

**VALIDATION OF ION CHROMATOGRAPHY FOR THE DETERMINATION OF
TRANSITION METAL IONS ALONG WITH ALKALI, ALKALINE
EARTH METAL ELEMENTS FOR URANIUM OXIDE FUEL**

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GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

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60	<i>Abstract :</i>	The present report describes the use of Ion chromatography (IC) methods with spectrophotometric and direct conductivity detection for the determination of transition metal elements and alkali alkaline earth metal ions in UO ₂ pellets. Transmet analytical column and Metrosep- cation 1-2 column were used for the separation of transition metal elements and alkali and alkaline earth metal elements respectively. Oxalic acid and mixture of pyridine 2,6-dicarboxylic acid (PDCA), Na ₂ SO ₄ and NaCl were used as mobile phase for the separation of transition metal ions and monitored after post - column reaction with 4,2-pyridylazo resorcinol (PAR) at 520nm spectrophotometrically. In the determination of alkali and alkaline earth metal ions the interference of transition metals are removed by complexing them with PDCA. Mixture of tartaric acid and PDCA employed in the separation of alkali and alkaline earth metal ions and monitored on direct conductivity detector. Mobile phase composition was optimised for the base line separation. Calibration plots of Fe ³⁺ , Cu ²⁺ , Ni ²⁺ , Co ²⁺ , Cd ²⁺ , Mn ²⁺ , Li ⁺ , Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ and Sr ²⁺ were linear over a wide dynamic range with regression coefficient better than 0.999. Detection limit of above ions were between 5-30ppb. To prevent the overloading of the cation exchange column, uranium matrix was removed from UO ₂ sample by solvent extraction with 30% TBP - TOPO/CCl ₄ . Ten sintered UO ₂ pellets of same lot were analysed and R.S.D. ±10% was obtained. These methods were validated by analysis of ILCE standards of UO ₂ .
70	<i>Keywords/Descriptors :</i>	URANIUM OXIDES; ION EXCHANGE CHROMATOGRAPHY; ALKALI METALS; PH VALUE; MIXED OXIDE FUELS; SOLVENT EXTRACTION; MATERIALS RECOVERY
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यूरेनियमडाइआक्साइड ईंधन में सं, मा तत्वों तथा गार एवं गारीय मृदा तत्वों े निर्धारण हेतू आयन,ोमेटोग्राफी (IC) ा प्रमा णी रण

सारांश :

वर्तमान रिपोर्ट में यूरेनियमडाइआक्साइड पेलेटों में सं, मा तत्वों तथा गार एवं गारीय मृदा तत्वों े निर्धारण हेतू स्पेक्ट्रोफोटोमीट्री एवं चाल ता पध्दति युक्त आयन,ोमेटोग्राफी ा वर्णन है। सं, मा तत्वों तथा गार एवं गारीय मृदा तत्वों े पृथक् रण े लिए ा मशः ट्रांसमेट और मेट्रोसेप धनायन 1-2 मु य ालम ा प्रयोगि या ाया। ऑक्सैलि अम्ल और पिरीडीन 2-6 डाइ ार्बोक्सिलि अम्ल, सोडियम सल्फेट एवं सोडियम क्लोराइड ा मिश्रण सं, मा तत्वों े पृथक् रण मे मोबाइल फेज़ णी तरह प्रयुक्त हुआ। सं, मा तत्वों ा निर्धारण ट्रांसमेट मु य ालम से पृथक् रण े पश्चात 4,2-पिरीडॉइल एजो रिसोर्सिनॉल से अभि, या र 520 nm पर स्पेक्ट्रोफोटोमीटर से ि या ाया। गार एवं गारीय मृदा तत्वों े निर्धारण में सं, मा तत्वों ा हस्त णेप पिरीडीन 2-6 डाइ ार्बोक्सिलि अम्ल े साथ ामप्लेक्सेशन े व्दारा हटाया ाया। टारटेरि अम्ल एवं पिरीडीन 2-6 डाइ ार्बोक्सिलि अम्ल ा मिश्रण गार एवं गारीय मृदा तत्वों े पृथक् रण मे मोबाइल फेज़ े रूप में प्रयुक्त हुआ। इन ा निर्धारण चाल ता पध्दति से ि या ाया। मोबाइल फेज़ े बेसलाईन से वियुक्ति े लिए इष्टतमि, त ि या ाया। Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Mn^{2+} , Li^{+} , Na^{+} , K^{+} , Mg^{2+} , Ca^{2+} तथा Sr^{2+} े अंशा न प्लॉट 0.999 से बेहतर समाश्रय ा िगां पर बृहद सांद्र ा रेंज े लिए र्णै थे। उपर्युक्त ायनों ि संसूचन सीमा 5-30 ppb े मध्य रही। धनायन विनिमय ालम े अतिभारण रो ने े लिए यूरेनियम मैट्रिक्स े 30% TBP-TOPO/ CCl_4 विलाय णि ष र्ष ा से पृथक्, त ि या ाया। सिंटरित UO_2 े ए णी लॉट े दस नमूनों ा अध्ययन ि या ाया तथा भिन्नता िगां $\pm 10\%$ रहा। ILCE UO_2 मान णे े तुलनात्म अध्ययन से इस वि सि त पध्दति ा आ लन ि या ाया।

मु य शब्द :

आयन,ोमेटोग्राफी, सं, मा तत्व, गार एवं गारीय मृदा तत्व, विलाय णि ष र्ष ा, पिरीडीन 2-6 डाइ ार्बोक्सिलि अम्ल, 4,2-पिरीडॉइल एजो रिसोर्सिनॉल, ILCE

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ABSTRACT:

The present report describes the use of Ion chromatography (IC) methods with spectrophotometric and direct conductivity detection for the determination of transition metal elements and alkali alkaline earth metal ions in UO₂ pellets. Transmet analytical column and Metrosep- cation 1-2 column were used for the separation of transition metal elements and Alkali & Alkaline earth metal elements respectively. Oxalic acid and mixture of pyridine 2,6-dicarboxylic acid (PDCA), Na₂SO₄ & NaCl were used as mobile phase for the separation of transition metal ions and monitored after post - column reaction with 4,2-pyridylazo resorcinol (PAR) at 520nm spectrophotometrically. In the determination of alkali and alkaline earth metal ions the interference of transition metals are removed by complexing them with PDCA. Mixtures of tartaric acid and PDCA employed in the separation of alkali and alkaline earth metal ions and monitored on direct conductivity detector. Mobile phase composition was optimised for the base line separation. Calibration plots of Fe³⁺, Cu²⁺, Ni²⁺, Co²⁺, Cd²⁺, Mn²⁺, Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺ and Sr²⁺ were linear over a wide dynamic range with regression coefficient better than 0.999. Detection limit of above ions were between 5-30ppb. To prevent the overloading of the cation exchange column, uranium matrix was removed from UO₂ sample by solvent extraction with 30% TBP- TOPO/CCl₄^[1]. Ten sintered UO₂ pellets of same lot were analysed and R.S.D. ±10% was obtained. These methods were validated by analysis of ILCE standards of UO₂.

Key words: *Ion chromatography, transition metal ions, alkali elements, alkaline earth elements, solvent extraction, PDCA, PAR, ILCE*

1. INTRODUCTION:

AFFF is fabricating various types of mixed oxide fuels, namely for PHWR, BWR, FBTR & PFBR. Chemical characterization of these fuels plays an important role in quantifying their specified impurities. During the various stage of fabrication, a number of metallic and non metallic impurities may get added up to the fuels. Presence of these impurities can cause adverse effects on fuel performance.

Presence of higher alkali and alkaline earth elements, transition metal elements can reduce the density of fuel. Ca and Fe have tendency to form preferential oxide there by affecting the O/M of fuel matrix^[2]. Higher presence of Fe, Co and Ni gives the indication of wear and tear of equipment used

during the fabrication process. Cd is important from neutron economy point of view. Alkali, Alkaline earth elements, Mn Co etc also form activation products after irradiation in the reactor.

Presently, trace metallic impurities in MOX fuels are analysed by using Atomic emission spectrometry techniques. Apart from being expensive, these techniques need skilled analyst and large sample size. While techniques like DC arc are dependent on imported electrodes, ICP suffers from drawbacks like clogging and spectral interference from radioactive material. DC- Arc is not suitable for rare earths determination with a good sensitivity. Ion chromatography may act as an alternative method due to its versatility of analysing metallic as well as non metallic impurities apart from being low cost and less sample size requirement. Ease of automation and online capability of separation make this method attractive in wide variety of routine trace analytical determinations.

Ion chromatography (IC) offers rapid separation, selectivity and sensitive analysis. It is a multi-elemental technique and was used in nuclear fuels in the front end^[3,4,5,6] as well as at the backend^[7]. Transition metal ions can be analysed by chelation ion chromatography^[8,9,10,11,12] Reversed phase ion chromatography^[13] and cation/anion exchange chromatography^[14,15] Separation of transition metals with ion exchanger requires a complexation of metal ions in mobile phase to reduce their effective charge density. Monovalent cations such as Na^+ or H^+ are unsuitable as eluent because the selectivity coefficient for transition metals of the same charge number hardly differ. A selectivity change can only be obtained by introduction of secondary equilibrium such as complexation equilibrium. Usually weak organic acids such as citric acid, oxalic acid, PDCA, reduces the positive charge of the metal cation and improves the speed and efficiency of separation. These acids form preferably anionic or neutral complexes with metal ions, which can be separated on anion or cation exchangers. In the present study, oxalic acid and PDCA are used as mobile phase. Ionic strength of the mobile phase is increased by using NaCl and Na_2SO_4 .

Stationary phase having both anion and cation exchange capacities are used for the separation of Transition metal ions^[16]. In the present study, transition metal ion are separated on TRANSMET ion exchange column(mixed bed capacity) and mixed with post column colour developing reagents (PCR) PAR and form chelate complex which absorb in the range between 490-530nm, determined spectrophotometrically. PCR is delivered pneumatically. Mobile phase composition is optimised by changing the concentration of PDCA and pH.

Alkali and alkaline earth metal ions can be determined by either suppressed conductivity detection mode^[5] or by direct conductivity detection mode after cation exchange separation. Silica based cation exchangers with sulphonic groups as ion- exchange site are not significant in the separation despite high chromatographic efficiency. With the advent of poly(butadiene- maleic acid) PBDMA group based silica columns it is possible to analyse alkali and alkaline earth metals simultaneously^[17]. In the present study spherical silica gel coated with PBDMA used for the separation of alkali and alkaline earth metals. If the sample contains the transition metal ions they interferes in the

determination of alkaline earth metal ions when we use tartaric acid as a mobile phase. UO_2 samples contains both the transition metal ions, alkali & alkaline earth metal ions. In the present study the interference of transition metal ions are removed by forming anionic complexes with PDCA. Mixture of tartaric acid and PDCA are used as mobile phase. Mobile phase composition is optimised by changing the concentration of both components.

After optimising the mobile phase composition for both the determinations calibration plots of different metal ions are obtained. Samples for the determination of transition and alkali & alkaline earth metal ions in UO_2 were prepared by dissolving it in conc. HNO_3 and removing the major matrix by solvent extraction with TBP/TOPO in CCl_4 . The separated aqueous phase contains analytes, it is evaporated to near dryness and redissolved in corresponding mobile phase. Method is validated by carrying out losses study and comparing the results with ILCE UO_2 standard.

2. INSTRUMENTATION:

2.1 Apparatus:

A schematic of the IC system used in the present work is given in Figure 1. It consists of 709IC pump, HPLC compact pump (Bischoff make), LC gradient mixer, Pulsation Dampener, 733 IC separation center with two Rheodyne sampling valves with $20\mu L$ loop, post column colour developing reactor with 732 IC conductivity detector and Lambda 1010 UV- VIS spectrophotometer. Samples were introduced through $20\mu L$ sample loop fitted with a Rheodyne injector. Separation of alkali and alkaline earth metal ions was achieved with an analytical column Metrosep cation 1-2 (125x4.1mm) [containing spherical silica gel with polybutadiene maleic acid (PDMA) groups] coupled with a guard column Metrosep RP Guard. The eluted ions were monitored with 732IC conductivity detector. While the transition metal ions were achieved with an analytical column Transmet (250x 4.6mm) [Latex anion exchanger with mixed anion & cation exchange capacity. Packing material: Surface sulfonated microporous Polystyrene/Divinylbenzene (2% cross-linked) with particle size $13\mu m$ electrostatically agglomerated totally aminated latex beads with particle size 150nm] with a guard column Transguard (30 x 4.6). The eluted ions were monitored after a post column reaction with a metallochromic reagent. Post column colour developing reagents were added pneumatically into the low dead volume-mixing tee. The signals from both the detectors were processed by a software and chromatograms were monitored on PC. The IC system was computer controlled through interface. All IC separations were isocratic and carried out at 1ml/min flow rate at room temperature.

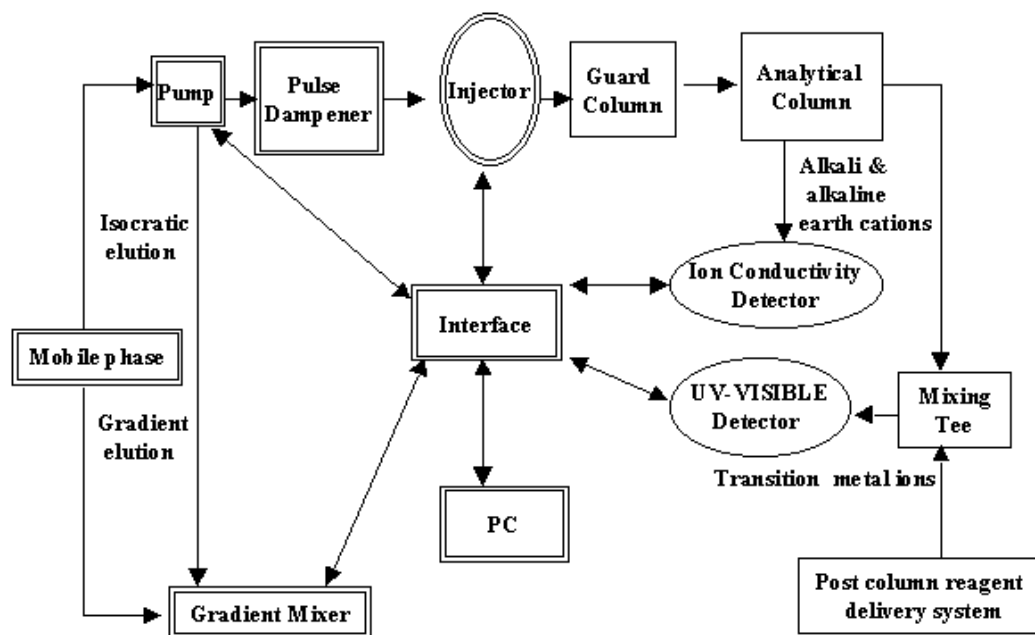


Figure 1. Schematic of the IC system (Metrohm make) used in the present work

2.2 Reagents and Materials:

Freshly deionised water (18.2M Ω) purified through a Milli Q system was used for all dissolutions and dilutions. Fluka make standard stock solutions for ion chromatography containing 1000ppm of Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺, Pb²⁺, Cu²⁺, Ni²⁺, Zn²⁺, Co²⁺, Cd²⁺ and Mn²⁺ were used for external standardization. Standard stock solutions (1000ppm) of Fe³⁺ was prepared by dissolving Fe(NO₃)₃·9H₂O. Tartaric acid, oxalic acid, NaCl, Na₂SO₄, Na₂CO₃, PDCA, Dimethyl amino ethanol, PAR were obtained from Fluka. All mobile phase and post column colour developing reagents were filtered through 0.45 μ m PTFE membrane filter and degassed before use.

2.3 Sample preparation for Transition, Alkali & Alkaline earth metal ions in sintered UO₂ pellets:

Sintered UO₂ pellet was crushed and about 5.0gm of sample was dissolved in conc. HNO₃. After complete conversion into uranyl nitrate it was further dissolved in conc. HNO₃. This solution was then evaporated to near dryness under IR lamp and redissolved in 4M HNO₃. Uranium matrix was removed by giving three contacts with 30%TBP in CCl₄ in 2: 1 ratio and finally with 0.2M TOPO in CCl₄ in 1:1 ratio. The aqueous layer was collected, diluted and filtered through 0.45 μ m PTFE injection filter. This aqueous layer was further studied for alkali and alkaline earth metal ions and transition metal ions after determining the U content in the same by RPIPC^[4]. The filtered aqueous layer contains soluble alkali & alkaline earth ions, transition metal ions, and lanthanide ions.

3. DETERMINATION OF TRANSITION METAL IONS:

Determination of Transition metal ions in UO₂:

For the determination of transition metal ions, aqueous phase obtained as described in 2.2, was evaporated to near dryness and redissolved in the mobile phase 2mM PDCA + 2mM Na₂SO₄ + 15mM NaCl, pH 4.8. A small quantity (~20 μL) of this solution was injected to IC and separation was carried out on Transmet column coupled with guard column Transguard with mobile phase 2mM PDCA + 2mM Na₂SO₄ + 15mM NaCl, pH 4.8 and detected after post column colour reaction with PAR in the 2:1 ratio. To obtain linear calibration plot for Pb²⁺, Fe³⁺, Cu²⁺, Ni²⁺, Zn²⁺, Co²⁺, Cd²⁺ and Mn²⁺ mixtures of standards were injected directly.

3.2 Results and discussion:

Initially oxalic acid was used for the separation of transition metal ions. Figure 3.2.1 shows typical chromatogram for standard mixture of transition metal ion when oxalic acid was used as mobile phase. Here Mn and Cd are co-eluted. But Fe(III) can't be eluted when oxalic acid was used as a eluent because Fe(III) forms stable Fe(ox)₃³⁻ (log K= 18.5) which can't be eluted with divalent oxalate.

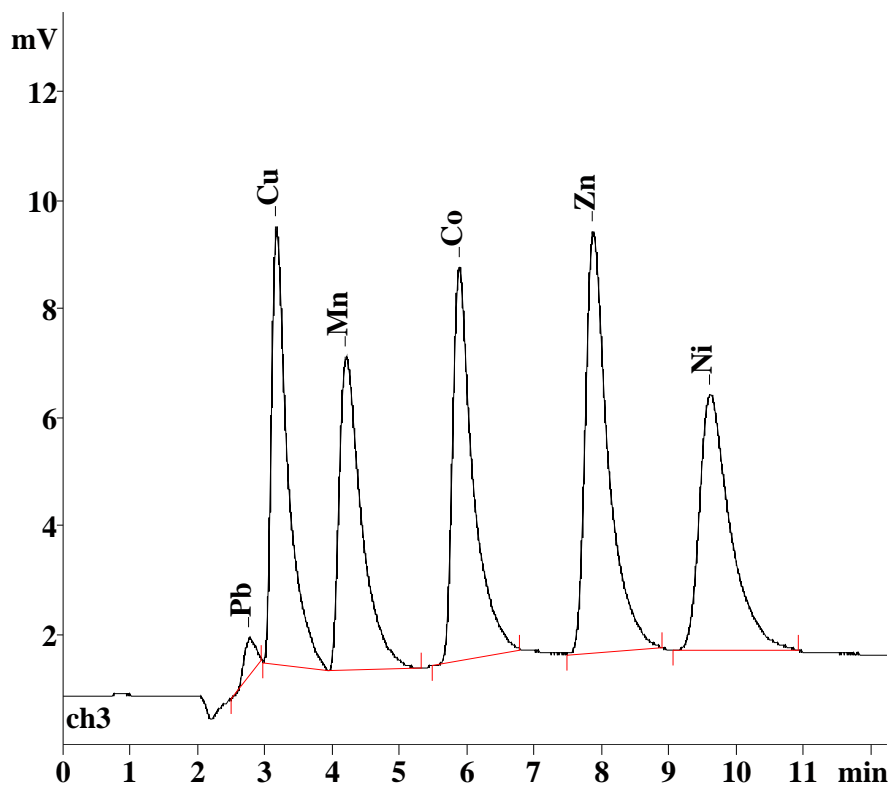


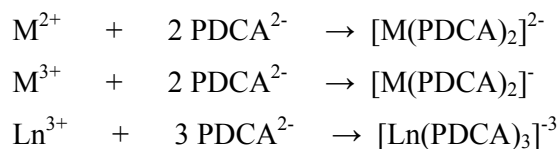
Figure 3.2.1. Standard chromatogram of Pb, Cu, Mn, Co, Zn, Ni in mobile phase of 80mM Oxalic acid + 100mM tetramethyl ammonium hydroxide +50mM KOH

Flow rate :1ml/min

PCR: 0.5mM PAR + 0.3M NaHCO₃ + 0.5M NH₄OH + 1M Dimethylaminoethanol

Flow rate : 0.5ml/min, Detection at 520nm

Hence PDCA is used as mobile phase in the separation of transition metal ions. Anion exchange is dominating separation mechanism when PDCA is used as complexing agent. PDCA or oxalic acid is used as complexing agent in the mobile phase which forms anionic complexes with di or trivalent transition metal as shown in the following scheme. Transition metal forms stable monovalent and divalent complexes with PDCA, while the complexes of lanthanides are trivalent. On the basis of charge difference transition metals can be eluted with PDCA, while the lanthanide ions which are present in the aqueous phase are retained at the top of the column and do not interfere in the analysis. The alkali and alkaline earth metal ions show very less tendency for complexation and they are mainly present as the cationic form and elute in the solvent front.



These metal ions are determined spectrophotometrically after post column colour development with PAR. Ligand exchange between the transport complex and PAR is aided by addition of ligands such as phosphate, sulphate, carbonate, bicarbonates or alkyl amines to the eluents. Hence 0.5mM PAR + 0.3M NaHCO₃ + 0.5M NH₄OH + 1M Dimethylaminoethanol is used as post column colour developing reagent during the analysis.

Preliminary work was focused in establishing the condition necessary for isocratic separation of transition metal ions at 1ml/min flow rate. Effect of PDCA concentration and pH on the retention of transition metal ions were studied.

Effect of PDCA concentration:

Concentration of PDCA was varied from 1mM to 5mM at pH 4.8 while keeping the Na₂SO₄ and NaCl concentration constant to 2mM and 15mM respectively. It was observed that an increase in the concentration of PDCA in the mobile phase reduces the retention time of transition metal ions. This can be attributed to increased interaction of PDCA with the adsorbed PDCA-Transition metal ion anionic complex on ion exchange bed. This effect is shown in figure 3.2.2. Fe & Cu and Co & Cd are not base line resolved when PDCA concentration was ≥ 5mM. It is clear from the figure that at 2mM PDCA concentration, optimum separation of these transition metal ions was achieved in a reasonable time. Hence 2mM PDCA + 2mM Na₂SO₄ + 15mM NaCl was chosen for further study.

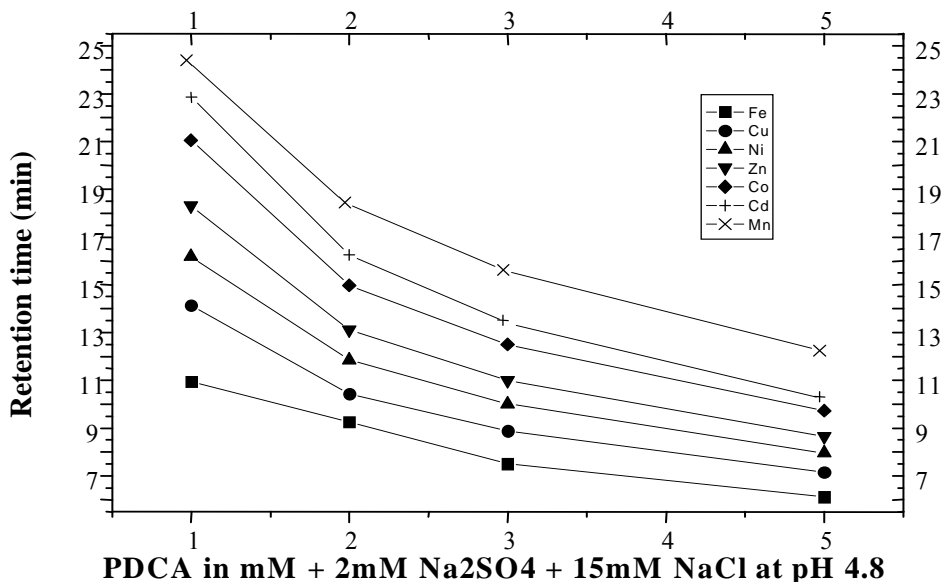


Figure 3.2.2 Effect of PDCA concentration on retention of Transition metal ions

Effect of pH:

After optimising the PDCA concentration to 2mM, effect of pH on the retention of eluting transition metal ions was studied. The pH of the mobile phase (2mM PDCA + 2mM Na₂SO₄ + 15mM NaCl) was varied from 3.5 to 5.5. Figure 3.2.3 shows this variation. It was observed that retention time decreases with the increase in pH. This behaviour can be explained on the basis of increased ionisation of PDCA, which is a weak acid. This increase in ionisation enhances its complexation tendency with transition metal ions which leads to decrease in the retention time. The pH of mobile phase was chosen to 4.8, as it could bring separation in minimum time. Higher pH values of the mobile phase leads to merging of peaks, e.g. at pH of 5.5, Cu & Ni and Co & Cd are not base line separated where as lower pH values result in prolonged elution time.

Thus mobile phase composition is optimised to 2mM PDCA + 2mM Na₂SO₄ + 15mM NaCl at pH 4.8 for quantitative analysis. Figure 3.2.4 shows a typical chromatogram of standard mixture of Fe³⁺, Cu²⁺, Ni²⁺, Zn²⁺, Co²⁺, Cd²⁺ and Mn²⁺ in 2mM PDCA + 2mM Na₂SO₄ + 15mM NaCl at pH 4.8.

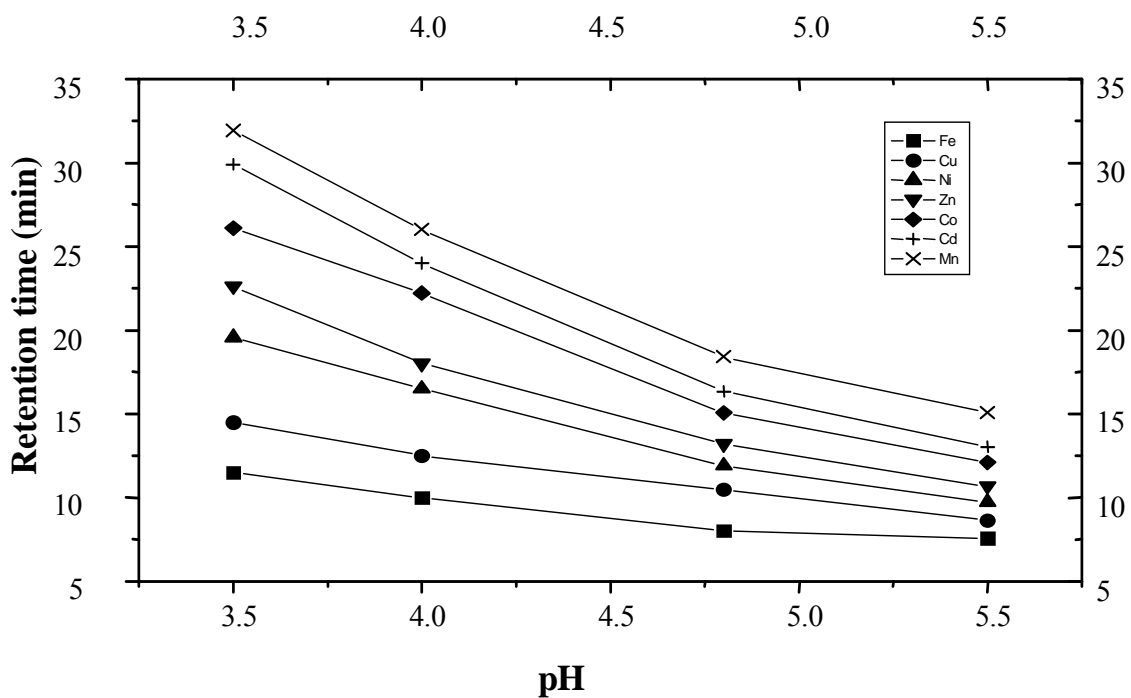


Figure 3.2.3 Effect of pH on the retention of transition metal ions

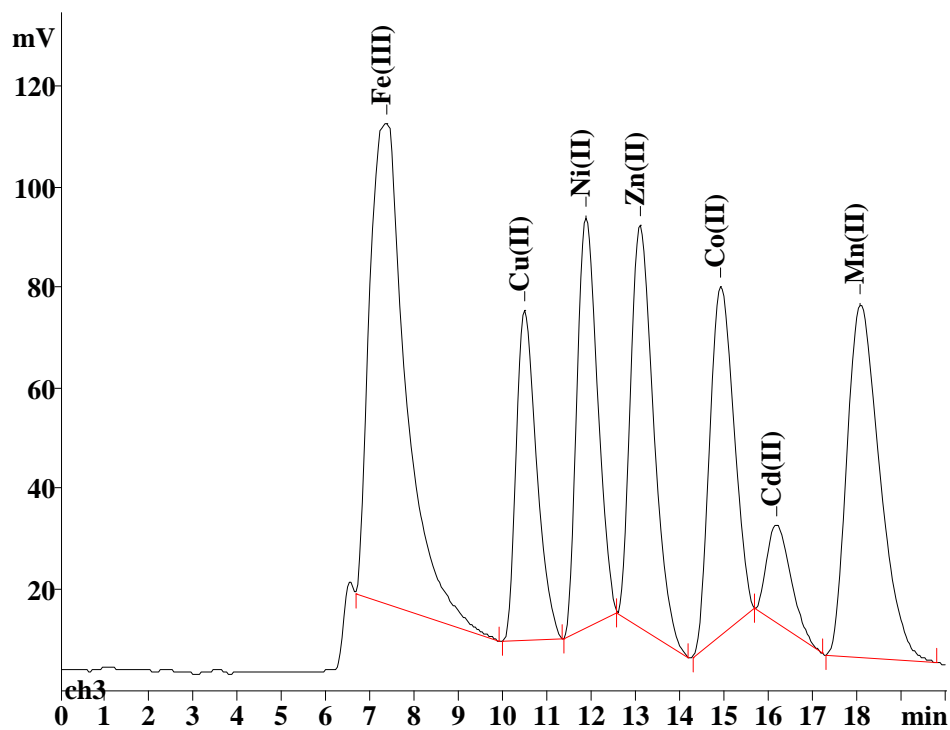


Figure 3.2.4 Standard chromatogram of Fe^{3+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Cd^{2+} and Mn^{2+}

Linearity, Repeatability:

The optimised mobile phase composition 2mM PDCA + 2mM Na₂SO₄ + 15mM NaCl was used to evaluate these parameters. The calibration plots of Fe³⁺, Cu²⁺, Ni²⁺, Zn²⁺, Co²⁺, Cd²⁺ and Mn²⁺ were obtained in the range 0.05-20ppm range. Table 4.2.1 shows the calibration data for the analysis of Fe³⁺, Cu²⁺, Ni²⁺, Zn²⁺, Co²⁺, Cd²⁺ and Mn²⁺ ions. The system was linear over a wide range of concentration. Detection limit obtained based on S/N =3 for these ions. The coefficients of variation obtained were better than ±6% in 10 replicates. The precision of the method was checked by repeatedly injecting a suitably diluted sample.

Table 3.2.1 Detection limit, calibration details and % RSD of Transition metal ions

Metal Ions	Conc. Range (ppm)	Detection limit (ppb)	Correlation coefficient	Slope	%R.S.D. for given concentration level (10 replicates)	
					Conc (ppb)	%RSD
Fe ³⁺	0.1-10	30	0.9988	0.0395	259	5.43
Cu ²⁺	0.05-5	10	0.9999	0.0355	524	3.08
Ni ²⁺	0.05-5	10	0.9979	0.0329	649	1.24
Zn ²⁺	0.05-5	9	0.9989	0.0264	676	1.83
Co ²⁺	0.05-5	13	0.9997	0.0259	471	2.33
Cd ²⁺	0.5-20	25	0.9967	0.0891	800	5.38
Mn ²⁺	0.05-5	15	0.9994	0.0171	472	2.75

Method validation:

The method of determination of transition metal ions was applied to sintered UO₂ samples. Recovery experiments were carried out to evaluate the method quantitatively. Known amounts of Fe³⁺, Cu²⁺, Ni²⁺, Zn²⁺, Co²⁺, Cd²⁺ and Mn²⁺ were added to aqueous phase obtained after solvent extraction of Uranium. Recovery of the added ions were calculated from the initial and final analyses (table 3.2.2) and found acceptable for all ions. Further to ensure that no loss of transition metal ions occurs during the sampling of UO₂ certified UO₂ powder sample was analysed. Table 3.2.3 shows the result obtained for all these ions agreed within 10% of the expected value. This table also shows the result of transition metal ions in sintered UO₂ pellet.

Table 3.2.2 Recovery of Fe³⁺, Cu²⁺, Ni²⁺, Zn²⁺, Co²⁺, Cd²⁺ and Mn²⁺ added to aqueous phase obtained after solvent extraction of UO₂

Conc. mg/L / Added ion		0.5	1	2	2.5	4	Average recovery %
Fe ³⁺	Obtained	0.48	0.931	1.886	2.487	4.08	96.98
	Recovery %	96	93.1	94.3	99.5	102.0	
Cu ²⁺	Obtained	0.477	0.925	2.074	2.364	3.824	96.35
	Recovery %	95.4	92.5	103.7	94.56	95.6	
Ni ²⁺	Obtained	0.53	1.173	2.352	2.352	3.996	110.44
	Recovery %	106	117.3	117.6	111.4	99.9	
Zn ²⁺	Obtained	0.51	0.987	1.968	2.784	3.9	101.59
	Recovery %	102	98.7	98.4	111.36	97.5	
Co ²⁺	Obtained	0.476	0.871	1.985	2.653	3.936	97.23
	Recovery %	95.3	87.1	99.25	106.12	98.4	
Cd ²⁺	Obtained	0.486	0.952	1.862	2.747	3.84	98.3
	Recovery%	97.3	95.2	93.1	109.9	96.0	
Mn ²⁺	Obtained	0.467	0.941	1.989	2.725	3.824	94.86
	Recovery%	93.4	94.1	99.5	91.7	95.6	

Table 3.2.3 : Results of Fe³⁺, Cu²⁺, Ni²⁺, Zn²⁺, Co²⁺, Cd²⁺ and Mn²⁺ for Sintered UO₂ pellets and ILCE certified UO₂ powder

Analyte ion present (ppm)	Sample type			
	Sintered UO ₂ pellets	ILCE UO ₂ powder		
		Obtained	Expected	Variation
Fe ³⁺	44.3 ± 3	87	92	5.4%
Cu ²⁺	1.2 ± 0.04	5.5	6.6	16.6%
Ni ²⁺	0.8 ± 0.02	14	15	6.6%
Zn ²⁺	2.7 ± 0.14	4.7	5.2	9.6%
Co ²⁺	6.3 ± 0.24	4.8	5.2	7.6%
Cd ²⁺	0.7 ± 0.04	0.09	0.07	28.5%
Mn ²⁺	1.1 ± 0.03	11.8	-	-

Figure 3.2.5 shows typical chromatogram of ILCE UO₂ powder after removal of Uranium matrix. It is clear that these cations can be quantitatively determined in these samples.

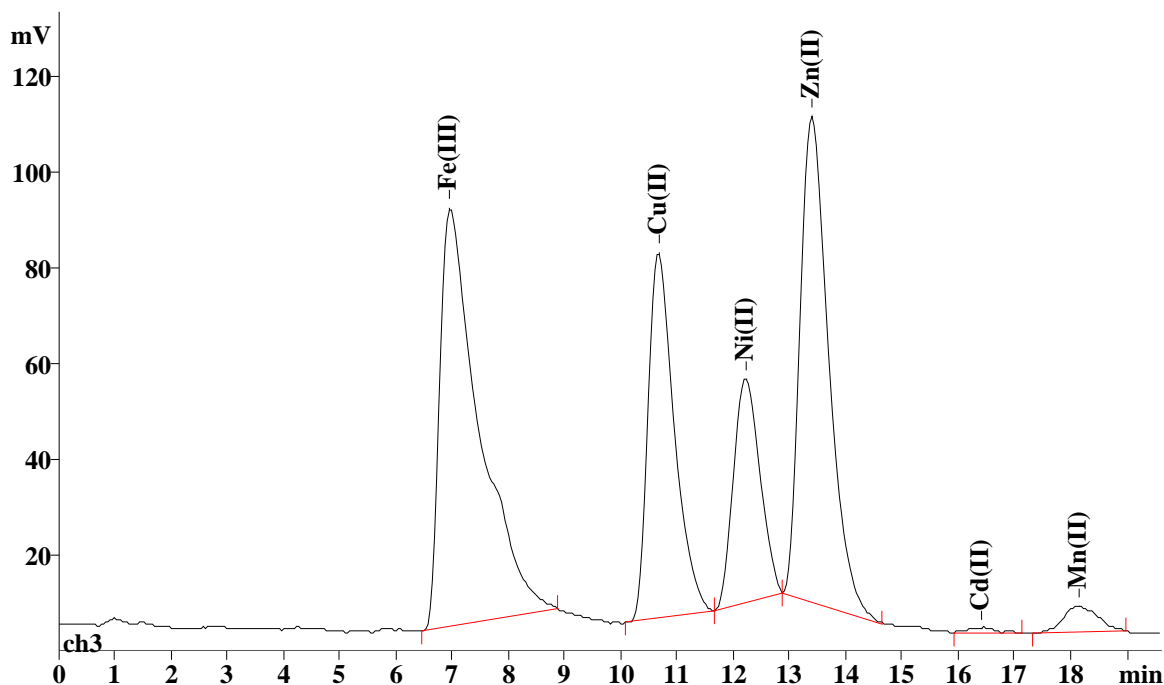


Figure 3.2.5 Chromatogram of ILCE UO₂ powder in mobile phase of 2mM PDCA + 2mM Na₂SO₄ + 15mM NaCl at pH 4.8

4. DETERMINATION OF ALKALI AND ALKALINE EARTH METAL IONS:

4.1 Determination of Alkali and Alkaline earth metal ions:

The aqueous layer obtained after solvent extraction of U contains both alkali, alkaline earth metal ions and transition metal ions. Therefore it was of interest to develop a method where alkali and alkaline earth metal ions can be determined without the interference of transition metal ions. The aqueous layer was taken in a quartz beaker and evaporated to near dryness. The residue was redissolved in corresponding mobile phase (4mM Tartaric acid + 1mM Pyridine 2,6- dicarboxylic acid) . 20 μ L of this solution was injected into IC and the separation was done with mobile phase 4mM Tartaric acid + 1mM Pyridine 2,6- dicarboxylic acid at flow rate of 1ml/min. To obtain the linear calibration plot for Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺ mixture of the standards were injected directly.

4. 2 Results and discussion:

Presence of two different types of carboxyl group (having different dissociation constants) on PBDMA facilitate the separation of alkali and alkaline earth metal ions simultaneously . Hence Metrosep cation 1-2 column (125 x 4.1mm) [containing spherical silica gel with polybutadiene maleic

acid (PDMA) groups] coupled with a guard column Metrosep RP Guard was used for the separation of alkali and alkaline earth metal ions. Preliminary work was concentrated in establishing the condition necessary for isocratic separation of alkaline earth and alkaline earth metal ions. Although only tartaric acid gives baseline separation of alkali and alkaline earth metal ions on Metrosep cation 1-2 column [19]. But our sample contains the transition metal ions, which interfere in the determination. Hence this interference has to be removed. Commercially available Longuard Cation cartridge containing iminodiacetic acid resin can suppress interfering transition metal elements [5]. Here, we have removed the interference by complexation using PDCA as complexing agent as it requires no extra hardware and of low cost. Transition metal ions and the lanthanide ions, which form anionic complexes, don't retain on to the cation exchange column and elutes in the solvent front. First the mobile phase composition was optimised by varying Tartaric acid and PDCA concentration to 1mM – 8mM and 0-2mM respectively.

Effect of PDCA concentration:

PDCA concentration was varied from 0-2mM by keeping the Tartaric acid concentration fix to 6mM. Figure 4.2.1 shows this variation. In the absence of PDCA elution trend is normal i.e. Li< Na<K<Mg<Ca< Sr. It is interesting to see that Ca²⁺ elutes prior to Mg²⁺ in the presence of PDCA. It may be due to complexation of Ca²⁺ by PDCA. At 6mM Tartaric acid + 2mM PDCA, K⁺ and Ca²⁺ gets co-eluted while at 6mM Tartaric acid + 0.5mM PDCA Ca²⁺ and Mg²⁺ are not baseline separated. Hence PDCA concentration was fixed to 1mM for complexation of transition metal ions.

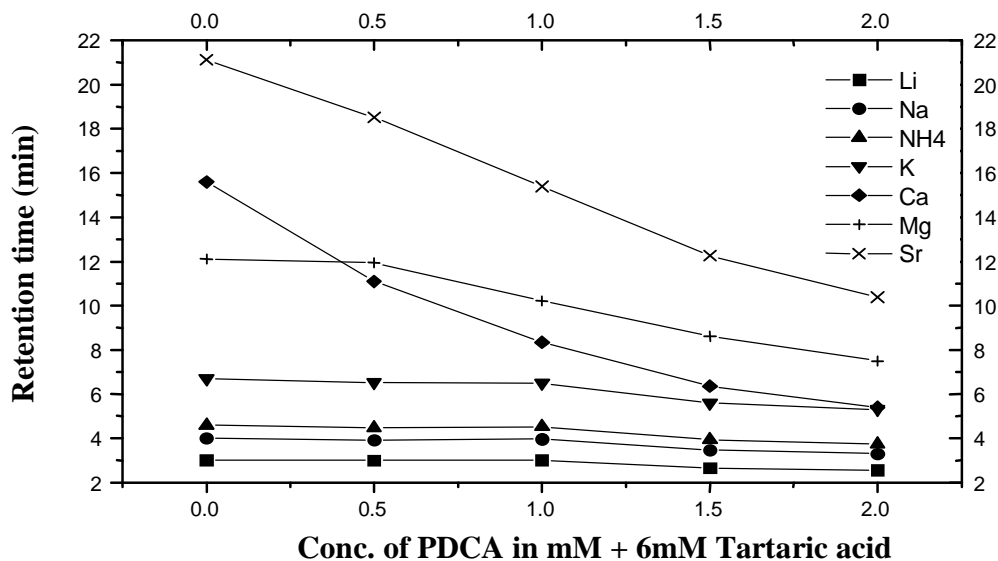


Figure 4.2.1 Effect of PDCA concentration on retention of alkali and alkaline earth metal ions

Effect of Tartaric acid concentration:

After fixing the concentration of PDCA in the mobile phase tartaric acid concentration was varied from 1mM to 8mM. Figure 4.2.2 shows the effect of Tartaric acid concentration on the retention of alkali and alkaline earth metal ions. Retention time decreases with the increase of tartaric acid concentration. This can be attributed to increased interaction of Tartaric acid with metal ions. Best base line separation was achieved at 4mM Tartaric acid + 1mM PDCA hence this composition of mobile phase is fixed for further quantitative analysis. Figure 4.2.3 shows typical chromatogram obtained in the standard mixture.

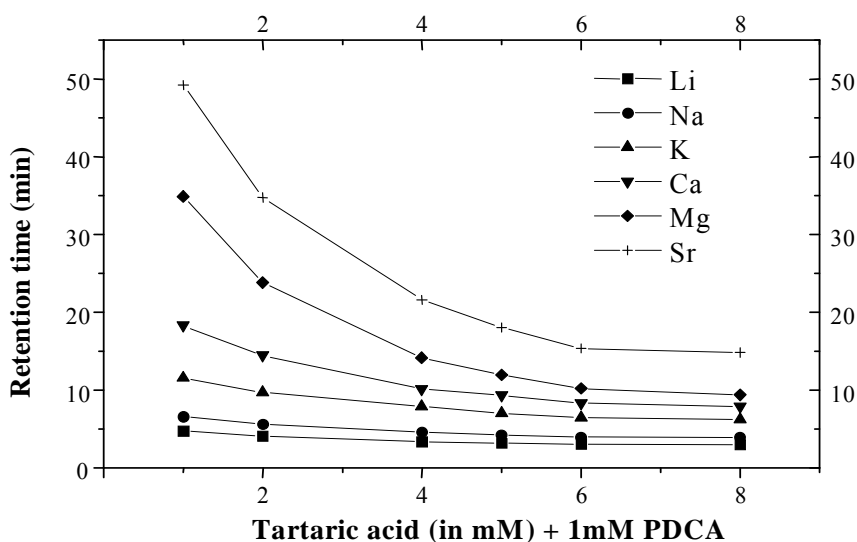


Figure4.2.2. Effect of Tartaric acid concentration on retention of alkali and alkaline earth metal ions

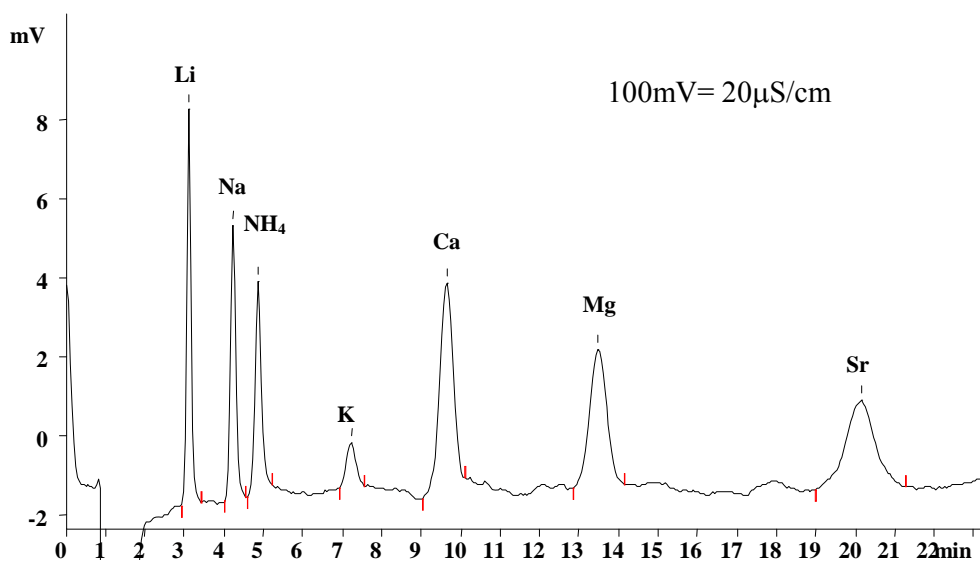


Figure4.2.3. Standard chromatogram of alkali and alkaline earth metal ions in mobile phase of 4mM Tartaric acid + 1mM PDCA

Linearity, Repeatability :

After optimising the mobile phase composition i.e. 4mM Tartaric acid + 1mM PDCA (background conductivity $\sim 690\mu\text{S}/\text{cm}$) the calibration plots of these elements obtained in the range 0.05-5mg/L. Table 4.2.1 shows the linearity regression data for non-suppressed analysis of Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Sr^{2+} . It is clear from the table that the calibration plots of above ions were linear over a wide dynamic range with coefficient of variation better than 0.999. These results are considered acceptable for the range covered. Detection limits obtained based on $\text{S}/\text{N}=3$ for common cations were between 5-30ppb. The coefficients of variation obtained were better than $\pm 5\%$ in 10 replicates. The precision of the method was checked by repeatedly injecting a suitably diluted sample. Table 4.2.1 show the results and the R.S.D. obtained by analysing 10 samples.

Method Validation:

Recovery experiments were employed to evaluate the method quantitatively. Known amounts of Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Sr^{2+} were added to final aqueous phase obtained after solvent extraction of Uranium. Recovery of the added ions was calculated from the initial and final analyses (Table 4.2.2) and found acceptable for all ions. Certified UO_2 powder samples were analysed after dissolving and giving same treatment as that of sample to ensure that no loss of alkali and alkaline earth metal ions under the different conditions used for dissolution and solvent extraction of UO_2 sintered pellet. Table 4.2.3 shows that the result obtained for the Ca^{2+} and Mg^{2+} ions agreed within 10% of the expected value.

Table 4.2.1: Linearity regression data for the non-suppressed analysis of cations

Metal Ions	Conc. Range (ppm)	Detection limit (ppb)	Correlation coefficient	Slope	%R.S.D. for given concentration level (10 replicates)	
					Conc (ppb)	%RSD
Li^+	0.005-5	5	0.9999	0.0111	53	3.06
Na^+	0.01-20	10	0.9999	0.0397	190	1.2
K^+	0.01-20	20	0.9997	0.0858	131	1.3
Ca^{2+}	0.01-20	20	0.9989	0.0439	547	0.9
Mg^{2+}	0.01-20	30	0.9999	0.0224	166	2.5
Sr^{2+}	0.05-20	30	0.9993	0.0908	505	2.9

Injection volume was $20\mu\text{L}$; $n=10$

Table 4.2.2: Recovery of Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺ and Sr²⁺ added to aqueous phase obtained after solvent extraction of UO₂

Conc. mg/L / Added ion		1	2	3	4	5	Average recovery %
Li ⁺	Obtained	1.11	2.015	2.97	4.085	4.824	101.85
	Recovery %	111	100.75	99	102	96.48	
Na ⁺	Obtained	1.14	2.015	3.09	4.077	5.047	106.11
	Recovery %	114	110.75	103	101.9	100.94	
K ⁺	Obtained	1.004	1.997	2.943	3.649	4.967	98.28
	Recovery %	100.4	99.85	98.1	93.72	99.34	
Ca ²⁺	Obtained	1.003	2.08	3.039	4.08	4.794	100.69
	Recovery %	100.3	104	101.3	102	95.88	
Mg ²⁺	Obtained	0.973	1.957	2.955	3.906	4.993	98.23
	Recovery %	97.3	97.85	98.5	97.65	99.86	
Sr ²⁺	Obtained	1.02	2.047	2.986	3.828	4.912	99.57
	Recovery %	102	102.35	99.56	95.7	98.24	

Table 4.2.3 : Results of Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺ and Sr²⁺ for Sintered UO₂ pellets and ILCE certified UO₂ powder

Analyte ion present (ppm)	Sample type			
	Sintered UO ₂ pellets	ILCE UO ₂ powder		
		Conc. Obtained	Conc. Expected	Variation
Li ⁺	0.1 ± 0.07	-	-	-
Na ⁺	21.43 ± 0.50	114.74	-	-
K ⁺	4.0 ± 0.05	7.3	-	-
Ca ²⁺	31.4 ± 0.63	107.5	108.0	0.46%
Mg ²⁺	11.1 ± 0.28	48.4	47.4	2.06%
Sr ²⁺	1.1 ± 0.05	5.2	-	-

Figure 4.2.4 a ,b shows typical chromatogram of different elements present in sintered UO₂ pellet after removal of Uranium matrix. It is clear that these cations can be quantitatively determined in these samples.

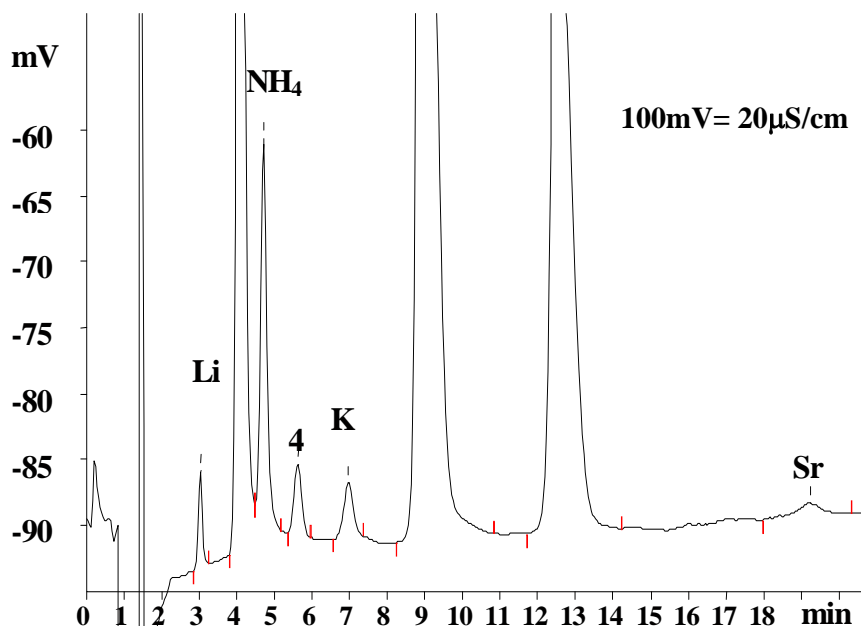


Figure4.2.4a Chromatogram of alkali & alkaline earth ions in sintered UO₂ pellet (mobile phase of 4mM Tartaric acid + 1mM PDCA)

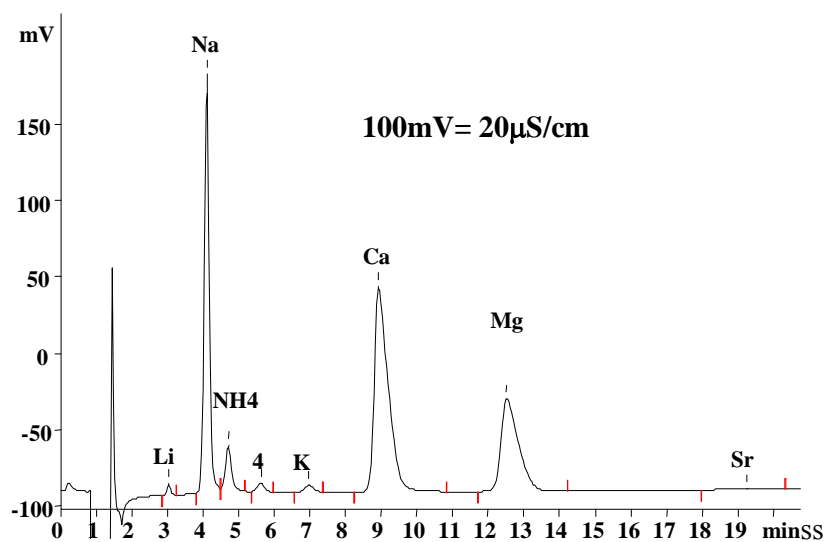


Figure4.2.4bChromatogram of alkali & alkaline earth ions in UO₂ pellet (mobile phase of 4mM Tartaric acid + 1mM PDCA)

5. CONCLUSIONS:

It has been demonstrated that IC technique can efficiently be used for the analyses of alkali, alkaline earth and transition metal ions in sintered UO_2 pellets. Alkali and alkaline earth metal ions and transition metal ions do not have inter elemental interferences. The same procedures can be extended for the analyses of these elements in ThO_2 , $(\text{U}, \text{Th})\text{O}_2$ and $(\text{U}, \text{Pu})\text{O}_2$ samples. Thus Ion chromatography may act as an alternative method for the determination of alkali alkaline and transition metal ion in uranium based nuclear fuels.

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