

Trace Level Determination of Alkaline Earth Metals in High Purity Uranium Using Ion Chromatography

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Summary: An improved ion chromatographic (IC) method has been developed for the determination of magnesium and calcium in high purity uranium. The extraction of alkaline earth metal ions present in samples were optimized using tributyl phosphate (TBP) as an extractant. Excellent recoveries of 99% were achieved for investigated alkaline earth metals at trace level. The relative standard deviations (RSD'S) for Mg^{2+} and Ca^{2+} ions for the ion chromatographic method were 0.5 and 0.8 ppm respectively. The analytes were also analyzed with atomic absorption spectroscopy (AAS) as a counter technique.

Introduction

The purity check on uranium is essential as certain metals at trace level in reactor fuel may pose problems in smooth running of nuclear reactor. These problems are absorption of thermal neutrons by the trace impurities and subsequent production of undesirable isotopes with enormous amount of activity. The permissible concentration of magnesium and calcium in nuclear grade sinterable uranium dioxide powder and in nuclear grade uranyl nitrate is 150 and 200 $\mu g/g$ respectively [1]. Various analytical techniques like titrimetry and atomic absorption spectroscopy

(AAS) are commonly used for analysis of only single element, whereas ion chromatographic technique is generally used for the analysis of complex samples. Different types of detectors such as photometric UV/VIS, refractive index, conductometric and fluorimetric are used in chromatographic analysis. Chromatographic separation coupled with conductometry is broadly classified into suppressed and non-suppressed ion chromatography (IC). When compared to other analytical techniques, IC is fast, sensitive and possesses universal applicability for the analysis of

ionic substances. Detection limits range from ppb to ppm levels [2-7]. This communication describes simultaneous assay of alkaline earth metals in a matrix like high purity uranium using non-suppressed IC. The sampling procedure has been optimized for the efficient recoveries of alkaline earth metals from the samples using TBP as an extractant. The validity of the proposed method has been tested by comparing its results with AAS.

Results and Discussion

The use of EDA has been described for the resolution of alkaline earth metal ions. However, it requires long elution time (15-20 minutes) for alkaline earth metal ions. Therefore, elution behaviour of alkaline earth metal ions was optimized by incorporating various concentration combinations of complexing and chelating agents. A mobile phase composing of 0.3mM EDA and 2mM tartaric acid of pH 3.5 eluted the whole alkaline earth metals within 7-8 minutes with reasonable peaks separation. The chromatographic separation of these metal ions using synthetic metal ions mixture is shown in Fig. 1. The linear response of Mg^{2+} and Ca^{2+} ions have been demonstrated in Fig. 2. However, the analysis of metals of interest in matrix like bulk uranium requires the prior removal of uranium from the dissolved sample. Otherwise, masking of Mg^{2+} and Ca^{2+} ions are observed by the uranium metal. In addition when sample is injected as such, it also loads the column and the chromatographic behaviour of the latter is changed. The bulk uranium can be extracted using proper extractant like TBP. The extraction of alkaline earth metals shows low distribution coefficient of these metals ions in TBP-Kerosene oil system [8]. The known quantities of Mg^{2+} and Ca^{2+} ions in presence of a fixed uranium concentration (as expected in actual sample) were extracted in TBP under various experimental conditions. A composition of 30% TBP-kerosene oil with 6M HNO_3 was found optimum for the recovery of Mg^{2+} and Ca^{2+} in the aqueous layer. The results of these investigated recoveries are summarized in Table-1. It was found that main source of error was the elimination of 6M HNO_3 , when treating it with formic acid. It can be minimized if long neck glass flasks are utilized for sampling rather than open beaker. The lowest detection limit for Mg^{2+} and Ca^{2+} ions were 0.5 and 2 ppm respectively. The reproducible chromato-

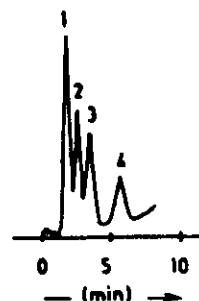


Fig. 1a: Separation of standard alkaline earth metal ion mixture.

Eluent: 0.3mM EDA+2 mM Tartaric acid
pH 3.5

Column: Wescan SCX (25 cmx4.6 mm)

Flow rate : 1.5 ml/min.

Peak identification : 1= Mg^{2+} ; 2= Ca^{2+} ;
3= Sr^{2+} ; 4= Ba^{2+}

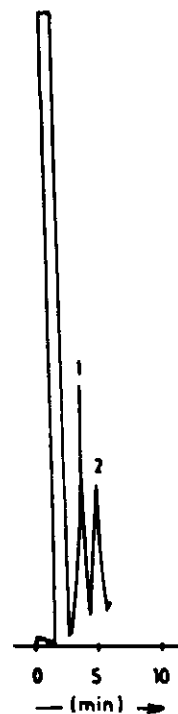


Fig. 1b: Separation of processed standard Mg^{2+} and Ca^{2+}

graphic behaviour of Mg^{2+} and Ca^{2+} for independently processed same sample is shown in Fig. 3. The processed samples were also analyzed with AAS. It can be seen that results are reasonably comparable as given in Table-2. The standard deviation in case of IC is higher as compared to

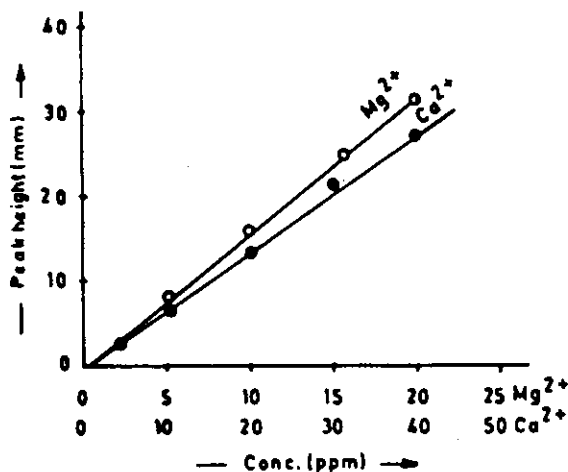


Fig. 2: Calibration curves of Mg^{2+} and Ca^{2+} as per conditions in figure 1.

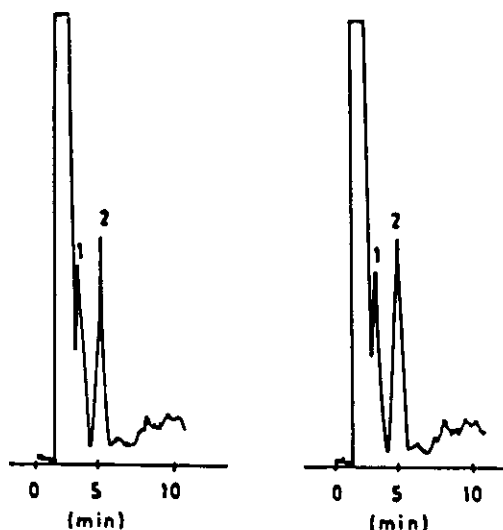


Fig. 3: Reproducible chromatographic behaviour for the analysis of Mg^{2+} and Ca^{2+} in high purity Uranium as per conditions in figure 1.

Table-1: Solvent extraction recoveries^a of Mg^{2+} and Ca^{2+} in 30% TBP-kerosene oil system

Recoveries of Magnesium (ppm)			Recoveries of Calcium (ppm)		
Added	Found ^a	Recovery %	Added	Found ^b	Recovery %
5.0	4.98	99.6	5.0	4.97	99.4
10.0	9.80	98.0	10.0	9.80	98.0
15.0	14.70	96.0	15.0	14.70	98.0
20.0	19.60	98.0	20.0	19.50	97.5
25.0	24.50	98.0	25.0	24.40	97.3
30.0	29.20	97.3	30.0	29.20	97.3
35.0	34.10	97.4	35.0	34.00	97.1
40.0	38.80	97.0	40.0	38.80	97.0

^a: Average of triplicate measurements.

^b: Determined by IC.

Table-2: Comparison of ion chromatographic and atomic absorption spectroscopic (AAS) results

Sample code	IC ^a $\mu g/g$		(AAS) $\mu g/g$	
	Mg^{2+}	Ca^{2+}	Mg^{2+}	Ca^{2+}
1	14.2 \pm 0.5	36.1 \pm 0.6	18.2 \pm 0.2	40.7 \pm 0.2
2	16.4 \pm 0.5	35.7 \pm 0.8	20.9 \pm 0.1	43.1 \pm 0.2

^a: Average of five determinations.

AAS values. However, IC has the advantage of multi-element analysis capability. Moreover, the measured values of Mg^{2+} and Ca^{2+} ions in samples proved the reliability of the proposed method for the analysis of alkaline earth metals in high purity uranium.

Experimental

Chemicals

Ethylene diamine (EDA) was of Fluka Switzerland. Tartaric acid, formic acid, nitric acid, TBP and salts used for preparing standard solutions were from E.Merck, Germany. Double deionized distilled water was used for the preparation of solutions.

Instruments

An ion-analyzer fitted with a Reodyne injector 7000, conductometric detector 213 A, analytical column SCX (25 cm x ϕ 4.6 mm) and a sample loop of 50 μ l were of Wescan Instrument, USA. The printer/plotter chromato-integrator, D-2500, and atomic absorption spectrophotometer Z-8000 were from Hitachi, Japan. A Pope pH meter, USA was used for pH measurements. All the measurements were made at ambient temperature i.e. 25 ± 1 °C.

Sampling procedure

Sample containing uranium metal was dissolved in 1:1 (~ 8 M) HNO_3 . One mL of the dissolved uranium was extracted in 30% TBP-Kerosene oil with 6M HNO_3 . The aqueous layer was collected in a teflon beaker and it was evaporated to almost dryness by slowly adding formic acid. The residue was collected in 1 mL of 0.1 M HNO_3 and was injected into IC for the analysis. The same aliquot was also analyzed with AAS.

Chromatographic parameters

Mobile phase consisting of 0.3mM EDA + 2mM tartaric acid of pH 3.5 was used for the

elution of alkaline earth metal ions with flow rate of 1.5 mL min^{-1} . Retention time data of standard cations was used for qualitative identification of these species in the sample. Peak height Vs concentration ratio (external calibration) method was used for the quantification of Mg^{2+} and Ca^{2+} ions.

References

1. Annual Book of ASTM; Vol., 12.01, Nuclear energy (1) C-753-81, p. 194 and ASTM C-788, p. 430 (1984).
2. M. Ahmed, A.R. Khan, S.B. Butt and Ehasn-ul-Haq; Ion Chromatographic Analysis of water and nuclear Materials. PINSTECH/NCD- 108 (1985).
3. H. Small, T.S. Steven and W.C. Beumen; *Anal. Chem.*, **47**, 1800 (1975).
4. J.S. Fritz, D.T. Gjerde and G. Schmucker, *J. Chromatogr.*, **186**, 509 (1980).
5. B.A. Colenutt and P.J. Trenchard, *Environ. Pollut.*, **10**, 77 (1985).
6. X. Zenyuan, X. Hongshen and W. Qian, *Xiagtan Daxue Ziran Kexue Xuebao*, **15**, 82 (1993).
7. P. Jones, M. Foulkes and B. Paull, *J. Chromatogr.*, **673**, 173 (1994).
8. A.I. Mikhailichenko, M.A. Klimenko and V.B. Bulgakova, *Russian Journal of Inorg. Chem.*, **16**, 1363 (1971).