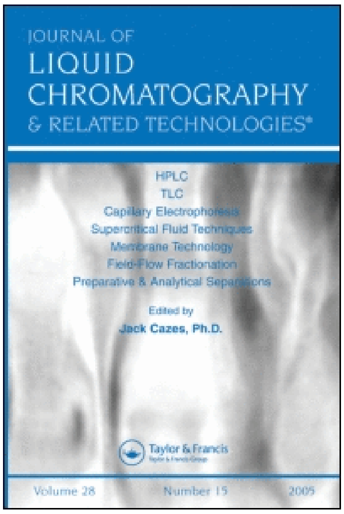

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Assay of Uranium in the Presence of Various Interfering Ions Using Ion Pair Liquid Chromatography

M. Riaz[a]; Shahid Bilal Butt[a]; Ehsan-Ul-Haq[a]
[a] Nuclear Chemistry Division PINSTECH, Islamabad, Pakistan

To cite this Article Riaz, M. , Butt, Shahid Bilal and Ehsan-Ul-Haq(1993) 'Assay of Uranium in the Presence of Various Interfering Ions Using Ion Pair Liquid Chromatography', Journal of Liquid Chromatography & Related Technologies, 16: 7, 1589 — 1599

To link to this Article: DOI: 10.1080/10826079308020975

URL: http://dx.doi.org/10.1080/10826079308020975

JOURNAL OF LIQUID CHROMATOGRAPHY, 16(7), 1589-1599 (1993)

ASSAY OF URANIUM IN THE PRESENCE OF VARIOUS INTERFERING IONS USING ION PAIR LIQUID CHROMATOGRAPHY

M. RIAZ, SHAHID BILAL BUTT, AND EHSAN-UL-HAQ
Nuclear Chemistry Division PINSTECH
P. O. Nilore
Islamabad, Pakistan

ABSTRACT

A sensitive and specific method for uranium(VI) determination using reverse phase ion-pair high performance liquid chromatography with UV detector has been developed. The developed method has been applied for the determination of uranium in a synthetic sample containing most of the interfering ions. Except iron most of the elements and anion which often interfere in uranium assay do not interfere in the present method. Interference of iron is masked by addition of 5mM/1 EDTA solution to the sample.

INTRODUCTION

The higher capital cost of uranium metal recovery from its ore compel scientists to develop more reliable analytical method for assay of uranium and to control on uranium wastage in nuclear industry. Moreover the necessity of a sensitive and reliable method for uranium assay in complex samples like blood/urine can not be ignored[1]. Different instrumental methods have been reported for determination of uranium in various matrices[2]. These methods have certain limitations such as interference of different metal ions, higher acidity of sample to be analysed, higher instrumental cost etc.

Liquid chromatography with pre, post and on column derivitization is used for estimation of uranium (VI) in various matrices[3-5]. Muller et al[6] utilised ion-pair liquid chromatrography for uranium assay using RP-2 column, tetrahexylammonium bromide as ion-pairing reagent and $NaHSO_4$ as ion developer. This methed has established the maximum acidity limit of 0.3M HNO_3 for analysis. It my cause problems when low contents of uranium are present in the higher acidity, where higher dilution of samples may limit the detection of uranium. Moreover, acidity above 0.3M HNO_3 strongly effects uranium lowest detection limit (LDL) of < 20 mgl^{-1} due to the interference of acidity peak[6] and samples need to be pre-neutralised. The presence of NO_2^- also strongly interfere and requires pre or on column oxidation by sulphamic acid.

In the present communication, the behaviour of tetrabutylammonium perchlorate ($TBAClO_4$) and NaH_2PO_4 as ion-pairing reagent, and as ion developer respectively using RP-8 column has been investigated for the assay of U(VI). The tolerance limit of acidity for samples is improved to 0.5M HNO_3. Moreover, the presence of NO_2^- in the sample does not require its prior oxidation by sulphamic acid. The incorporation of NaH_2PO_4 has completely resolved the acidity and U(VI) peaks, and the trace quantities of uranium (<20 mgl^{-1}) can be performed without pre-neutralization step as reported elswhere[6] .

EXPERIMENTAL

Reagents

Tetrabutylammonium perchlorate was obtained from Fisher scientific Company USA. Uranyl nitrate for preparation of U(VI) standard and stock solutions, NaH_2PO_4 , H_3PO_4, acetonitrile (ACN) and Na_2EDTA of analytical grade were from E-Merck Germany. Deionized water was prepared using sybron deionizer (USA).

Instrumentation

Solvent delivery system was perkin Elmer Series 10 fitted with a 6 μl loop and a Rheodyne 7120 sample injector, USA. The detector was UV Spectrophotometer, Dupont, USA. Chromatograms were recorded on a Hitachi D-2500 chromato-integrator, Japan. The analytical column was ET 250/8/4 Nucleosil c_8 (25cmx4.6mm) of Macherey Nagel, Germany. All the measurements were carried out at room temperature, (22±1C°).

PRINCIPLE OF URANIUM ION-PAIRING

Kaplan and co-worker[7] have spectrophotometrically confirmed trinitrate complex of uranyl ion in HNO_3. The reaction sequence in aqueous solution is as follows:

$$UO_2^{++} \overset{NO_3^-}{\rightleftarrows} UO_2NO_3^+ \overset{NO_3^-}{\rightleftarrows} UO_2(NO_3)_2 \xrightarrow{NO_3^-} \left[UO_2(NO_3)_3\right]^-$$

Concentration of above complexes depends upon the concentration of water and nitrate. Muller et al[6] have established the existence of a 1:1 complex of uranyl trinitrate with quaternary amine as per equation

$$[UO_2(NO_3)_3]^- + R_4N^+ \rightleftarrows [R_4N\ ]\ [UO_2(NO_3)_3]$$

In the present procedure, the ion-pairing ability of uranyl trinitrate with $TBClO_4$ has been explored in HPLC for the improvement in the existing method for the assay of U(VI)

RESULTS AND DISCUSSION

Optimization of Mobile Phase

The nitrate and the complex $[R_4N]\ [UO_2(NO_3)_3]$ have λ max at 220nm and 254nm respectively. Detection of uranium was carried out at

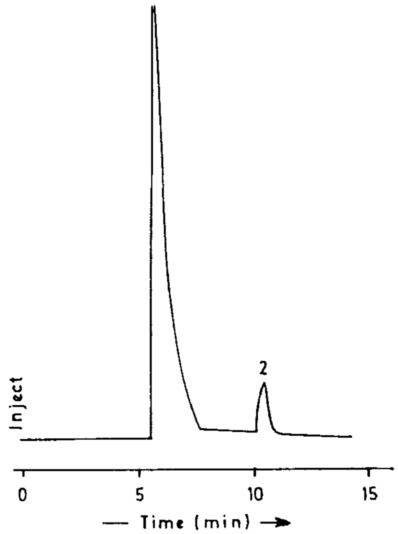

Fig.1 Chromatogram of standard Uranium in the Eluent.

Peak identification : 1 = U = 100 mg l^{-1} ; 2 = NO_3^-
Column = Nucleosil. C_8 ; Detector UV = 254 nm
Flow rate = 0.4 ml min^{-1};
Eluent = ACN : 15 % ; H_2O : 85 % ;
$TBAClO_4$: 10×10^{-3} M ; NaH_2PO_4 : 25×10^{-3} M .

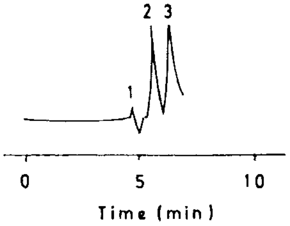

Fig. 2 Resolution of acidity and Uranium peak in 0.5 M HNO_3
Peak identification : 1 = Solvent peak, 2 = Acidity peak,
3 = Uranium peak (20 mg l^{-1})

254nm having a molecular extinction coefficient of ion-pairing complex (ε=846). The mobile phase 25% ACN-water, 5mM/l of $TBAClO_4$ and $NaHSO_4$ each has resolved 0.1M HNO_3, U(VI), water and NO_3^- components in the same order. However, for sample acidity of 0.5M HNO_3, the above mobile phase containing $NaHSO_4$ from 5-15mM/l could not separate the acidity and uranium (VI) components. Another ion-developer NaH_2PO_4 with varied concentrations of 5-50mM/l at pH 3 has been incorporated in place of $NaHSO_4$. 25mM/l of NaH_2PO_4 has resolved 0.5M HNO_3 acid and uranium (VI) with a retention time difference of 0.5 minute but at the same time the base line is slightly shifted positively. This shifting is controlled by reducing the ACN concentration to 15% and increasing $TBAClO_4$ to 10mM/l, which resulted in an improved resolution of 0.8 minute between U(VI)/0.5M HNO_3 (Fig.2). 50mM/l NaH_2PO_4 deteriorates the resolution of the components of interest. Similarly 15mM/l of $TBAClO_4$ with 15% ACN-H_2O and 25mM/l NaH_2PO_4 resulted in the loss of resolution between 0.5 M HNO_3 acidity and U(VI) peak and in addition to that increase number of peaks and loss of sensitivity for U(VI) was also observed. The pH of the mobile phase 15% ACN-water, 25mM/l NaH_2PO_4 and 10mM/l $TBAClO_4$ was varied from 3-2 with 10% H_3PO_4 in order to investigate its effect on the resolution of acidity and U(VI). At pH 3 the U(VI) peak height reduced significantly, however the resolution improved as compared to pH 2. The lowering of U(VI) signals at pH 3 may be either partly due to the hydrolysis of U(VI) or it may be because of a decrease in U(VI) trinitrate complex concentration for a constant NO_3^- At pH 3 only < 1% of the U(VI) is hydrolysed as reported[8]. Therefore, the later reasoning prevail over the former for the lowering or U(VI) response at pH 3. The optimum composition of investigated mobile phase at pH 3 having flow rate of 0.4 ml min^{-1} is as under,

Mobil phase:	ACN:	Water:	$TBClO_4$:	NaH_2PO_4
	15%	85%	10mM/l	25mM/l

Chromatogram in Fig.1-2 show the elution behaviour of 100 mgl^{-1}standard U(VI) in the eluent and 20 mgl^{-1}in 0.5M HNO_3 respectively. Whereas Fig.3 shows the calibration curve of peak area vs

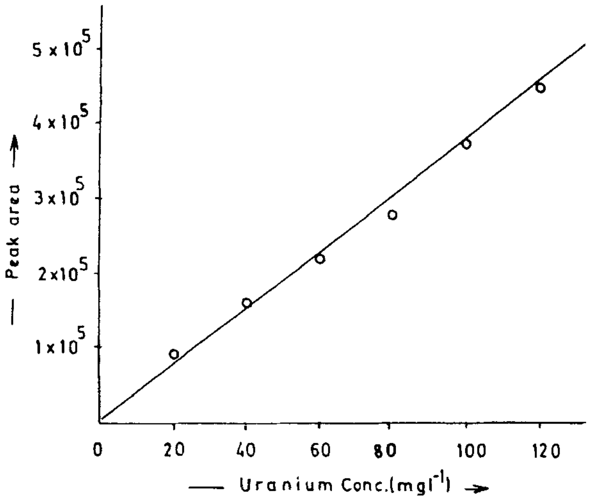

FIG. 3 CALIBRATION CURVE OF URANIUM (Peak area vs conc.)

TABLE.I

Synthetic Sample of Interfering ions

Total Cation Concentration 136.4 $g.l^{-1}$

Element	$g.l^{-1}$	Element	$g.l^{-1}$
Na	44.0	Ru	0.3
Mg	10.0	Rh	0.3
Ca	0.2	La	2.0
Sr	0.2	Ce	0.4
Ba	1.4	Pr	2.2
Al	40	Nd	3.4
Cr	0.1	Gd	0.2
Mn	10.5	Th	2.5
Fe	10.2	Boron	0.3
Ni	2.2	Fluoride	3.2
Cu	0.4	Nitrate	250
Zr	4.0	H^+ ion	2M
Mo	1.9		

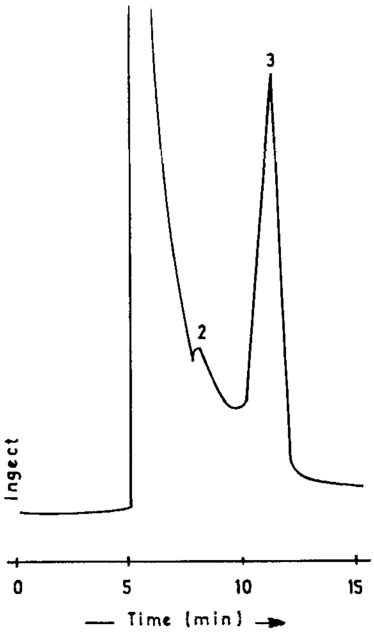

Fig.4 Chromatogram shows masking of Uranium by Iron in 0.5 M HNO_3

Peak identification: 1 = Iron-Uranium peak. (Fe^{+3} = 100 mgl^{-1}, U = 100 mgl^{-1})

2 = Unknown. 3 = NO_3^-

U(VI) Concentration in 0.5 HNO_3. The response of detector is linear in the range of 5-120 mgl^{-1} U(VI) with a correlation coefficient of 0.99. The peak area/concentration ratio i.e. external calibration method was used for quantification of uranium.

STUDY OF INTERFERENCES

The interference of various elements as given in table 1 was investigated. To minimize the acidity effects and overloading of U(VI)

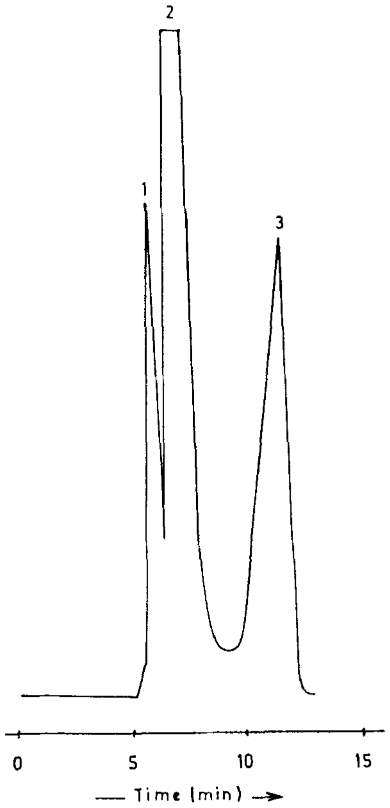

Fig.5 Chromatogram shows demasking of Iron by using 5mM/l Na_2EDTA in 0.5 M HNO_3

Peak identification: 1 = Uranium. 2 = Iron-EDTA complex peak. 3 = NO_3^-

Conc of U (vi) and Fe^{+3} are same as in Fig.4

TABLE.2

Analysis of IAEA-Uranium Ore and Synthetic U(VI) Solutions

Sample Code	Certified Value/ known Conc mgl^{-1}	HPLC VALUE mgl^{-1}	RSD	Photometeric Value mgl^{-1}	RSD
S_1	13.17[a]	13.8±0.10	0.7	16.1±0.60	3.7
S_2	7.2[b]	7.6±0.2	2.6	8.7±0.4	4.6
S_3	20.0	19.5±0.2	1.1	21.1±0.4	1.9
S_4	35.0	34.2±0.2	0.6	35.8±0.2	0.6
S_5	80.0	78.9±0.4	0.5	82.4±0.3	0.4

$s_1 - s_2$ = Torbernite (U_3O_8) SRM, IAEA a = 0.471%, b =0.313%
$s_3 - s_5$ = Synthetic U(VI) Solutions.

on chromatographic column the standard and sample solution were diluted with distilled water in order to keep the maximum acidity level of 0.5M HNO_3. It has no effect on peak symmetry or on quantification of Uranium. The consituents in Tabel-1 were 20 times diluted for 1 µl injection volume and 100 times diluted for 6 µl with distilled water and injected individually. Only Fe^{+3} /Fe^{+2} with (RT 5.52 minutes) were eluted close to uranium peak (RT 6.35 minutes). Iron has a tolerence limit of 10 mgl^{-1}. Above this limit iron completely overlaps the uranium peak as shown in Fig.4. Interference of iron has been avoided by the addition of 5mM/l Na_2EDTA to the sample, that does not effect the response and elution behavior of U(VI) as shown in Fig.5 alongwith a separated Iron-EDTA complex peak. Rest of the investigated ions do not interfere. With a 6 µl injection the lowest detection limit (LDL) for standared U(VI) and for U(VI) with the interfering metal ion was 2 mgl^{-1} and 5 mgl^{-1} respectively.

ANALYSIS OF STANDARD REFERENCE MATERIAL (SRM) AND SYNTHETIC U(VI) SOLUTION

The developed method has been applied for the analysis of SRM IAEA-Uranium ore Torbernite received from IAEA, Austria. These samples were dissolved in aqua-regia and finally stored in 0.5 M HNO_3. The results of SRM and standard U(VI) solutions containing all the investigated interfering ions (Synthetic U(VI) Solution) analysed by the reported and extractive photometric method[9] are compared in Table 2. The results for samples S_1 and S_2 obtained by the present method are well in agreement with the certified values of SRMs, however the photometric values differ appreciably for $S_1$and S_2. The analytical results of standard U(VI) solutions using photometric method are close to those obtained by the present chromatographic procedure.

CONCLUSION

The developed method is applicable to the analysis of uranium in complex matrices like uranium ore etc. The reliability of the present procedure has been evaluated by analysing IAEA (SRMs) The data show good precision and accuracy of the measurements within ± < 6% . The method reported herein is relatively simple, sensitive and free of most of the ions investigated.

REFERENCES

1. T.J. Miller. Anal. Letters, 24, 657-664 (1991).
2. R.H. Atallah, D.G. Christianand S.D. Hartenstein Analyst 113(3), 463-469 (1988).
3. J.J. Byerley, J.M. Scharer and G.F. Atkinson. Analyst. 112(1),41-44(1987).
4. K. Andrew, K. S. William and A. Michael. Anal. Chem. 60(24), 2729-2733 (1988),

5. I. Jancarova, H. Krizora and V. Kuban, Talanta. 38(10), 1093-1097, (1991).
6. J.P. Muller, J.Cojean and A.Deloge. Analusis. 15,209-216 (1987).
7. L. Kaplan. R.A. Hildeprand and M. Ader US Atomic Energy Commission report ANL 4250,(1950).
8. C.F. Baes Jr and R. E. Mesmer. The Hydrolysis of Cations. John Wiley and sons. pp.179-182, 1976.
9. D.A. Johnson and T.M. Florence, Anal. Chim. Acta, 53, 73-79, (1971).

Received: August 20, 1992
Accepted: September 4, 1992