the ionic radius of the anion part for alkali halides: (•) positive spectra; (◆) negative spectra.

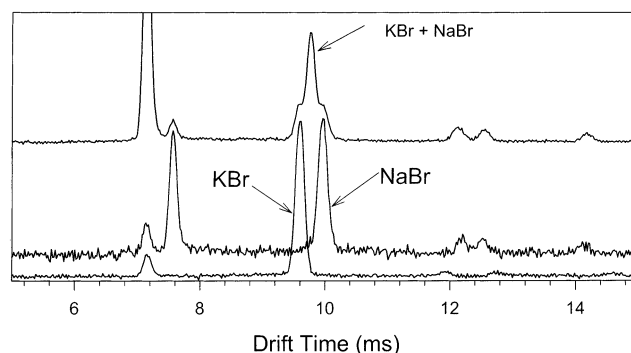


Figure 6. Thermal ionization ion mobility spectra of sodium bromide, potassium bromide, and their mixture. A new peak appeared in the mixture spectrum just between the first product ions of KBr and NaBr.

dimers AH^+A and BH^+B , a new asymmetric dimer of the form AH^+B is also formed. The asymmetric dimer appears just between the two symmetric dimers.²⁰ A mixture of KBr and NaBr was loaded on the filament, and the ion mobility spectrum was recorded. The result is presented in Figure 6, where the spectra of pure KBr and NaBr are also given. A new peak has emerged in the mixture spectrum just between the second peaks of KBr and NaBr. Similar behavior was observed for other pairs of salts. This supports the assignment of the second peak in positive spectra of alkali halides to $M^+(MX)$. In a manner similar to conventional IMS, the first peak (M^+) may be called RIP and the others will be product ions. Each group of salts, containing the same cation, has its own common RIP, but their product ions differ within that group.

(b) Negative Thermal Ionization. If the adsorbed particles on a metal surface possess electron affinity, then they may be desorbed as negative ions.¹⁰ In negative polarity, the filament

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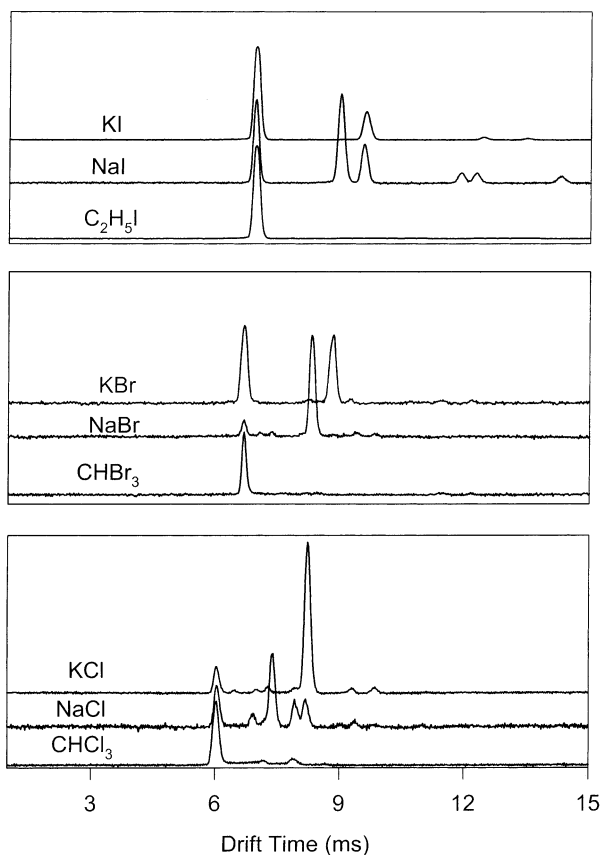


Figure 7. Negative thermal ionization ion mobility spectra of some alkali halides together with ion mobility spectra of halomethanes recorded with negative corona discharge at the same conditions.

potential was negative, with respect to the first guard ring. The blank heated filament did not show any ion emission. However, when the filament potential was increased up to ~ 1.4 kV, negative corona discharge occurred and free electrons were observed. At reduced filament potentials, when the filament was loaded with sodium or potassium halides and heated, the corresponding halide ion peaks were observed. The negative TI-IMS spectra of selected salts are shown in Figure 7. To identify the negative ions, the spectra of chloroform, bromoform, and ethyl iodide were recorded with corona discharge ionization source at the same conditions as those of thermal ionization. These halogenated compounds produce negative halide ions via dissociative electron capture reaction. It follows from Figure 7 that the salts have produced their corresponding negative halide ions under negative thermal ionization. Here again the halide ion may be called RIP. The other peaks or product ions may be formed via the attachment of the halide ion to the desorbed neutrals from the surface.

The drift time of the major product ions increases with the size of the counteranion of the salts, as demonstrated in Figure 5. If the first major product ion is assumed to be $X^-(MX)$, then thermal ionization of a mixture of XM and $X'M$ salts should give rise to formation of $X'MX$. This was examined for the pair of KCl and KI. The results are demonstrated in Figure 8. As can be seen, a new peak appeared in the mixture spectrum just between the product ions of KCl and KI. The new peak arises from $Cl^-(KI)$ or $I^-(KCl)$. The mobility of such ion lies between those of $Cl^-(KCl)$ and $I^-(KI)$ ions.

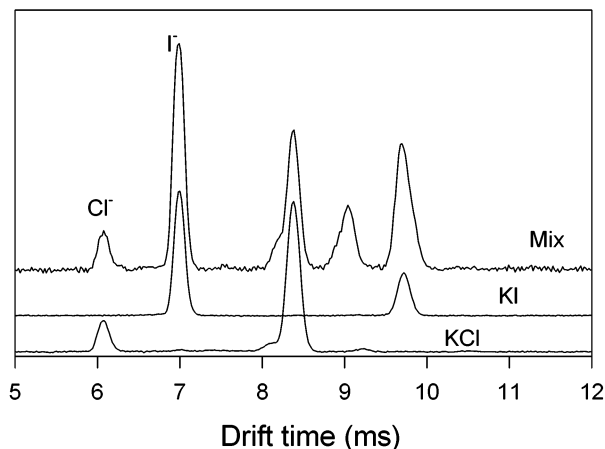


Figure 8. Negative thermal ionization ion mobility spectra of potassium chloride and potassium iodide as well as their mixture. A new peak appeared in the mixture spectrum just between the first product ions of KCl and KI, which is thought to be due to formation of $Cl^-(KI)$ ion.

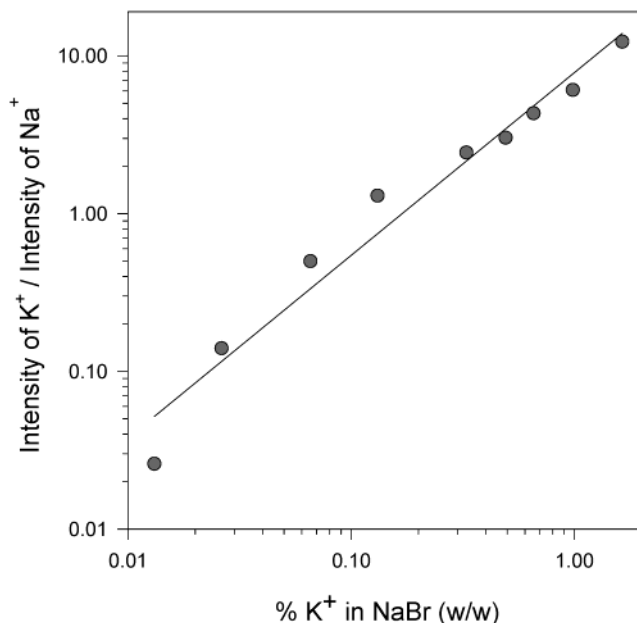


Figure 9. Ratio of potassium peak intensity to sodium peak intensity against potassium concentration in sodium bromide.

(c) Quantitative Analysis. Thermal ionization rate is exponentially proportional to the negative of the ionization potential. Potassium has a lower ionization potential (4.34 eV) than sodium (5.14 eV); thus, potassium is more efficiently ionized than sodium upon thermal ionization. Accordingly, trace impurity of potassium in sodium salts is expected to be detectable. To practically examine this, a series of standard solutions of sodium bromide with added potassium bromide as impurity were prepared and their corresponding TI-IMS spectra were recorded. The ratio of the intensity of potassium ion to that of sodium ion peak was plotted against the potassium percentage in the mixture. The calibration curve (Figure 9) has a linear dynamic range of 3 orders of magnitude with a slope of 1.1 on the log–log plot. The practical detection limit was obtained to be below 0.01% K^+ in NaBr. Iodide impurity in chloride salts may also be analyzed using negative thermal ionization IMS, because the electron affinity of iodine (3.05 eV) is lower than that of chlorine (3.61 eV).

CONCLUSIONS

Alkali elements are easily ionized due to low ionization potential. Halides are also converted to negative ions upon thermal ionization because they possess high electron affinity. The spectra presented in this work show that at least sodium and potassium cations as well as halide anions can easily be identified in inorganic samples by thermal ionization ion mobility spectrometry. Furthermore, the capability of the method in quantitative analysis was demonstrated. Determination of ultratrace levels of potassium and sodium ions in water can readily be performed. Since there is no need for vacuum in this technique, the use of IMS for such identifications is simple, rapid, and inexpensive compared to other techniques such as mass spectrometry or atomic absorption.

Just as in thermal ionization mass spectrometry, other elements may be ionized as long as their ionization potentials do not exceed that of the drift gas and water. To observe other elements, filaments with higher work function, higher working temperature

at atmospheric pressure, and better design are required. In addition, devices to detect weak ion signals down to a fraction of a picoampere at atmospheric pressure are needed. Study of other salts is being carried on, and the results will be described in future.

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