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Capture of air particulate matter and gaseous Hg⁰ by ionic liquids analyzed by PIXE

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Particle induced X-ray emission (PIXE) has been extensively employed to study the elements associated to air particulate matter (PM). However, the atmosphere is a very complex system and inorganic pollutants may be also in gaseous phases. Aerosol monitoring does not allow the determination of all the volatile inorganic compounds, since they are not retained in the filters, or if they are trapped, the analysis under vacuum results in a partial or total loss of them. In order to extend the applications of PIXE there is a need to develop new methods to simultaneously capture particulate matter and volatile substances.

Ionic liquids (IL) result from combinations of organic cations and anions that may be liquid at room temperature. The physicochemical characteristics of ILs allow them to absorb atmospheric trace metals present in solid and gaseous phases, a task normally performed with independent sampling methods. In this work we explored this capability of ILs as monitors of chemical species which can be found in the gas phase and as particulate matter. The tested ILs included 1-Butyl-3-Methyl-Imidazolium-Hexafluorophosphate [BMIM][PF₆] for PM and Hg capture; and 1-Butyl-3-methylimidazolium thiocyanate [BMIM][SCN] only for Hg capture. Elemental analysis of both experiments was performed by Particle Induced X-ray emission (PIXE). Changes in the molecular structure on BMIM PF₆ due to the Hg binding were followed by infrared (IR) spectroscopy. [BMIM][PF₆] proved to be successful as passive collector of PM. However when both were used for Hg capture, [BMIM][SCN] showed better selectivity. These preliminary results showed the potential of IL's for simultaneous uptake of PM and volatile inorganic compounds.

Keywords: Ionic liquids; passive monitoring; PIXE.

La emisión de rayos X inducida por partículas (PIXE) se ha empleado ampliamente para estudiar los elementos asociados al material particulado suspendido en el aire (MP). Sin embargo, la atmósfera es un sistema muy complejo y los contaminantes inorgánicos pueden también estar en fase gaseosa. El monitoreo de aerosoles no permite la determinación de todos los compuestos inorgánicos volátiles, ya que no se conservan en los filtros, o se pierden durante el análisis al vacío. A fin de ampliar las aplicaciones de PIXE es necesario desarrollar nuevos métodos para capturar simultáneamente partículas y sustancias volátiles. Los líquidos iónicos (LI) se obtienen al combinar cationes orgánicos y aniones y pueden ser líquidos a temperatura ambiente. Las características fisicoquímicas de los ILs les permiten absorber metales traza presentes en el aire en fase sólida o gaseosa, una tarea que normalmente se realiza con métodos de muestreo independientes. En este trabajo exploramos esta capacidad de ILs como monitores de especies químicas presentes como gases o asociados a partículas. El IL usado para la captura de PM y Hg es el 1-Butyl-3-Methyl-Imidazolium-Hexafluorophosphate [BMIM] [PF₆] y para la captura de Hg el 1-butyl-3-methylimidazolium [BMIM] [SCN]. El análisis elemental en ambos experimentos se hizo con la técnica de PIXE. Los cambios en la estructura molecular del [BMIM][PF₆] debido a la incorporación de Hg, se siguieron por espectroscopia infrarroja (IR). [BMIM][PF₆] demostró para ser exitoso como colector pasivo de MP. Sin embargo cuando se usaron ambos para captura de Hg [BMIM] [SCN] mostró una mejor selectividad. Estos resultados preliminares mostraron el potencial de los LI para la captación simultánea de PM y compuestos inorgánicos volátiles.

Descriptores: Líquidos iónicos; monitoreo pasivo; PIXE

PACS: 78.70.Ck; 61.25.hk

1. Introduction

Particle induced X-ray emission (PIXE) has been extensively employed in atmospheric pollution research since trace element analysis is performed in a rapid, non-destructive, and multi-element analytical way. PIXE is ideal for the analysis of aerosol filters, since it has all the necessary characteristics to analyze with a high degree of sensitivity inorganic pollutants associated to particulate matter (PM). However, the atmosphere is a very complex system and inorganic pollutants may be also in gaseous phases. Aerosol filters cannot retain all the volatile inorganic compounds and, if they are trapped,

PIXE analysis under vacuum results in a partial or total loss of them. Part of the problem comes from the fact that all sorption substrates are designed to retain only inorganic species in particulate matter and are unable to retain gaseous forms. Collection of gaseous inorganic species must be performed independently either by a direct collection in a container or through sampling during a time-period where the gas is concentrated onto a solid or liquid absorbent. New materials and methods need to be developed if solid and volatile substances are collected simultaneously.

Ionic liquids (ILs) are materials being actively used in environmental studies and show high gas absorption. These

compounds are organic salts that result of the combination of organic cations and inorganic anions that remain as ions in liquid phase up to 100°C. They are able to dissolve a variety of organic and inorganic compounds, biological molecules and metallic ions [1-3]. There is a great variety of substances that can be used to make IL's, but most of them are based on a combination of organic cations (e.g. imidazolium, pyridinium, phosphonium, quaternary ammonium, pyrrolidinium, guanidinium, and triazolium) with a variety of anions (e.g. Cl⁻, Br⁻, I⁻, AlCl₄⁻, NO₃⁻, PF₆⁻, BF₄⁻, CF₃COO⁻, SCN⁻). Their low vapor pressure makes them very suitable to capture volatile compounds and some IL's have been used to remove CO₂, SO₂, PAHs, O₃ and metallic Hg from air [4-5]. Also, the presence of ligand ions and the ability of ILs to complex metallic cations, makes them potential candidates in the development of new materials capable of collecting particulate matter. With the proper selection of anion and cation, IL's could be designed to simultaneously collect inorganic ions associated to PM or in their gaseous phase. Their properties and thermal stability may then be used to develop new passive monitors based on ionic liquids.

The purposes of this study were twofold: to explore the performance of ILs i) to capture particulate matter (PM) suspended in air and ii) to absorb and retain a volatile inorganic species such as gaseous Hg⁰. In the first approach, ILs were directly exposed to the air at two small towns in the Tula industrial zone using the ILs as passive monitors of PM. In the second approach, a laboratory experiment was designed to test the ability to capture and retention of metallic gaseous Hg⁰ by ILs, since it cannot be retained by filters and 95% of the Hg in the atmosphere is under the gaseous phase [6].

We tested 1-Butyl-3-Methyl-Imidazolium-Hexafluorophosphate [BMIM][PF₆] IL for PM; and [BMIM][PF₆] as well as 1-Butyl-3-methylimidazolium thiocyanate [BMIM][SCN] for Hg capture. Quantitative analyses of the pollutants deposited in the ILs were determined by PIXE. Changes in the molecular structure of [BMIM][PF₆] due to the Hg binding were followed by infrared (IR) spectroscopy.

2. Material and Methods

2.1. Sensitivity in the PIXE analysis

The relative sensitivity in the PIXE analysis was measured by testing [BMIM][PF₆] samples containing different concentrations of a reference material (Chicago aerosol RM-NIST1548A).

2.2. Field study

Passive collection of atmospheric particulate matter by ILs was performed using a sampler shown in Fig. 1. A known volume of [BMIM][PF₆] was deposited in a clock glass and the samplers were placed in the roof of a house at two locations of the Tula Industrial corridor: Tula and Tepeji del Río, Hidalgo. Major and trace elements were quantified after 24

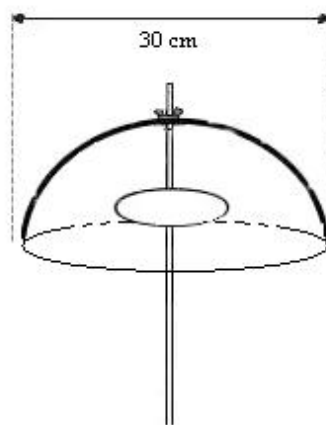


FIGURE 1. A schematic diagram of the passive collection of PM in a 6 cm clock glass containing the IL. The clock glass is covered with a protective semispherical plastic screen to avoid big particles to enter in collector.

and 37 days of exposure. After exposure, ILs were taken to the laboratory and analyzed by PIXE.

2.3. Mercury capture

Mercury capture by ILs was explored in a laboratory experiment. Elemental Hg (1 g) was introduced in a 70 mL test tube creating an artificial atmosphere of gaseous elemental Hg. A drop of 20 μ L of [BMIM][PF₆] IL deposited in a prolene film was introduced in the test tube. After 6 weeks of exposure the IL was removed, encapsulated as described below, and stored until PIXE analysis.

2.4. Encapsulation of ILs and PIXE analysis

Because of its high viscosity, ILs can be easily encapsulated between two layers of film and the analysis can be performed with a relatively high beam current (about 50 nA). Therefore, a drop of IL (20 μ L) containing the reference material, particulate matter or Hg, was encapsulated between two layers of prolene (4 μ m thick) forming a sandwich and immobilized in a Mylar holder, as reported previously [5]. PIXE analyses were carried out using a 2.5 MeV proton beam in a Van der Graaff tandem at the National Institute of Nuclear Research (ININ).

2.5. IR analysis

The exact nature of the interactions between Hg and ILs (e.g., complex formation or electrostatic interactions) is still unknown. Infrared spectrometry may be useful to follow changes in the IL structure after binding Hg and was applied in this study. Spectra of ILs exposed to gaseous Hg and were obtained in a Vector 33 Bruker spectrometer at a resolution of 4 cm⁻¹ and 32 scans with a single reflection ATR accessory equipped with a diamond crystal, at the Applied Physics and Advanced Technology Center, UNAM.

3. Results

3.1. General

The variations of relative sensitivity in the PIXE analysis of ILs samples loaded with different concentrations of the Chicago aerosol reference material were carried out. Ionic liquids alone have a negligible background. Table I shows the obtained results for some selected elements that were detected by PIXE. The concentrations obtained experimentally are in good agreement with the actual concentrations.

In the field experiment, major and trace elements present in atmospheric particulate matter captured by [BMIM][PF₆] from Tula and Tepeji del Río were quantified after several days of exposure. Figure 2 shows a PIXE spectrum of an IL exposed for 37 days at Tula Hidalgo. Elements such as S, Cl, Ca, Ti, Fe, Cu, Zn, Pb and Sr were easily detected. Other elements such as V, which is associated to oil refinery industry were also present in most samples. Figure 3 shows the accumulation for Ca, Fe, V, and Zn, in Tula as well as in Tepeji del Río after 24 and 37 days of exposure. Except for V, levels of the selected elements are higher in Tula. As expected, the elemental concentration increased with time of exposure. The high levels of Ca observed in both sites are explained by the limestone quarries present in the Tula industrial corridor.

TABLE I. Element concentration of selected elements in [BMIB]PF₆. Twenty μ L were taken from a preparation of 50 mg of Chicago aerosol (RM-NIST 1548a) in 1 mL of IL.

Element	Certified mg/kg	Experimental mg/kg	Error (%) (peak fitting)	LOD mg/kg mg/kg
Ca	58400	55500	5	70
Ti	4021	4150	7	40
Mn	790	674	5	12
Fe	39300	39800	5	15
Zn	4800	4740	10	12

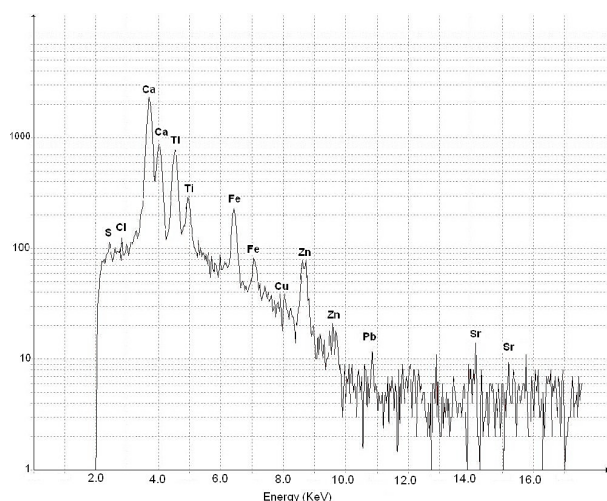


FIGURE 2. PIXE spectrum of [BMIM][PF₆] after exposure for 37 days at Tula Hidalgo.

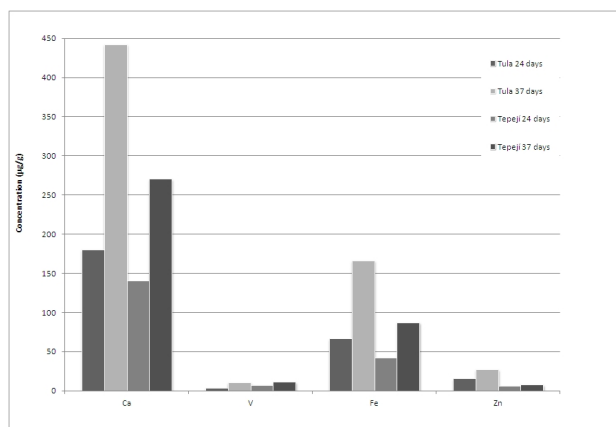


FIGURE 3. Accumulation of Ca, V, Fe and Zn in el [BMIM][PF₆] at 24 and 37 days of exposure at Tula and Tepeji del Río (TR).

[BMIM][PF₆] is one of the most frequently IL used in environmental studies [7]. Therefore we tested it for Hg capture. Figure 4 shows the infrared spectra of this IL after several weeks of exposure to Hg⁰. There were no changes in peak position in the infrared spectra. The lack of changes in neither peak positions nor bandwidths indicates that there is no interaction with Hg. Similar results were obtained with PIXE, where low amounts of Hg were detected after several weeks. Therefore we considered the use of an IL carrying SCN⁻ as the anion portion, which is known to be a good ligand for transition metals. Figure 5 shows the PIXE spectra of [BMIM][PF₆] and [BMIM][SCN] after 6 weeks of exposure to Hg⁰. It can be observed that SCN⁻ is much more effective for Hg capture where the L X-ray emission lines characteristic of Hg are clearly seen, indicating the higher affinity of Hg by thiocyanate. PIXE sensitivity is good enough to show the presence of traces of Fe, Cu and Zn present in the Hg reagent grade used.

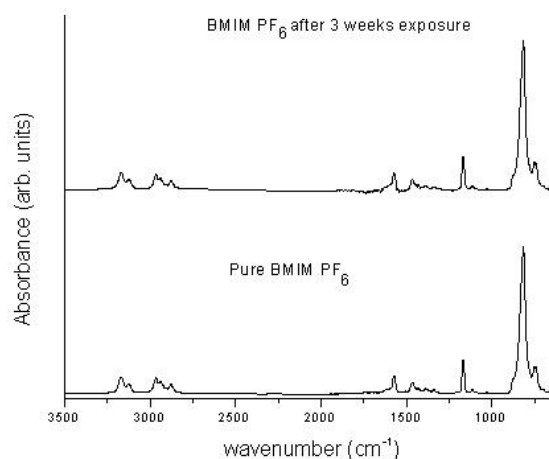


FIGURE 4. Infrared spectra of pure BMIM PF₆ and after 3 weeks of exposure to Hg⁰, from 3500 to 600 cm⁻¹.

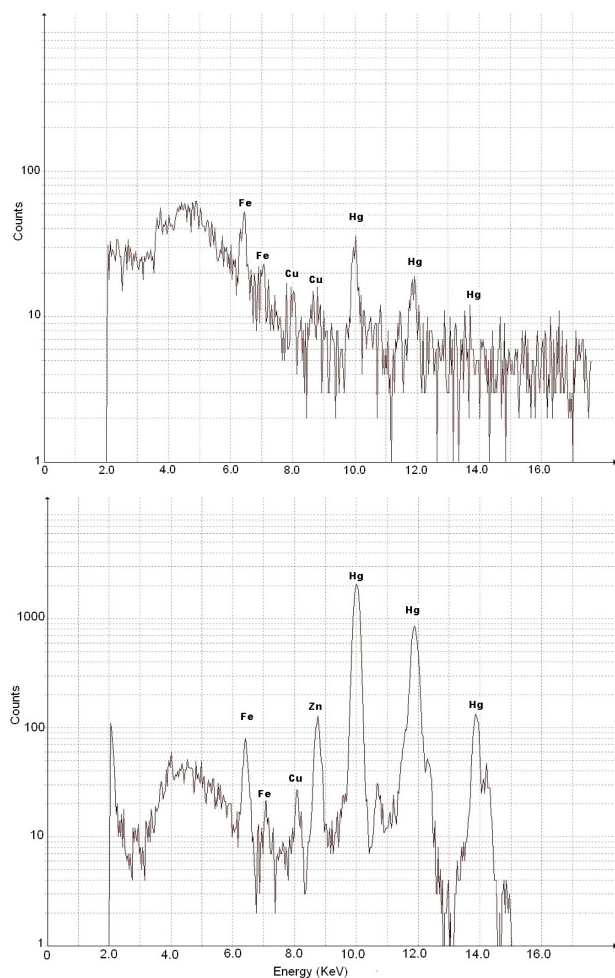


FIGURE 5. PIXE spectrum of IL in prolene after 6 weeks of exposure. Top: BMIM-PF₆, Bottom: BMIM-SCN.

4. Conclusions

We propose the use of ILs as passive monitors of airborne PM and volatile inorganic species such as gaseous Hg⁰. [BMIM][PF₆] exposed to two locations from the Tula industrial corridor was able to capture air particulate matter. Accumulation of some elements in ILs varied as a function of the exposure time and site in response to their presence in the atmosphere. Particulate matter incorporation tested with Chicago aerosol reference material did not show important matrix effects in PIXE analysis. Mercury uptake was tested with [BMIM] with PF₆ and SCN as anions. [BMIM][PF₆] was not effective in the capture of gaseous Hg⁰. Its low capacity to form bonds with mercury was confirmed by infrared spectroscopy, since spectra did not change at least during 3 weeks of exposure to Hg⁰. [BMIM][SCN] resulted significantly more effective for Hg⁰ capture and therefore may be considered as a promising IL for simultaneous uptake of PM and volatile inorganic compounds. Experiments for simultaneous capture with this and other ILs are under way. Infrared and Raman will be very helpful to understand the nature of interaction of Hg with IL, but more work is needed before ILs can be applied for real study cases.

Acknowledgments

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