

Liquid Chromatographic Determination of Uranium in Laki Hot Springs Using *Bis*(Salicylaldehyde)propylenediimine as Derivatizing Reagent

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Summary: Preconcentration of uranium from water samples of Laki hot springs has been examined with aluminium oxide, followed by acid dissolution of the precipitate. Precolumn derivatization is carried out with *bis*(salicylaldehyde)propylenediimine (H_2SA_2Pn). Elution and separation have been examined from YMC Pack ODS 5 μm column with a mixture of methanol:acetonitrile:water (60:10:30 v/v/v). Detection UV was at 260 nm. Iron and copper are also detected and are simultaneously quantized with uranium. The amounts of metal ions obtained are within 11-89 $\mu g/L$ with coefficient variation (C.V) 2.6-4.5 after preconcentration of 390 times.

Introduction

A number of analytical methods have been reported for the determination of uranium in acid digests of rocks [1] natural ground water [2], nuclear reprocessing solutions [3,4] and waste stream samples [4], technological waters [5], hot spring water [6], phosphoric acid [7], sea water [8] and urine [9], using spectrophotometry [1,3,9-12], spectrofluorimetry [13-15], liquid chromatography (ion exchange [16,17], ion [18], ion pair [19,4,5] adsorption [20] and reverse phase [2,21,23]), neutron activation analysis, [6,24] gamma-ray spectrometry [25], laser induced fluorescence and thermal lensing spectroscopy [26] and photo-acoustic spectroscopy [27]. The complexing reagents used for the determination of uranium include 1-(2-pyridylazo)-2-naph-thol [28], 4 (2'-pyridylazo) resorcinol [29], arsenazo III, [2,5,7, 16], 2-(5-bromo-2-pyridylazo)-5-diethyl-aminophenol [3], 5-(aryloxy) quinolin-8-ols [9], *N*-(*o*-sulphonic benzoylsodium salt)-*N*-phenylhydroxylamine [11], hydroxamic acid [1], hydrazones [10,12,21-23] and tetradentate Schiff bases [30,33].

For the determination of uranium from water samples, the enrichment of uranium has been carried out on reversed phase cartridge [2], ion [18] or ion pair HPLC [4-5]. The detection is by UV [4] or by post column derivatization with arsenazo III [2,5,18]. The detection limits are reported 2 $\mu g/mL$ [2], 0.1 $\mu g/ml$ [4] and 0.18 mM [5] uranium.

The reagent H_2SA_2Pn (Fig. 1) has been extensively studied as complexing reagent for copper(II), nickel(II), palladium(II), platinum(II).

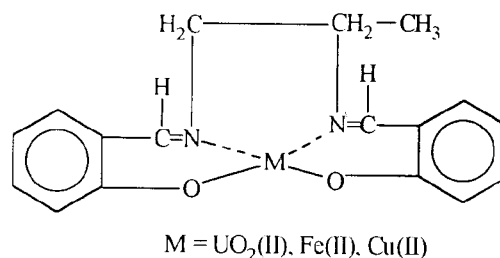


Fig. 1: Structural diagram of metal chelates.

oxovanadium(IV), cobalt(II) and iron(II) [32-37]. The dioxouranium(VI) complex of H_2SA_2Pn has also been reported [38] and its structure has been assigned.

Kikawada *et al.* [8] have determined uranium by co-precipitation of uranium with aluminium, followed by neutron activation analysis. In the present work uranium has been preconcentrated with aluminium, followed by off column derivatization with H_2SA_2Pn , reverse phase PHLC separation and UV determination.

Results and Discussion

Reagent H_2SA_2Pn reacts with dioxouranium(VI), iron(II), iron(III) and copper(II) to form coloured complexes. The complexes are extractable in chloroform, isobutyl methyl ketone and ethyl acetate. The uranyl complex absorbs maximally at 476 nm ($\epsilon=1714 \text{ L mole}^{-1} \text{ cm}^{-1}$). Effect of pH on the extraction of dioxouranium(VI), iron(II) and copper(II) with H_2SA_2Pn in chloroform was examined spectrophotometrically. The optimal extraction of uranium, iron and copper was observed at pH 6.6 and 7 respectively. It was therefore the simultaneous extraction of uranium, iron and copper was carried out at pH 6. Uranyl complex obeys the Beer's law at final concentration of 8-40 $\mu\text{g/ml}$ chloroform.

The elution and separation of uranium, iron and copper complexes were examined on YMC ODS column and the complexes easily eluted with binary mixture of methanol + water. The reagent eluted first and did not affect the analytical response of metal chelates. The optimal separation between the reagent, dioxouranium (VI), iron(II) and copper(II) was obtained when eluted isocratically with a mixture of methanol:acetonitrile:water (60:10:30 v/v/v) with a flow rate of 0.6 ml/min and detection at 260 nm. The resolution factor (R_s) between two adjacent peaks was observed > 1.6 (Fig. 2). However at this conditions optimized for the determination of uranium, iron(II) and copper(II), nickel(II) coeluted with copper(II) and iron(III) coeluted with iron(II).

Linear calibration curves for simultaneous extraction of uranium, iron and copper, recorded as average peak height ($n=3$) were with 20-100 $\mu\text{g/ml}$,

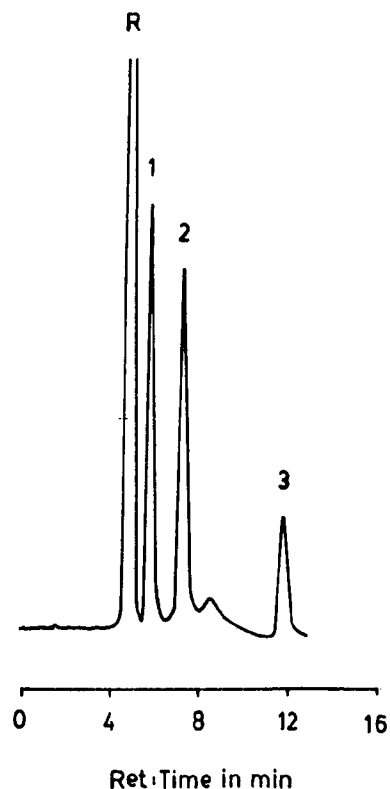


Fig. 2: HPLC separation of $R = H_2SA_2Pn$, and its (1) dioxouranium(VI) (2) iron(II) and (3) copper(II) chelates on a column (150 x 4.6 mm id) of YMC-Pack ODS AQ 5 μm with elution with methanol:acetonitrile: water (60:10:30 v/v/v) at a flow rate of 0.6 ml/min. and detection at 260 nm.

with coefficient of correlation (r) from $n=5$ points 0.996, 0.987, 0.994 respectively. The detection limits measured atleast three times the background noise was 2.5 $\mu\text{g/ml}$ each of the metal, corresponding to 12.5 $\mu\text{g/injection}$ (5 μl).

For the determination of uranium in natural hot spring water samples required preconcentration procedure and preconcentration by coprecipitation with aluminium oxide was examined, followed acid dissolution of the precipitates and precolumn derivatization with H_2SA_2Pn . Aluminium was selected for coprecipitation, because it does not react with H_2SA_2Pn and could be masked from precipitation at pH 6 with fluoride.

Recovery of the uranium by coprecipitation was examined by taking different amounts of uranium (50, 100, 200 μg) and coprecipitation procedure (B) was followed. The amounts of uranium was evaluated from calibration curve prepared from the known amounts of uranium following extraction procedure (A). The amounts of uranium recovered were within the range of 90-92% with coefficient of variation (C.V) 4.2-4.9 with preconcentration of 650 time.

The chemical analyses of Laki hot spring were temperature 42, 41°C, pH 6.6, 6.8, sulphide 152 and 142 mg/L, conductivity 7300, 5300 us/cm, chloride 3370, 3710 mg/L, alkalinity 99, 88 mg/L, total hardness 820, 700 mg/L, sulphate 137 and 136 mg/L for springs 1 and 2 respectively.

Laki hot spring water samples were analysed for the contents of uranium, iron and copper and amounts were evaluated from the calibration curves prepared by preconcentration by coprecipitation. The amounts of uranium found were 28.0 and 24.6 $\mu\text{g/L}$, iron 84.6 and 69.6 $\mu\text{g/L}$ and copper 11.0 and 12.8 $\mu\text{g/L}$ in springs 1 and 2 respectively. The amounts of uranium and copper were also evaluated by standard addition technique (Fig. 3) and amounts found were 27.4 and 22.4 $\mu\text{g/L}$ uranium and 10.0 and 11.2 $\mu\text{g/L}$ copper in springs 1 and 2 respectively. The results obtained by HPLC for iron and copper were also compared with atomic absorption. The results (Table-1) show close correlation.

Table-1: Analysis of uranium, copper and iron in Laki natural hot springs water samples

| S.No. | Amount of metal found $\mu\text{g/L}$ by HPLC (C.V) | | | Amount of metal found $\mu\text{g/L}$ by A.A(C.V%) | |
|-------|--|---------------|---------------|--|---------------|
| | Uranium | Copper | Iron | Copper | Iron |
| 1. | 28.0 (3.7) | 11.0 (4.2) | 84.6 (4.5) | 14.2 (1.4) | 88.3 (2.6) |
| 2 | 29.6 (4.6) | 12.8 (3.8) | 69.2 (4.2) | 15.5 (1.1) | 72.3 (1.8) |

Experimental

The reagent $\text{H}_2\text{SA}_2\text{Pn}$ was prepared as reported by heating together salicylaldehyde and 1,2-propylenediamine in 2:1 molar ratio [32].

A. Solvent extraction procedure

An aliquot of solution 10-20 ml containing uranium (0-200 μg) or copper, iron and uranium (0-

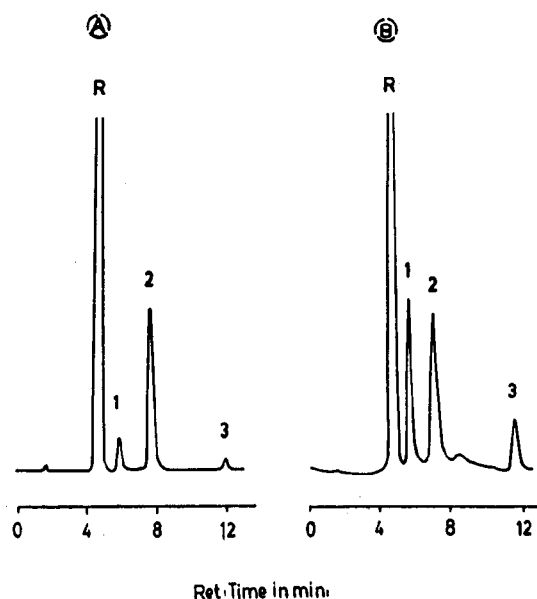


Fig. 3: Simultaneous determination of (1) uranium (2) iron (3) copper in (A) Laki hot spring sample No. 1. (B) Laki hot spring sample No. 1 spiked with uranium 100 μg and copper 40 μg . Conditions as Fig. 2.

200 μg each) was transferred to round bottom flask and was added ascorbic acid 3-4 mg, sodium acetate-acetic acid buffer pH 6 and reagent solution (3.0 ml, 1% w/v in ethanol). The mixture was warmed at water bath for 10 min and cooled contents were transferred to separating funnel. Chloroform (4 ml) was added and contents were mixed well. The layers were allowed to separate and organic layer was collected. Extract (2 ml) was transferred to sample vial and solvent was evaporated and residue was dissolved in methanol (1 ml). The solution (5 μl) was injected on column YMC-Pack, ODS, AQ, 5 μm (150 x 4.6 mm id) and complexes were eluted with a ternary mixture of methanol: acetonitrile: water (60:10:30 v/v/v) with a flow rate of 0.6 ml/min. Detection UV was at 260 nm.

B. Procedure for preconcentration

Double distilled water (1300 ml) was transferred to a tall beaker and was added uranium (0-200 mg) or a mixture containing copper, iron and uranium (0-200 μg each). It was added nitric acid (10 ml, 65%) and solid aluminium(III) sulphate (10 g). The solution was mixed well and warmed at (70-

80°C) for 15 min. The solution was cooled at room temperature and was added ammonia solution (20 ml, 35%) with constant stirring. The solution was allowed to stand at room temperature overnight. The precipitate was filtered and was transferred to a beaker. Hydrochloric acid (80 ml, 37%) and nitric acid (20 ml, 65%) were added and contents were heated to near dryness. Nitric acid (20 ml, 65%) was added and was again heated to near dryness. The residue was dissolved in nitric acid (5 ml, 0.1N) and pH was adjusted to 6 ml and was added sodium flouride solution (5 ml), 1% w/v in water). Further procedure was followed as A.

C) Analyses of uranium, iron and copper in laki hot springs

Laki hot springs highly impregnated with sulphur are situated in Laki hills of Khirther mountains range, near Laki village about 85 kilometers North West of Hyderabad, about 150 feet above sea level. The area is dry and arid. The laki hot springs are known since long for the cure of certain diseases.

Clear and transparent water of the main spring 1 (Southern) and relatively small spring 2 (Northern) were sampled and collected in clean 2.5 L bottles from the middle of the pools and sample collecting depth was about 5-10 inches. The samples were transferred to laboratory and analysed next-day.

Laki hot spring samples (1) and (2) 1300 ml were taken in tall beakers and were treated as B. The residue was dissolved in nitric acid (0.1N) and volume was adjusted to 25 ml. Solution 15 ml was taken and pH was adjusted to 6 and was added sodium flouride (5 ml, 1% water). Further procedure was followed as A.

D. Analyses of uranium, copper and iron in laki hot spring water sample using standard addition technique

Laki hot spring water samples (1) and (2) 1300 ml each was taken in tall beaker and was added 100 µg uranium and 40 µg copper and procedure was followed as C.

Hitachi 655A liquid chromatograph connected with variable wavelength UV monitor,

Rheodyne 7125 injector and Hitachi 2500 Chromato-integrator was used.

Column YMC-Pack ODS, AQ 5 µm (150 x 4.6 mm id) (YMC, Co Ltd. Japan) was used throughout the study.

Spectrophotometric studies were carried on Hitachi 220-Spectrophotometer. Varian Spectr AA-20 atomic absorption spectrometer with air-acetylene flame was used.

Solutions containing 1 ml/ml uranium, iron and copper were prepared from G.R. grade uranyl nitrate, ammonium iron(II) sulphate and copper(II) chloride (Merck). Hydrochloric acid, nitric acid, chloroform, acetone, methanol G.R. (E. Merck) were used. Freshly prepared double distilled water was used for HPLC studies.

Laki spring samples were examined for temperature, pH, conductivity, sulphide, chloride, alkalinity, hardness and sulphate using standard procedures [39].

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