



Translocation of uranium from water to foodstuff while cooking



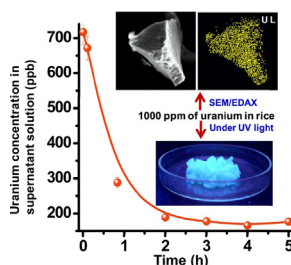
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HIGHLIGHTS

- Rice can efficiently uptake uranium from water contaminated with uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), while cooking.
- Unusual uranium uptake to the extent of about 1000 ppm is observed when rice is cooked in highly concentrated uranium contaminated water (1240 ppm).
- Nature of interaction of uranium with carbohydrates is probed using small monosaccharides like glucose and mannose.
- Electrospray ionization mass spectrometry showed UO_2^{2+} to be the most stable species in water in such solutions which can form complexes with sugars.
- The species (UO_2^{2+}) is also observed in the case of water exposed to the common mineral, uranium oxide (UO_2) and similar type of complexation is observed with sugars.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work reports the unusual uranium uptake by foodstuff, especially those rich in carbohydrates like rice when they are cooked in water, contaminated with uranium. The major staple diet in South Asia, rice, was chosen to study its interaction with UO_2^{2+} , the active uranium species in water, using inductively coupled plasma mass spectrometry. Highest uptake limit was checked by cooking rice at very high uranium concentration and it was found to be a good scavenger of uranium. To gain insight into the mechanism of uptake, direct interaction of UO_2^{2+} with monosaccharides was also studied, using electrospray ionization mass spectrometry taking mannose as a model. The studies have been done with dissolved uranium salt, uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), as well as the leachate of a stable oxide of uranium, $\text{UO}_2(\text{s})$, both of which exist as UO_2^{2+} in water. Among the eight different rice varieties investigated, Karnataka Ponni showed the maximum uranium uptake whereas unpolished Basmati rice showed the minimum. Interaction with other foodstuffs (potato, carrot, peas, kidney beans and lentils) with and without NaCl affected the extent of chemical interaction but was not consistent with the carbohydrate content. Uranium interaction with D-mannose monitored through ESI-MS, under optimized instrumental parameters, identified the peaks corresponding to uranyl adduct with mannose

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monomer, dimer and trimer and the species were confirmed by MS/MS studies. The product ion mass spectra showed peaks illustrating water loss from the parent ion as the collision energy was increased, an evidence for the strong interaction of uranium with mannose. This study would constitute the essential background for understanding interaction of uranium with various foods. Extension of this work would involve identification of foodstuff as green heavy metal scavengers.

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1. Introduction

Heavy metal contamination of the environment and livestock has been a growing concern of multidisciplinary interest, the impact of which has socio-political to scientific implications. The legacy of metal contamination so far comprises mostly of arsenic [1,2] followed by lead, [3–7] cadmium [4,6–10] and mercury [7,11] with more elements being identified as industrial exploitation increases. Extensive studies have been carried out on arsenic contamination of water resources, soil, vegetation and various environmentally relevant systems. Studies on the adverse effects of Cd, Pb and Hg have also been carried out and effective treatment methods have evolved [3,6,7,11–19]. Many documented cases of contamination due to other transition and rare earth elements also exist [1,20,21]. Other heavy metals including radioactive ones are also drawing attention lately [20,22–29]. Uranium has received significant attention over the last few decades owing to its promising applicability as a prospective energy power. These studies are important in India where it is estimated that uranium production will increase, as a result of the use of pressurized heavy water reactor technology utilizing enriched uranium. The principal ores of uranium are urania (mostly UO_2) and coffinite ($\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$). Solubility products of these oxides (in terms of $\log K_{\text{sp}}$) are in the range of -8.5 . In natural waters it exists as uranyl hydroxide and carbonate species. Recently efforts have been made to find the basis of uranium mobility and its effects on the environment have been reported. Pompe et al. [30] have investigated the interaction of UO_2^{2+} with humic acids (HAs) with and without modification and found that phenolic OH groups decide the complexation behavior of HAs. Uranium complexes formed after the uptake by plants were studied by Nitsche et al. [28]. In another work, the authors have reported different uranium speciation in water near to uranium mines by experimental determination as well as by modelling for the different U(VI) species, at specific pH range [29]. Compounds of relevance include $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (aq) in carbonate- and calcium-containing mine waters from Schlema, Germany at pH 7.1. Uranium speciation changes depending on the pH and the ions and concentrations present in water. They have found that in carbonate-containing and calcium-poor tailing water from Helmsdorf at pH 9.8, $\text{UO}_2(\text{CO}_3)_3^{4-}$ is the most abundant uranium species, while UO_2SO_4 (aq) was the most abundant uranium species from sulfate-rich mine water in Königstein, Germany at pH 2.6 [29].

Even though respiratory intake and epidermal contact of uranium can cause health issues, it is through drinking water and food consumption the major propagation and biomagnification of uranium takes place in animals [31]. Recent studies on other mammals like rats and rabbits suggest that even the non-radioactive isotopes can cause hazardous effects in biosphere [23]. Studies based on the intake of uranium by animals showed that solubility of uranium is a crucial factor that determines its metabolism in the body. It appears that the amount of soluble uranium accumulated internally is proportional to the intake from ingestion or inhalation [22,32]. Igarashi et al. [26] has reported that the maximum allowed limit of uranium in humans is $40 \mu\text{g/kg}$ with approximate 40% present

in the muscles, 20% in the skeleton and 10%, 4%, 1% and 0.3% in the blood, lungs, liver and kidneys, respectively. Health hazards caused by exposure to uranium in rats and rabbits were evaluated by several research groups and changes in organs including kidney and liver were monitored [23,24]. Effect on humans consuming uranium contaminated drinking water in countries all over the world especially in Canada, Finland, Sweden, Ireland and USA suggested renal tissues are affected primarily [25].

The uranium poisoned environment and ecosystem demand effective remediation which should start with research on the basics of uranium interaction with biomolecules. From previous studies, it was found that many heavy metals bind with various carbohydrate moieties and contribute to the spread of contamination in environment and health hazards in vegetation [33,34]. Our investigation substantiates the need to list uranium in the category of heavy metals capable of strongly interacting with foodstuff. Since rice is the staple food in many countries (mainly Asian countries), even small uptake of uranium by the same deserves an extensive study as the permissible World Health Organization (WHO) limit for drinking water is 15 microgram/L. To study the mechanism of uranium-rice interaction, we chose D-mannose as a model monosaccharide and investigated the product using electrospray ionization mass spectrometry (ESI-MS).

2. Experimental section

2.1. Materials

Uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was purchased from Thomas Bakers. Glucose and mannose were purchased from Sigma-Aldrich and Sisco Research Laboratories Pvt. Ltd., respectively. All the rice varieties and other foodstuff used in the study were obtained from the local market. All the chemicals were used without further purification and deionized water was also used throughout the experiment. Urania (UO_2) was gifted by IGCAR, India.

2.2. Instruments

Inductively coupled plasma-mass spectrometry (ICP-MS) measurements of the samples were done with a PerkinElmer NexION 300X instrument. Prior to ICP-MS analysis, the non liquid samples were digested using an Anton Paar microwave digester at 800 W for 20 min. Scanning electron microscopy (SEM) and energy dispersive analysis of the X-ray (EDAX) images were collected using an FEI QUANTA-200. X-ray photoelectron spectroscopy (XPS) studies were conducted with an Omicron ESCA probe spectrometer with polychromatic Mg $K\alpha$ X-rays ($h\nu = 1253.6 \text{ eV}$). Electrospray ionization mass spectrometry (ESI-MS) analysis was carried out using Applied Biosystems 3200 QTRAP LC/MS/MS system in the mass range of m/z 80 to 1700. The optimized conditions used are as follows: declustering potential (DP) = 60 V, entrance potential (EP) = 10 V, ion spray voltage (IS) = 3 kV, collision energy (CE) = 10–60 V, collision cell exit potential (CXP) = -1 V .

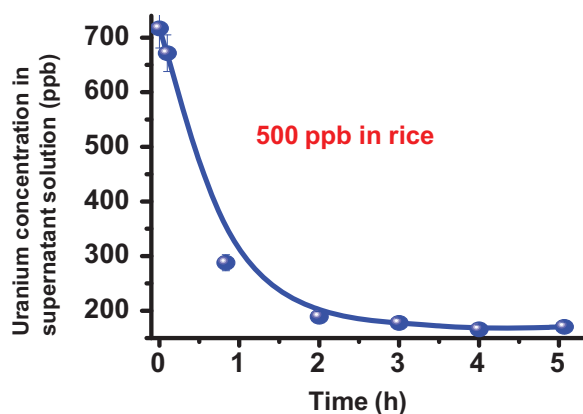


Fig. 1. Decrease in the uranium concentration in the supernatant solution with time during cooking of Karnataka Ponni rice in water containing 720 ppb of uranium.

2.3. Methods

2.3.1. Uranium interaction with rice and other foodstuffs

Eight different rice varieties were chosen for the study including polished and unpolished of each variety. For each one, 2 g of rice was weighed and cooked in 40 mL of 1 ppm $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution at 80°C (solution temperature) in a teflon beaker for a period of 2 h. Simultaneously a blank of the rice sample without uranium salt was also cooked under the same conditions. For ICP–MS analysis, it was collected 1 mL of the supernatant (starch) solution with regular time interval (0.5 h) and 43.4 μL of concentrated nitric acid was added (to make it 5% as standards are also made by this procedure for our instrument). After complete cooking, the entire rice was divided in two equal parts in two digestion tubes, followed by the addition of 1 mL water, 2 mL H_2O_2 and 5 mL concentrated HNO_3 and digested using a microwave digester, working at high pressure and temperature (reference method). The digested samples were diluted and subjected to ICP–MS analysis. A sample of the cooked rice was analyzed to estimate the uranium content in it using SEM, EDAX and XPS methods. For this, a small amount of the cooked rice was oven dried and ground into a fine powder prior to analysis.

UO_2 was stirred in water for 1 h, centrifuged and collected the supernatant which was analyzed for its uranium content. This solution was used as stock solution for reactions with UO_2 .

2.3.2. Uranium interaction with a simple carbohydrate as the model system

In order to explore the chemistry of uranium–rice interaction, it was synthesized uranium–mannose adduct following a previously reported method [35]. A 20 mL solution of 2 mM $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to a hot solution of D-glucose (1 mM) in deionized water (30 mL) and heated for 30 min at 80°C . The solution was diluted using deionized water and samples of concentration ranging from 5 ppb to 50 ppm were prepared and analyzed by ESI–MS.

3. Results and discussion

3.1. Uptake of uranium by rice

The results of the investigated uranium interaction with eight different rice samples cooked in water contaminated with uranium is presented in Figs. 1 and 2 and Table 1. Fig. 1A shows a continuous and fast decrease in the uranium concentration in supernatant solution, upon cooking Karnataka Ponni rice which tends to reach a constant value. This implies that rice is uptaking uranium from water while being cooked. Other rice varieties also show more or less similar trend as shown in Fig. 2. Degree of uranium uptake

Table 1

Uranium uptake by different rice varieties per g of the sample. P, UP, B stand for polished, unpolished and boiled, respectively.

Rice variety	Uranium uptake/g of rice (in ppb)
T.N. Ponni (P, B)	314
T.N. Ponni (UP, B)	595
Basmati (P)	465
Basmati (UP)	340
Karnataka ponni	734
Kerala rice	402
Idli rice	375
IR 20	429

depends both on uranium concentration and variety of rice used. Almost all the uranium was uptaken within 2 h which is reflected by a drastic decrease in uranium concentration in the supernatant solution (Fig. 1). After 3 h of cooking, the process attains equilibrium with no significant change in the concentration thereafter confirming that the rice has attained its maximum uranium uptake capacity (see later in Fig. 3). After 5 h of cooking, the rice was digested and analyzed, following the method described above, to estimate the uranium concentration inside and it was found to be in a good agreement with the supernatant solution concentration as the initial concentration of uranium was 720 ppb while after 5 h of cooking, in the supernatant it was found to be 180 ppb and about 500 ppb in the cooked rice. Uranium uptake experiments were performed with different rice varieties considering both polished and unpolished rice. Uranium concentration in rice after cooking is given in Table 1. Among all, Karnataka Ponni (polished) rice showed highest uranium uptake capacity, whereas T.N. Ponni (polished) has the lowest capacity to concentrate uranium from the solution. Compared to the unpolished variety, polished variety of Basmati rice scavenges uranium more readily from solution whereas for T.N. Ponni, the case is opposite. Therefore, it cannot draw any conclusion whether the polish (rice bran) is affecting or not the uranium uptake. This capability seems strongly depends on the rice variety (see Fig. 2).

Although it was seen that rice can uptake high amounts of uranium, the concentration reached in the experiments (Table 1: above 500 ppb) are not adequate to conduct studies using EDAX, XPS, etc. To overcome this problem, it was tried to find the limit of uptake of uranium in rice. For this study, a 1240 ppm uranium solution (prepared from $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was used and cooked rice was soaked in it. After 4 h of soaking, only 245 ppm of uranium was left in the solution. Under visible light the rice color is yellow and shows light green fluorescence under UV light due to uranium (Fig. 3A). The fluorescence might be masked due to inherent blue fluorescence from rice. A sample of the cooked rice was oven dried, ground and used for XPS, SEM and EDAX analyses and the corresponding data are represented in Fig. 3B–D, respectively. The SEM–EDAX analysis of a small portion of rice shows the presence of uranium along with other elemental components and it is evenly distributed throughout the rice as seen from elemental mapping (Fig. 3B). From XPS analysis, binding energies of U 4f7/2 and 4f5/2 were found to be 381.5 eV and 392.3 eV, respectively with spin–orbit coupling (Δ) of 10.8 eV (standard Δ = 10.89 eV for U), confirming U(VI) state in the rice sample (See Fig. 3 and Fig. S2). Please note that, this study has no relevance to normal cooking and was performed to check maximum uranium uptake limit of rice. This opens up a new possibility of extracting uranium from uranium concentrates by rice or other foodstuff.

3.2. Effect on other metal ion concentration

It is known that other metal ions like iron, manganese, etc., are present in rice in very small quantities. The binding of these met-

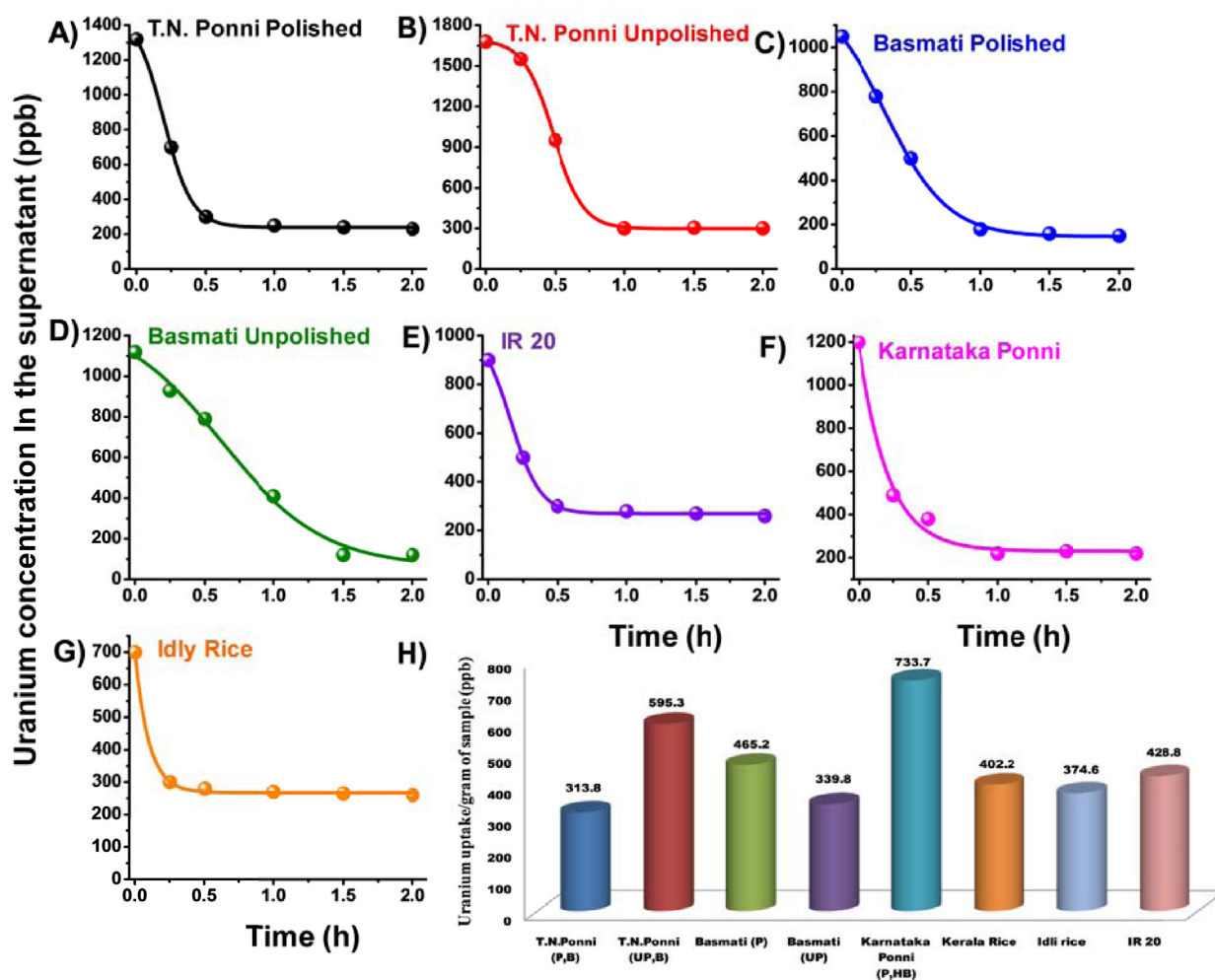


Fig. 2. A–G) Change in uranium concentration in the supernatant solution with time when 2 gram of different rice was cooked at 80 °C. Polynomial fits of the data points are also shown. H) Uranium concentration per g of rice cooked in uranium contaminated water.

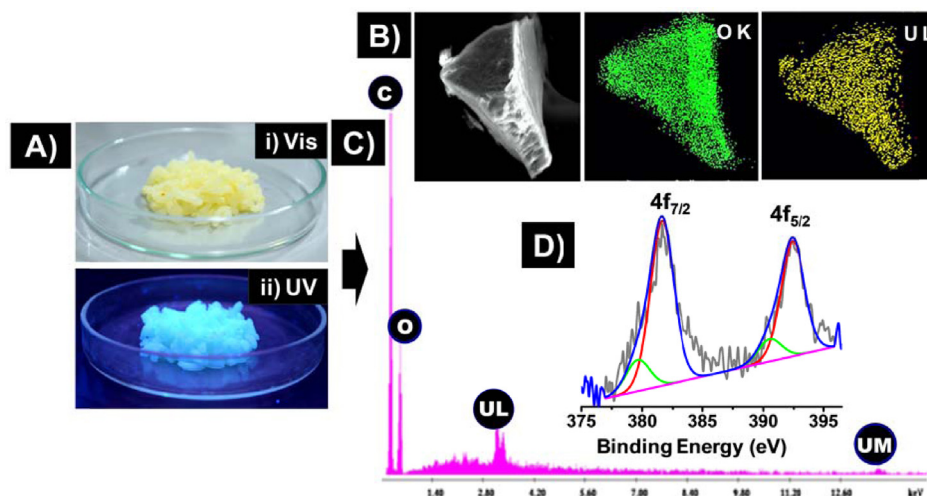


Fig. 3. A) Photographs of cooked rice soaked in highly concentrated uranium-containing water under visible (i) and UV light (ii). B) SEM image and elemental mapping of a cooked rice grain. Corresponding EDAX spectrum is shown in C. Presence of uranium was further proved by XPS in the U 4f region, is shown in D.

als to rice is still to be explored. Another goal of the study was to investigate whether the uptake of uranium affects the concentration of metal ions already present in rice. For this purpose the

concentration of different metal ions such as manganese, iron, nickel, copper, zinc and chromium in rice we monitored in the supernatant solution during regular intervals using ICP–MS. Com-

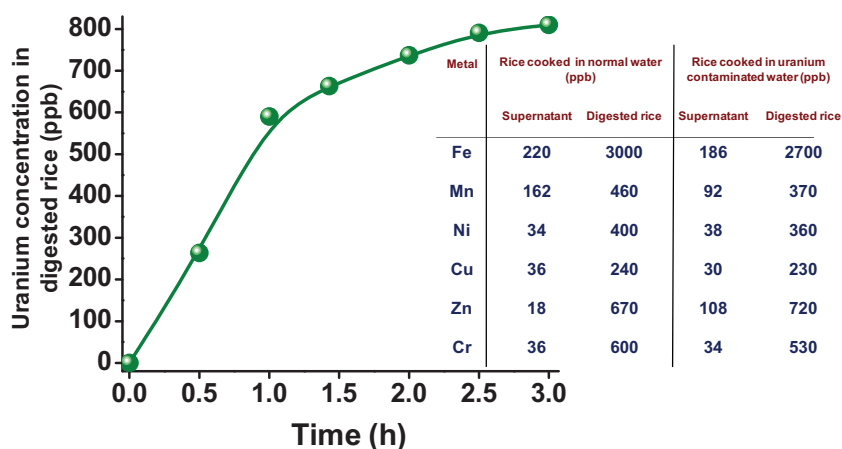


Fig. 4. Change in uranium concentration in the digested rice with time during cooking of Karnataka Ponni rice in water containing 1 ppm of uranium.

paring the concentration change of the transition metal ions during cooking with and without uranium, it was found that uranium uptake does not alter the binding of other metals to any significant extent as evident from Fig. 4.

3.3. Uranium interaction with monosaccharide

The experiments indicate that rice is scavenging uranium from water containing uranium in the form of uranyl ion. The next step was focused on exploring the chemistry of the interaction at the molecular level using mass spectrometry. As it is difficult to monitor directly rice or the supernatant by ESI-MS, the experiments were performed with a simple carbohydrate, mannose as our model system and tried monitoring its interaction with uranium. As it is interesting to probe if uranium naturally interactions occurred in contaminated areas it was used a common uranium mineral, urania (mostly UO_2) as the uranium source. It was found that uranium species existing in water are the same irrespective of whether they are generated from UO_2 or from a suitable commercially available uranium salt as shown in Fig. 5. Uranyl bound mannose monomer, dimer and also trimer were observed in ESI-MS along a few water detachment products from mannose. Uranium can be tetra or hexa-coordinated [35]. Hydroxyl groups in mannose can participate in complexation to give tetra co-ordination for single and hexa co-ordination for double mannose attachment. From previous reports it was known that sugar can coordinate with U through two -OH groups [35]. In aqueous solution UO_2^{2+} is mostly found to be hydrated as most intense peak is due to $\text{UO}_2(\text{OH})^+$. Since the solubility of uranium oxide in water is very low, it was found more appropriate to carry out further mass spectral analysis of uranium carbohydrate interaction using $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as the uranium source. The mass spectra generated for $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, mannose solution and uranyl-mannose adduct in positive ion mode are shown in the Fig. 6(A). The ESI-MS of mannose in water usually forms Na adduct and the corresponding peak is observed at m/z 203 ($\text{M-Na})^+$ which gives an overall positive charge.

Same tendency was found for mannose dimer and trimer also as shown in Fig. 6C. MS/MS of Na attached dimer or trimer leads to the mannose monomer. Uranyl nitrate can lose one or both the nitrate groups and can form UO_2^{2+} and $\text{UO}_2(\text{NO}_3)^+$. The UO_2^{2+} can capture one electron and can appear as UO_2^+ in positive ion mode. We have observed both the ions $[\text{UO}_2]^+$ and $[\text{UO}_2(\text{NO}_3)]^+$ in positive mode (see Fig. 6B). Corresponding nitrate ion was also observed in the negative ion mode at m/z 62. The UO_2^{2+} can form adduct with water and $\text{UO}_2(\text{OH})^+$ is a well known species and was detected at m/z 287. Uranium has three natural isotopes U^{234} , U^{235} and U^{238} . Among

them, U^{238} is the most abundant one (around 99.3%). The other (radioactive) isotopes, U^{234} (0.0053%) and U^{235} (0.72%) are very hard to detect through ordinary mass spectrometry. The MS/MS study of $\text{UO}_2(\text{OH})^+$ leads to free UO_2^+ but it never decay to free uranium ion which can be explained in terms of the stability of the ion in solution as well as in the gas phase. The important peaks found exclusively in the uranyl-mannose sample compared to the precursor spectra are m/z 449 and m/z 629. They correspond to uranyl adduct with mannose monomer and dimer, respectively. And at higher concentration, a trimer adduct at m/z 809 was also spotted. Detection of a peak at m/z 449 suggests that the species must have been formed by the loss of a proton from one of the hydroxyl groups coordinating UO_2^+ and the as-formed complex is stable in solution as well as in the gas phase.

In order to have more information regarding the species corresponding to m/z 449 and 629 peaks, the MS/MS spectra were also recorded, as shown in Fig. 7 from which it confirmed the adduct formation and strong binding of uranium with mannose.

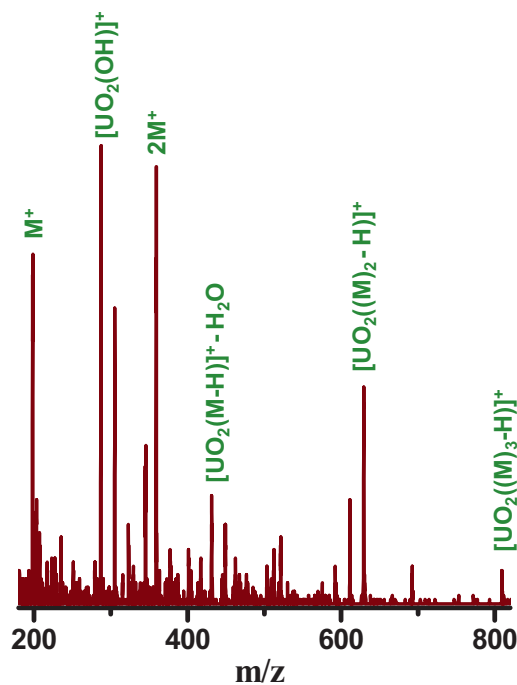


Fig. 5. ESI MS of uranyl-mannose adduct (prepared using urania) in positive ion mode.

In CID (collision induced dissociation), with increasing collision energy (CE), it was found that the intensity of the parent peak decreases and new peaks appear which are separated by m/z 18 due to water loss which is a common fragmentation pattern in all the sugars. The peak at m/z 629 also shows similar kind of water loss at lower collision energy. At higher CE, one mannose unit loss was observed and subsequent water loss species have

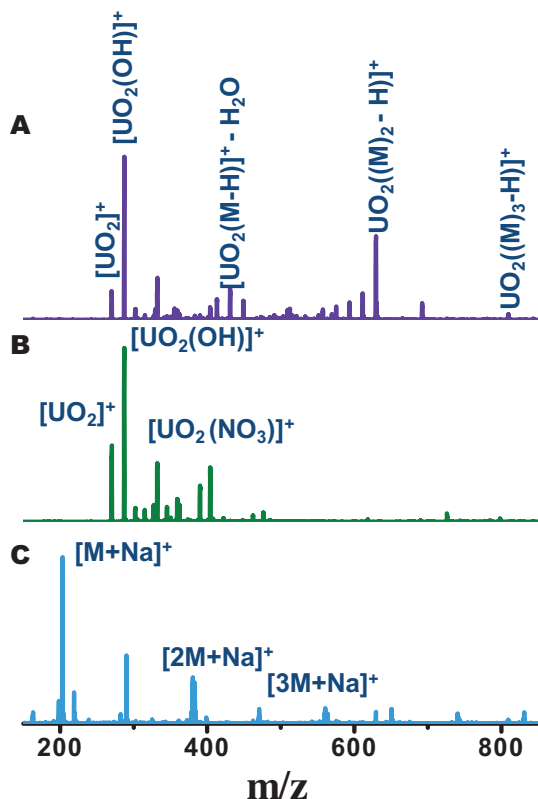


Fig. 6. ESI MS of (A) uranyl-mannose adduct (prepared using $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), (B) $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and (C) mannose in positive ion mode.

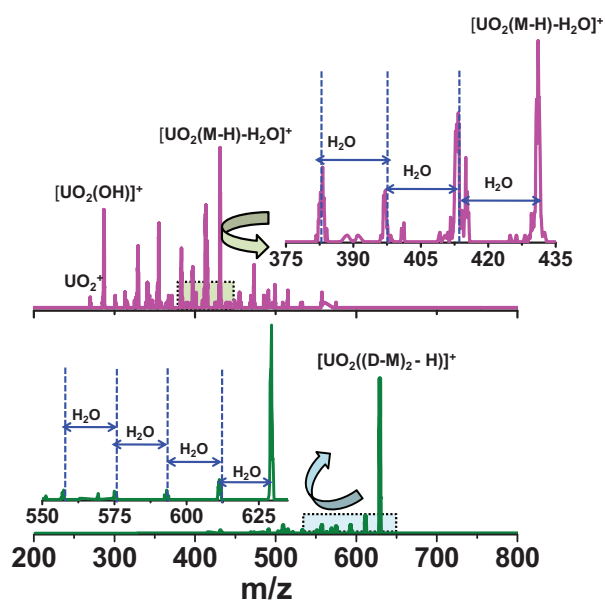


Fig. 7. ESI MS/MS of uranyl-mannose adduct with increase in collision energy (CE) showing water loss products at lower CE. At higher CE, mannose as well as water loss were observed.

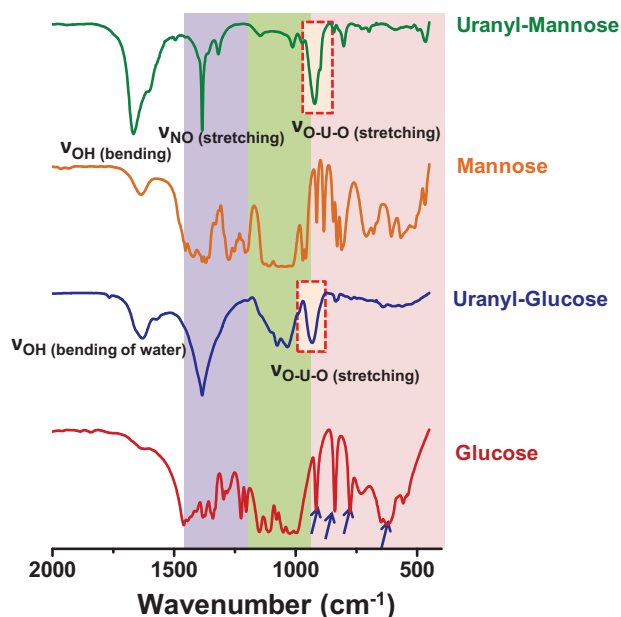


Fig. 8. IR spectra of glucose-uranyl and mannose-uranyl complexes, showing significant differences from the parent glucose and mannose. The arrows are showing the finger print peaks for sugars. Some of peaks at 3140–3460 and 990–1130 cm^{-1} are saturated.

also been formed as shown in Fig. 7. Note that similar kind of adduct formation was observed previously with glucose and the complex was studied using infra-red (IR) and nuclear magnetic resonance (NMR) but not observed in mass spectrometry suggesting that the species might not be stable in the gas phase [35]. It was also monitored glucose, mannose and the corresponding complex formation by IR spectroscopy. The anomeric structure of glucose and mannose can be confirmed from the 950–500 cm^{-1} region where signature peaks of D-glucose were observed around 915, 850, 780 and 600 cm^{-1} (Fig. 8 and Fig. S3 marked with blue arrow). Huge changes were observed in this region confirming appreciable interaction of uranium with glucose/mannose. A strong peak was observed at 930 cm^{-1} which can be attributed as O–U–O stretching in uranyl-glucose/mannose complex as marked in Fig. 8. Several bands due to CH_2 , C–OH and C–CH bending modes come in the 1460–1200 cm^{-1} region. Most of the peaks were absent or shifted after complexation with uranyl. Several other peaks were observed in the 1150–950 cm^{-1} region due to ring C–O stretching vibrations which also changed significantly after complexation. A strong absorption at 1384 cm^{-1} can be confirmed for N–O stretching frequency of nitrate ion which was originally absent in glucose/mannose and appeared only after complexation with uranyl ions. Peak around 1650 cm^{-1} is due to the H_2O bending mode. Significant changes were observed in the 4000–3000 cm^{-1} region where several OH and CH stretching frequencies overlap confirming involvement of OH groups in complexation with UO_2^{2+} . These data are in good agreement with the previously reported glucose-uranyl complex [35].

3.4. Interaction of uranium with other foodstuffs

Unusual uranium uptake by rice inspired to widen the study to different vegetables with varying carbohydrate content. Potato, carrot, peas, lentils and kidney beans were chosen for the purpose. The results presented in Fig. 7 show that not only starchy food but also other foods with less carbohydrate content (potato, carrot, kidney bean, lentil and peas) uptake reasonable quantities of uranium; in some cases uranium uptake is comparable with some rice

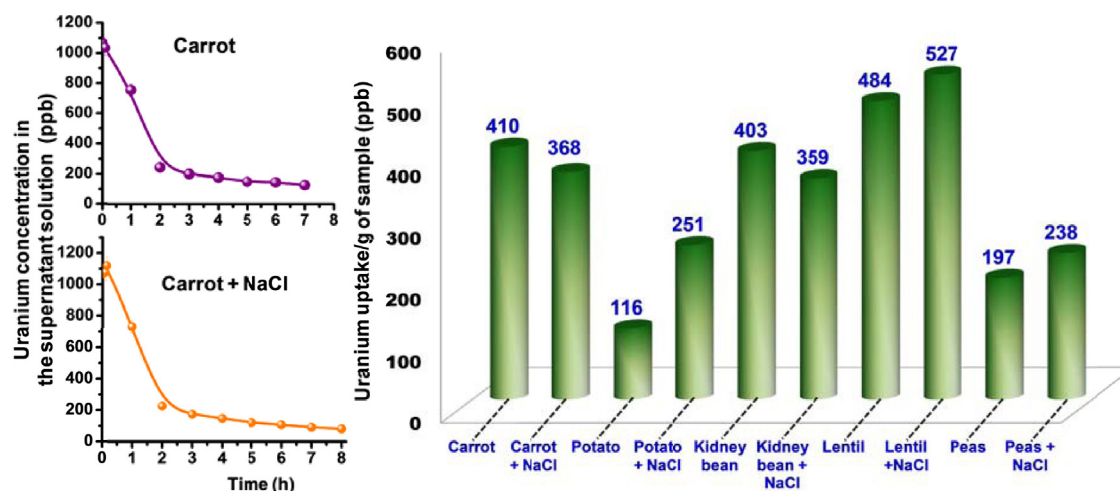


Fig. 9. (A) Decrease of uranium concentration in the supernatant solution with time during cooking of carrot with and without NaCl in water containing uranium. (B) Uranium concentration per gram of the food cooked in 1 ppm uranium contaminated water.

varieties. In the tested foodstuffs, some of them create color in the solution and moreover, they get boiled easily leaving some particles in the solution making it difficult by ICP–MS analysis. Therefore, it was not possible to monitor the release of uranium concentration into the supernatant, except for carrot which results are presented in Fig. 9A. For carrot, just after 2 h of cooking, uranium concentration in the solution decreased to 240 ppb (initial uranium concentration was 1070 ppb) and was saturated within 3 h (190 ppb at 3 h and 125 ppb after 7 h). Cooked carrot sample showed about 410 ppb of uranium.

When cooking, all these foodstuffs are in presence of salt and other ingredients. As the use of all the ingredients can create additional colors and other effects in foods, the experiments were done to check the effect in uranium uptake were restricted to NaCl. Each of the food samples was cooked with and without NaCl (50 ppm). Even though the presence of salt changes the uranium uptake (Fig. 9B), it was not possible to have a conclusion as in some cases uptake increased and in others decreased.

4. Summary and conclusions

In the present study, it was investigated the interaction of uranium (1 ppm) with different cooked foodstuffs. Among the eight different rice varieties Karnataka ponni showed the maximum uranium uptake whereas unpolished basmati rice showed the minimum but all of them uptake maximum uranium content from water after 2 h of cooking. Interaction with other foodstuffs (potato, carrot, peas, kidney beans and lentils) with and without NaCl affected the extent of chemical interaction but was not consistent with the carbohydrate content. The monitored uranium interaction with D-mannose through ESI–MS, under optimized instrumental parameters, identified the peaks which corresponded to uranyl adduct with mannose monomer, dimer and trimer which were also confirmed by MS/MS study. The product ion mass spectra showed peaks illustrating water loss from the parent ion as the collision energy was increased, an evidence for the strong interaction of uranium with mannose. This study would constitute the essential background for understanding interaction of uranium with various foodstuffs. Further extension of this work would be carried out with various heavy metals and other contaminants present in water as many such species are being reported in the recent past.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2015.04.041>.

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