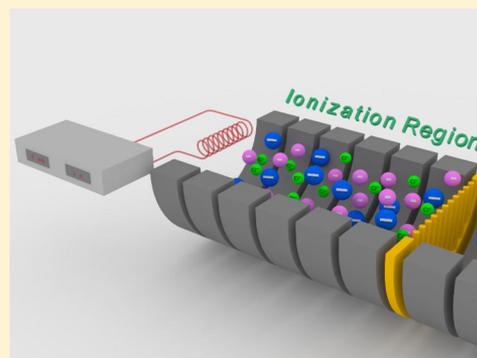


Ion Mobility Spectrometry of Heavy Metals

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S Supporting Information

ABSTRACT: A simple, fast, and inexpensive method was developed for detecting heavy metals via the ion mobility spectrometry (IMS) in the negative mode. In this method, Cl^- ion produced by the thermal ionization of NaCl is employed as the dopant or the ionizing reagent to ionize heavy metals. In practice, a solution of mixed heavy metals and NaCl salts was directly deposited on a Nichrome filament and electrically heated to vaporize the salts. This produced the IMS spectra of several heavy-metal salts, including CdCl_2 , ZnSO_4 , NiCl_2 , HgSO_4 , HgCl_2 , PbI_2 , and $\text{Pb}(\text{Ac})_2$. For each heavy metal (M), one or two major peaks were observed, which were attributed to $\text{M}\cdot\text{Cl}^-$ or $[\text{M}\cdot\text{NaCl}]\text{Cl}^-$ complexes. The method proved to be useful for the analysis of mixed heavy metals. The absolute detection limits measured for ZnSO_4 and HgSO_4 were 0.1 and 0.05 μg , respectively.



Heavy metals and transition metals naturally occur in the Earth's crust, drinking water, airborne particulates, dust, and living organisms in the form of single elements, complexes, or ions. Some heavy metals such as cadmium (Cd), mercury (Hg), and lead (Pb) are toxic and cause damage to DNA, thereby affecting the immune, renal, nervous, and hematopoietic systems.^{1–4} However, small amounts of such metals as zinc (Zn) or iron (Fe) are essential for the metabolic activities and blood cell production in organisms.^{5,6} Therefore, the detection and measurement of metals in foods, drinks, vegetables, and blood samples are of great interest.

A significant effort has been devoted to the development of techniques and innovative methods of heavy-metal detection. Such methods as Fourier transform infrared (FTIR) spectroscopy,^{7,8} electron spin resonance (ESR) spectroscopy,⁹ chemiluminescence (CL),^{10,11} capillary electrophoresis (CE),¹² ion chromatography,^{13,14} extended X-ray absorption fine structure spectroscopy (EXAFS),¹⁵ and spectropolarimetry¹⁶ have been used for the detection and analysis of transition metals. The conventional methods employed to measure heavy-metal ions in aqueous solutions or in the solid phase include inductively coupled plasma–mass spectrometry (ICP-MS),^{17,18} instrumental neutron activation analysis (INAA),¹⁹ atomic absorption spectroscopy (AAS),²⁰ X-ray fluorescence (XRF) spectroscopy,²¹ and anodic stripping voltammetry (ASV).²² Despite their accuracy and sensitivity, these methods are usually expensive and require complicated sample preparation procedures in some cases. The present article presents a simple and cost-effective method for the analysis of certain heavy and transition metals by ion mobility spectrometry (IMS).

IMS is a fast, simple, and inexpensive technique for the detection and analysis of organic volatile compounds.^{23–29} In IMS, the sample is initially vaporized and ionized. A continuous current of ions is then pulsed by a shutter grid and drifted

under a constant electric field at atmospheric pressure. While in the drift region, the ions are separated according to their mobility, which, in turn, is dependent on their mass, charge, and size. The arrival times of ions are registered by a Faraday cup to yield the ion mobility spectrum.

IMS is usually used for the analysis of volatile organic compounds. However, inorganic compounds have rarely ever been studied by IMS, because of their high melting points. Subjecting metals to IMS was first reported by Hill et al.,³⁰ who used an electrospray to produce cations in the gas phase. Detection of solid inorganic samples with high melting points requires a proper means for bringing them into the gaseous phase. Laser vaporization has been employed by Fye and Jarrold³¹ to vaporize and analyze metal-coated fullerenes by IMS. In addition, the use of thermal ionization (TI) for the study of alkali salts by IMS was first reported in our previous work.³² To the best of the authors' knowledge, no other study of ion mobility spectra of heavy metals has been reported in the literature. As the continuation of our TI-IMS work,³² in the present work, we attempted to extend the application of IMS to a wider range of cations by introducing a simple and fast method for the detection of transition and heavy metals in the negative mode. For this purpose, a Nichrome filament was employed for the vaporization process, and NaCl was used as the ionizing reagent.

EXPERIMENTAL SECTION

Ion Mobility Spectrometry. The IMS equipment used in this work was manufactured by TOF Tech. Co. (Iran).³³ The

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IMS cell that was constructed, 16 cm in length, consisted of aluminum rings. The cell temperature was 200 °C, with a drift field of 467 V/cm. A Bradbury–Nielsen shutter grid, with an opening time of $\sim 100 \mu\text{s}$ at 20 ms intervals, was mounted on the fourth ring to pulse the ions into the drift region (11 cm). A thin Nichrome filament was also used to vaporize the heavy-metal salts and to ionize the alkali salts. The filament was mounted at the beginning of the IMS tube, with a potential of 200 V, with respect to the first ring (Figure 1). The filament

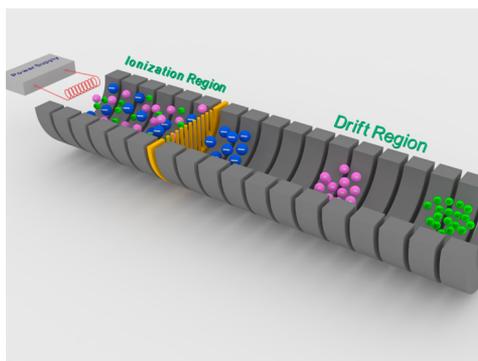


Figure 1. Schematic setup of the thermal ionization–IMS used for the detection of heavy metals.

was electrically heated by an isolated power supply with its voltage adjustable in the range of 0–10 V. Dry air was used as the drift gas after its residual water content had been removed by a 13X molecular sieve (Fluka) trap. No carrier gas was needed in this work. More instrumentation details can be found in the relevant literature.^{32,34}

Sample Preparation. The selected heavy-metal salts were purchased from Sigma–Aldrich, except for lead acetate and zinc sulfate, which were obtained from William & Hopkins. The NaI, NaBr, NaCl, and NaF used were Fluka products. Deionized distilled water was used as the solvent in all the solutions prepared.

For each experiment, a solution was prepared containing the heavy-metal salt (1%) and NaCl (1%) as the ionizing reagent or the dopant. Ten microliters (10 μL) of the solution was deposited dropwise on the filament to be heated by applying a voltage of 4–5 V until its solvent evaporated and a solid mixture of the heavy metal salt and NaCl remained on the filament surface. The filament was then inserted into the ionization region of the IMS tube (Figure 1) and heated electrically. In this situation, the IMS equipment was operating in the negative mode, so that only the anions would be detected. Additional experiments were carried out in the positive mode to find that most of the metal salts did not show any stable or strong signals in the positive mode in the presence or absence of NaCl. Furthermore, blank experiments were also carried out in the negative mode without the ionizing reagent (NaCl), and no signal was observed. Clearly, the selected metals would then be optimally detected in the negative mode and in the presence of NaCl as the ionizing reagent. The efficiencies of NaF, NaBr, and NaI used as ionizing reagents were also investigated. The most-intense and less-interfered spectra were only observed when NaCl was used as the dopant.

RESULTS AND DISCUSSION

Ion Mobility Spectra. Figure 2 shows the ion mobility spectra of both pure NaCl and NaCl mixed with CdCl₂,

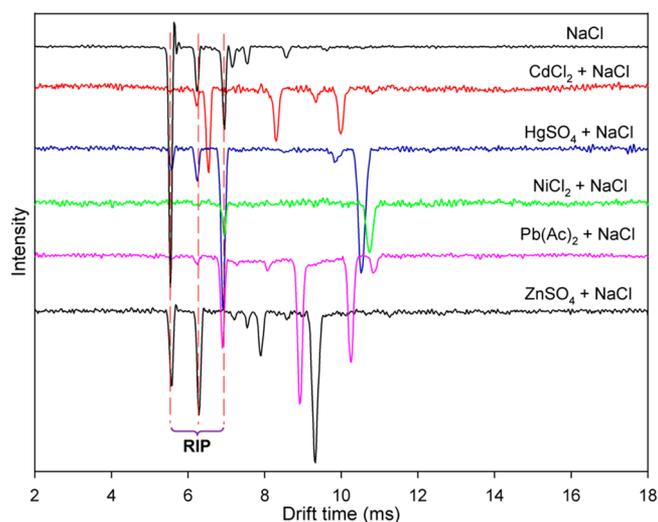


Figure 2. Ion mobility spectra of pure NaCl and mixtures of metal salts and NaCl in the negative mode.

HgSO₄, NiCl₂, Pb(Ac)₂ (where Ac denotes acetate), and ZnSO₄ in the negative mode. The upper spectrum belongs to pure NaCl with its peak at 5.6 ms and a reduced mobility of 2.5 cm² V⁻¹ s⁻¹, probably because of the presence of the [NaCl]Cl⁻ species, rather than the Cl⁻ anion, because the Cl⁻ peak produced by the corona discharge characteristically appears at a lower drift time of ~ 4.5 ms in the negative mode. Other peaks in the NaCl spectrum could be related to the different complexes of NaCl with Cl⁻, such as [NaCl]_nCl⁻.³² Since the heavy-metal salts did not exhibit any signals in the absence of NaCl, it was concluded that the peaks observed in the spectra must have been related to the adduct ions of the heavy metals and [NaCl]_nCl⁻ ions. Similar to normal ion mobility spectra, the first few peaks, denoted by dashed lines, could be regarded as reactant ion peaks (RIPs).

It is observed in each spectrum that the heavy metals exhibited strong additional product ion peaks, in addition to those of NaCl-RIPs. Two strong sharp peaks were also observed for CdCl₂, Pb(Ac)₂, and ZnSO₄ in each case, while NiCl₂ and HgSO₄ showed only one product peak. The drift times of the observed peaks, relative to the first NaCl peak, are reported in Table 1.

Table 1. Drift Times of the Peaks Observed for the Selected Metals and NaCl, Relative to That of the First NaCl Peak

compound	Drift Time		
	Peak 1	Peak 2	Peak 3
NaCl	1	1.12	1.25
CdCl ₂	1.5	1.81	
Pb(Ac) ₂	1.61	1.85	
ZnSO ₄	1.69	1.43	
NiCl ₂	1.93		
HgSO ₄	1.90		

Peak Assignment. Precise assignment of the observed peaks can be accomplished using a mass spectrometer, which is coupled with an IMS system. However, some structural information about the reactant and the product ions may be obtained from the thermal ionization mass spectrometric studies of alkali salts reported in the literature and further

supplemented by only a few additional experiments. The first reactant ion peak originating from NaCl is probably $[\text{NaCl}]\text{Cl}^-$, which is the product of NaCl thermal ionization on the filament. Because of the high concentration of NaCl on the filament, the Cl^- peak was not observed. The other RIPs were assumed to originate from the combination of Cl^- and gaseous NaCl molecules, as described in ref 32. Other peaks appearing in the presence of metal salts could be considered to be the product ion peaks (PIPs). Since these peaks appeared only in the presence of NaCl, and also because the intensity of the NaCl reactant ion peaks was reduced, at the same time, it was concluded that their corresponding product ions either formed via the charge transfer from RIPs or they were the adduct ions formed by the attachment of Cl^- or its clusters to the heavy metals. Given the fact that chlorine has a high electron affinity, relative to metals or metal salts, no charge transfer from the Cl^- ion or its clusters could have occurred; thus, the attachment assumption seems to be the more likely event in which the adduct ions ($\text{M}\cdot\text{Cl}^-$) were produced via Cl^- transfer from the $[\text{NaCl}]_n\text{Cl}^-$ ions to the metals. Alternatively, it could be postulated that a product ion of ($\text{M}[\text{NaCl}]_n\text{Cl}^-$) was produced because of the attachment of $[\text{NaCl}]_n\text{Cl}^-$ to the metals. However, since it is difficult for product ions with a large n to form, the observed PIPs must have been formed due to either $\text{M}\cdot\text{Cl}^-$ or $\text{M}[\text{NaCl}]\cdot\text{Cl}^-$.

In the case of adduct formation, a different product ion is produced if the reactant ion is changed. This was investigated by performing experiments with different reactant ions, and different sodium halide salts were used as the dopants. Then, ZnSO_4 was added to each sodium halide salt and the resulting spectrum was recorded. The background spectra of pure alkali salts in the negative mode are shown in the Supporting Information (Figure S1(a)). New major product ion peaks are denoted by asterisks in Figure 3 to compare the IMS spectra of ZnSO_4 with those of NaF, NaCl, NaBr, and NaI as ionizing reagents. In all of the spectra, the first peaks were assumed to originate from the $[\text{NaX}]\text{X}^-$ anions ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$)³² with the drift times in the order of

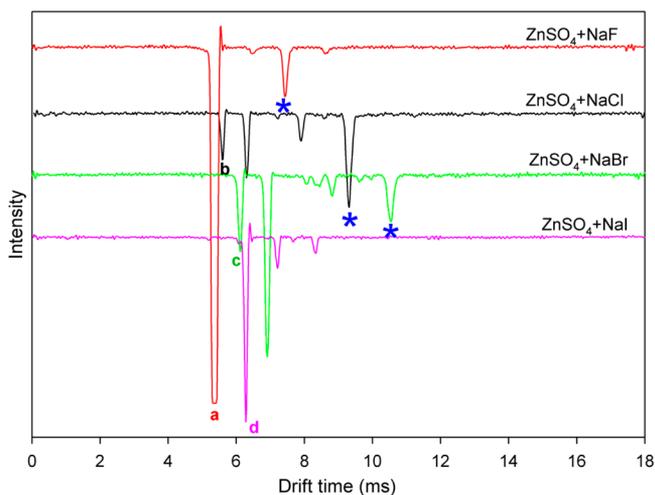
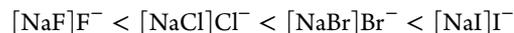


Figure 3. IMS spectra of ZnSO_4 with NaF, NaCl, NaBr, and NaI used as ionizing reagents. Different ionizing reagents exhibit different product ion peaks (denoted by asterisks). The reactant ions coming from NaF, NaCl, NaBr, and NaI peaks are shown by the letters “a”, “b”, “c”, and “d”, respectively.



These peaks have been marked as “a”, “b”, “c”, and “d”, respectively, in Figure 3. The order of the new product ion peaks in the drift time scale was also found to be similar to that observed for the reactant ions. It was revealed that the product ion was an adduct containing the halide reactant ion and the metal. Similar behavior was observed with other metals.

No product ion was observed when NaI was used as the dopant. Nevertheless, comparison of the spectra shown in Figure 3 and the similar trend observed with other metals indicate that $[\text{NaCl}]\text{Cl}^-$ is a better ionizing reagent than $[\text{NaF}]\text{F}^-$ and $[\text{NaBr}]\text{Br}^-$, because it provides stronger and more separated peaks.

Based on the observations in Figure 3, we may assume that at least one product ion was in the form of $\text{M}\cdot\text{Cl}^-$ or $\text{M}[\text{NaCl}]\text{Cl}^-$. If the latter is true, a mixture of NaF and NaCl must produce two different product ions, that is, $\text{M}[\text{NaF}]\text{F}^-$, $\text{M}[\text{NaCl}]\text{Cl}^-$, and a new species— $\text{M}[\text{NaF}]\text{Cl}^-$ or $\text{M}[\text{NaCl}]\text{F}^-$, which expectedly appeared between the two original product ion peaks. To explore the possibility of the formation of $\text{Zn}[\text{NaCl}]\text{F}^-$ or $\text{Zn}[\text{NaF}]\text{Cl}^-$, the IMS spectrum of ZnSO_4 was recorded in the presence of a mixture of NaF and NaCl as the ionizing reagent. Figure 4 compares the spectra of $\text{ZnSO}_4 +$

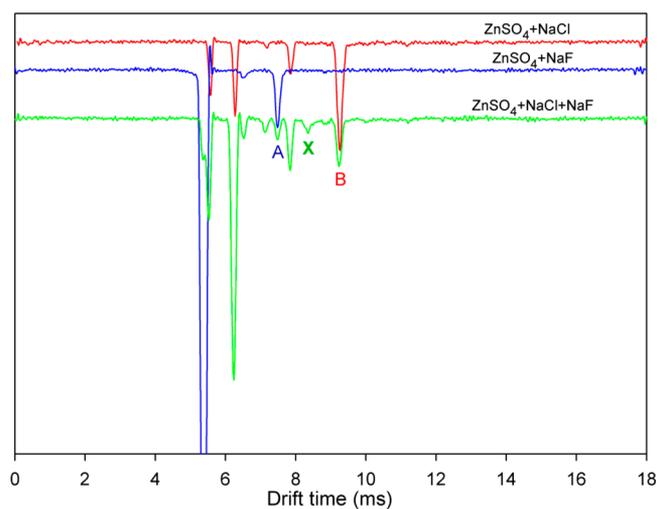


Figure 4. Comparison of the spectra of $\text{ZnSO}_4 + \text{NaF}$, $\text{ZnSO}_4 + \text{NaCl}$, and $\text{ZnSO}_4 + \text{NaF} + \text{NaCl}$. The product ion peaks “A” and “B” appeared at 7.45 and 9.25 ms, respectively. The new peak “X” was observed at 8.35, exactly in the middle of the two peaks; hence, the new product ion was in the form of $\text{Zn}(\text{NaF})\text{Cl}^-$ or $\text{Zn}(\text{NaCl})\text{F}^-$.

NaF and $\text{ZnSO}_4 + \text{NaCl}$ with that obtained in the presence of a mixture of NaF and NaCl. If the observed peaks “A” (7.45 ms) and “B” (9.25 ms) were due to $\text{Zn}[\text{NaF}]\text{F}^-$ and $\text{Zn}[\text{NaCl}]\text{Cl}^-$, respectively, a new peak $\text{Zn}[\text{NaCl}]\text{F}^-$ or $\text{Zn}[\text{NaF}]\text{Cl}^-$ would then be expected to have appeared within a drift time of ~ 8.35 ms. It is clear from Figure 4 that the new peak (“X”) emerging in the spectrum of the mixture was located exactly on the drift time of 8.35 ms. This new peak was not observed in any background spectra of NaCl, NaF, or even NaCl + NaF (see the Supporting Information).

The product ion peaks observed in Figure 4, denoted by the letters “A” and “B”, cannot be related to $[\text{ZnF}]^-$ and $[\text{ZnCl}]^-$, since the emergence of the new peak in the spectrum of ZnSO_4 with a mixture of NaF + NaCl would not be justified. In other words, based on the drift times of peaks A, B, and X, at least the

existence of two Cl or two F atoms in complexes A and B is necessary to observe a heterogeneous $[\text{ZnNaFCl}]^-$ complex. Therefore, the major anionic complexes of heavy metals with the NaCl reagent can be assigned to $M[\text{NaCl}]_n\text{Cl}^-$, where M denotes the heavy metal. These results confirm that the first peak in the NaCl spectrum as the main RIP is $[\text{NaCl}]_n\text{Cl}^-$, rather than Cl^- .

Qualitative Analysis. Figure 5 shows the IMS spectra of the two pairs of salts, $\text{PbI}_2/\text{Pb}(\text{Ac})_2$ and $\text{HgSO}_4/\text{HgCl}_2$, with

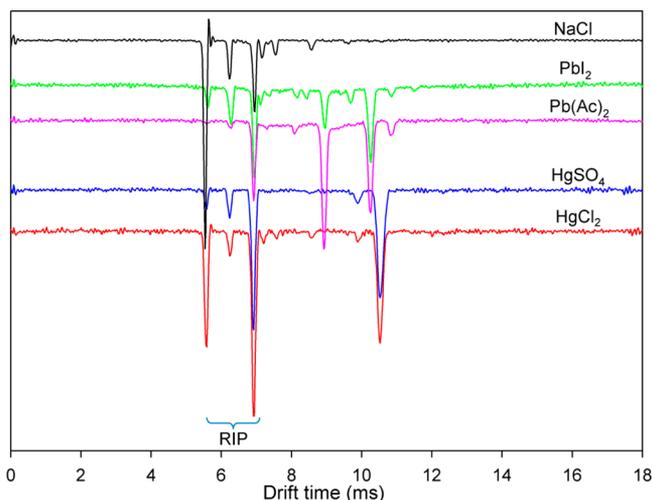


Figure 5. IMS spectra of NaCl and two pairs of salts with the same metal but different counterions: $\text{PbI}_2/\text{Pb}(\text{Ac})_2$ and $\text{HgSO}_4/\text{HgCl}_2$. The product ions were similar for each pair.

similar metals but different counterions. The product ion peaks observed in the spectra for the Pb salt pair were the same, although their counterions were different. This was also true in the case of Hg salts. This observation implies that the counterion in the metal salt is not responsible for the formation of the negative product ion complex. In addition, heavy-metal salts decompose at high temperatures, releasing metal atoms.^{35,36} Hence, the metal counterions are not stable to form independent negative ions or to participate in the negative complex ion. Therefore, it may be concluded that the observed product ion peak was due to the heavy-metal element in the form of an adduct with the reactant ion species $[\text{NaCl}]_n\text{Cl}^-$.

Mixtures. This method was employed to analyze heavy-metal mixtures. For example, Figure 6 shows the IMS spectra for the mixture of ZnSO_4 and HgSO_4 (with similar counterions), as well as that of ZnSO_4 and $\text{Pb}(\text{Ac})_2$ (different counterions), with NaCl as the ionizing reagent. The product ion peaks for Zn, Hg, and Pb in their pure spectra were present in the mixture spectra. No additional peak was observed in the spectrum for the mixture, indicating no combination of heavy ions in the complex. Figure 6 is also important from an analytical viewpoint, indicating that the proposed method can be used for the detection of heavy-metal mixtures without any interference.

Quantitative Analysis. The calibration curve for ZnSO_4 obtained by the thermal ionization–IMS method is linear from 0.1 μg to 1.0 μg and saturates at $\sim 10 \mu\text{g}$. An experimental absolute detection limit of 0.1 μg was obtained for ZnSO_4 . The measurement was also repeated for HgSO_4 to obtain a detection limit of 0.05 μg . The detection limits obtained using this method are not as good as those reported for ICP-

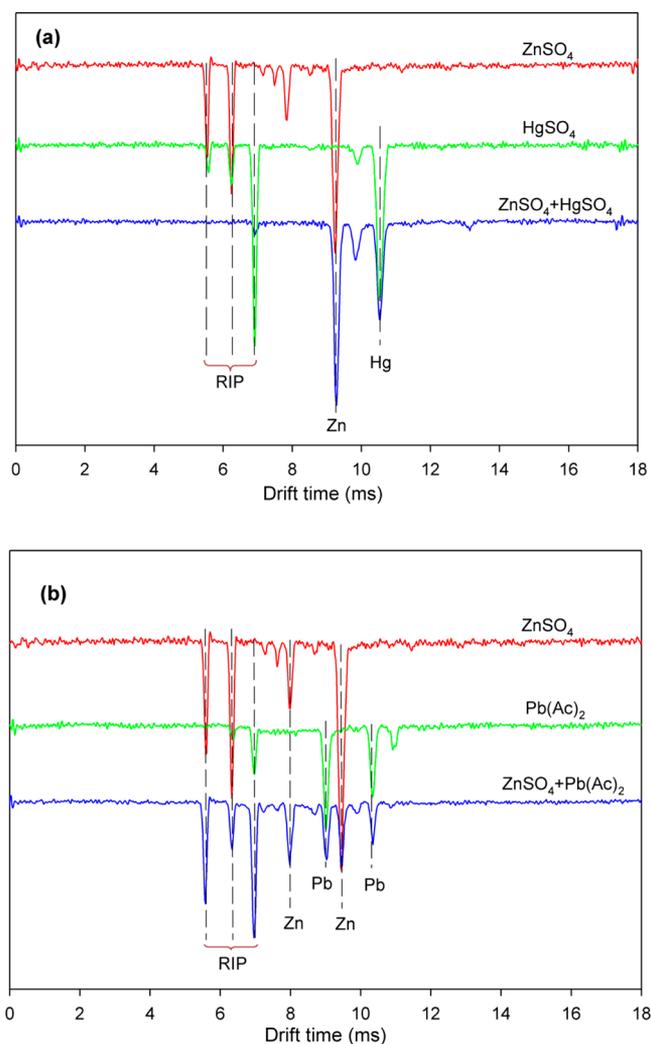


Figure 6. Analysis of heavy-metal mixtures, showing the IMS spectra for mixtures of (a) ZnSO_4 and HgSO_4 and (b) ZnSO_4 and $\text{Pb}(\text{Ac})_2$, with NaCl as the ionizing reagent.

MS¹⁷ and AAS.³⁷ However, the thermal ionization–IMS method is fast, simple, and inexpensive, and it works well at atmospheric pressures without the need for any vacuum equipment.

CONCLUSION

In this work, a method was proposed that extends the application of IMS to the identification of inorganic compounds, specifically metal salts. The technique relies on heating and evaporating the inorganic salt, together with the NaCl reagent in the negative mode. The $[\text{NaCl}]_n\text{Cl}^-$ ion thus released acts as the reactant ion to form an adduct ion with the metal in the gaseous phase. The product ions are believed to be in the form of $M[\text{NaCl}]_n\text{Cl}^-$ complexes, although a mass spectrometer is required to identify the ions exactly.

It was demonstrated that each metal, regardless of its counterion, generated unique peaks characteristic of that metal. Therefore, this can be a promising technique for the analysis and identification of transition metals and heavy metals by IMS. However, organic compounds cause no interference in this technique, since they are burned and vaporized on the filament before the metal peak appears.

In addition to being inexpensive, the technique is simpler to perform than most conventional methods. Moreover, it does not require complicated sample preparation procedures, since the sample is directly deposited on the filament. Another advantage of the method is its rapidity, as compared to most existing methods. Future research may focus on the detection of trace levels of heavy metals such as cadmium, mercury, and lead in environments such as water, beverages, and food.

Apart from the analytical purposes the proposed method serves, it is useful for the study of the reactions between halide ions and heavy metal compounds under atmospheric conditions. The kinetics and thermodynamics of such reactions may be studied in the gas phase by IMS to provide informative and interesting results that are useful in environmental chemistry.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.6b01664.

IMS spectra of NaF, NaCl, NaBr, and NaI in the negative mode and at 200 °C, as well as a comparison of pure NaF and NaCl spectra with their mixture spectrum (Figure S1) (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Verstraeten, S. V.; Aimo, L.; Oteiza, P. I. *Arch. Toxicol.* **2008**, *82*, 789–802.
- (2) Jarup, L.; Akesson, A. *Toxicol. Appl. Pharmacol.* **2009**, *238*, 201–208.
- (3) Johnson, F. M. *Mutat. Res., Rev. Mutat. Res.* **1998**, *410*, 123–140.
- (4) Hyman, M. *Altern. Ther. Health Med.* **2004**, *10*, 70–75.
- (5) Hambidge, K. M.; Krebs, N. F. *J. Nutr.* **2007**, *137*, 1101–1105.
- (6) Rouault, T. A. *PLoS Biol.* **2003**, *1*, e79.
- (7) Salmain, M.; Vessieres, A.; Jaouen, G.; Butler, I. S. *Anal. Chem.* **1991**, *63*, 2323–2329.
- (8) Salmain, M.; Vessieres, A.; Top, S.; Jaouen, G.; Butler, I. S. *J. Raman Spectrosc.* **1995**, *26*, 31–38.
- (9) Burns, D. T.; Dalgarno, B. G.; Flockhart, B. D. *Anal. Chim. Acta* **1989**, *218*, 93–100.
- (10) Jones, P.; Williams, T.; Ebdon, L. *Anal. Chim. Acta* **1990**, *237*, 291–298.
- (11) Ussher, S. J.; Milne, A.; Landing, W. M.; Attiq-ur-Rehman, K.; Seguret, M. J. M.; Holland, T.; Achterberg, E. P.; Nabi, A.; Worsfold, P. *J. Anal. Chim. Acta* **2009**, *652*, 259–265.
- (12) Zhu, R.; Kok, W. Th. *Anal. Chim. Acta* **1998**, *371*, 269–277.
- (13) Nordmeyer, F. R.; Hansen, L. D.; Eatough, D. J.; Rollins, D. K.; Lamb, J. D. *Anal. Chem.* **1980**, *52*, 852–856.
- (14) Mohamed, R. A.; Abdel-Lateef, A. M.; Mahmoud, H. H.; Helal, A. I. *Chem. Spec. Bioavailab.* **2012**, *24*, 31–38.
- (15) Dewald, H. D.; Watkins, J. W., II; Elder, R. C.; Heineman, W. R. *Anal. Chem.* **1986**, *58*, 2968–2975.
- (16) Palma, R. J., Sr.; Reinbold, P. E.; Pearson, K. H. *Anal. Chem.* **1970**, *42*, 47–51.
- (17) Tormen, L.; Gil, R. A.; Frescura, V. L. A.; Martinez, L. D.; Curtius, A. J. *Anal. Chim. Acta* **2012**, *717*, 21–27.
- (18) McCormick, S. P.; Moore, M. J.; Lindahl, P. A. *Biochemistry* **2015**, *54*, 3442–3453.
- (19) Almeida-Silva, M.; Canha, N.; Freitas, M. C.; Dung, H. M.; Dionisio, I. *Appl. Radiat. Isot.* **2011**, *69*, 1586–1591.
- (20) Bannon, D. I.; Murashchik, C.; Zapf, C. R.; Farfel, M. R.; Chisolm, J. J. *Clin. Chem.* **1994**, *40*, 1730–1734.
- (21) Margui, E.; Queral, I.; Hidalgo, M. *TrAC, Trends Anal. Chem.* **2009**, *28*, 362–372.
- (22) Armstrong, K. C.; Tatum, C. E.; Dansby-Sparks, R. N.; Chambers, J. Q.; Xue, Z. *Talanta* **2010**, *82*, 675–680.
- (23) Iceman, C.; Rue, C.; Moision, R. M.; Chatterjee, B. K.; Armentrout, P. B. *J. Am. Soc. Mass Spectrom.* **2007**, *18*, 1196–1205.
- (24) Langejuergen, J.; Allers, M.; Oermann, J.; Kirk, A.; Zimmermann, S. *Anal. Chem.* **2014**, *86*, 7023–7032.
- (25) Ewing, R. G.; Atkinson, D. A.; Eiceman, G. A.; Ewing, G. J. *Talanta* **2001**, *54*, 515–529.
- (26) Fernandez-Maestre, R.; Harden, C. S.; Ewing, R. G.; Crawford, C. L.; Hill, H. H., Jr. *Analyst* **2010**, *135*, 1433–1442.
- (27) Vautz, W.; Sielemann, S.; Baumbach, J. I. *Anal. Chim. Acta* **2004**, *513*, 393–399.
- (28) Borsdorf, H.; Fiedler, P.; Mayer, T. *Sens. Actuators, B* **2015**, *218*, 184–190.
- (29) Tabrizchi, M.; Ilbeigi, V. *J. Hazard. Mater.* **2010**, *176*, 692–696.
- (30) Dion, H. M.; Ackrman, L. K.; Hill, H. H., Jr. *Int. J. Ion. Mobility Spectrom.* **2001**, *4*, 31–33.
- (31) Fye, J. L.; Jarrold, M. F. *Int. J. Mass Spectrom.* **1999**, *185*–187, 507–515.
- (32) Tabrizchi, M. *Anal. Chem.* **2003**, *75*, 3101–3106.
- (33) *TOF tech. Pars Co.*; www.toftech.ir, 2015.
- (34) Bahrami, H.; Tabrizchi, M. *Talanta* **2012**, *97*, 400–405.
- (35) Tariq, S. A.; Hill, J. O. *J. Therm. Anal.* **1981**, *21*, 277–281.
- (36) Patnaik, P. *Handbook of Inorganic Chemicals*; McGraw-Hill: New York, 2003.
- (37) Fen, Y. W.; Yunus, W. M. M. *Sens. Rev.* **2013**, *33*, 305–314.