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Short communication

Simultaneous solvent extraction and high-performance liquid chromatographic determination of uranium, iron, nickel and copper in mineral ore samples and phosphate rock residues using N,N′-ethylenebis(salicylaldimine) as complexing reagent

M.Y. Khuhawar*, S.N. Lanjwani

Institute of Chemistry, University of Sindh, Jamshoro, Pakistan

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Abstract

The reagent N,N-ethylenebis(salicylaldimine) (H_2SA_2en) has been examined for precolumn derivatization, followed by solvent extraction in chloroform and HPLC determination of uranium, iron, nickel and copper on a Hypersil ODS 3 μm column. Complexes were eluted isocratically using a ternary mixture of methanol–acetonitrile–water and UV detection was at 260 nm. The detection limit was 12 ng/injection for each of the elements. The method has been applied for the determination of metals in mineral ore samples and phosphate rock residues. The results obtained are compared using atomic absorption.

Keywords: Mineral ores; Complex formation; Derivatization, LC; Fluoroapatite; Uranium; Iron; Nickel; Copper; Metals; Ethylenebis(salicylaldimine)

1. Introduction

The interest in the selective extraction, separation and quantitative determination of uranium continues. A number of complexing reagents have been recommended for the solvent extraction, spectrophotometric and spectrofluorimetric determination of uranium with varying degrees of success [1–6]. High-performance liquid chromatographic (HPLC) methods combined with precolumn derivatization are interesting, when an appropriate complexing reagent is involved. Selective complexation with a limited number of metal ions, followed by solvent extraction enables the separation of the desired constituents from the matrix. The high potential of HPLC for the separation of metal ions can be used for simultaneous quantitative determinations.

HPLC methods for the determination of uranium involve mostly ion-exchange, ion-pair or ion chromatography, followed by post-column derivatization with Arsenazo III or 4(2-pyridylazo) resorcinol [7–13]. Cosoli et al. [14] have reported the HPLC determination of uranium on a LiChrosorb RP-2 column. The proposed method is based on the extraction of uranyl ion into dichloromethane as neutral complex of 2,6-diacetylpyridinebis(benzoylhydrozone). Linear calibration is reported with 5–100 ng of uranium injected. Main and Fritz [15]

*Corresponding author.

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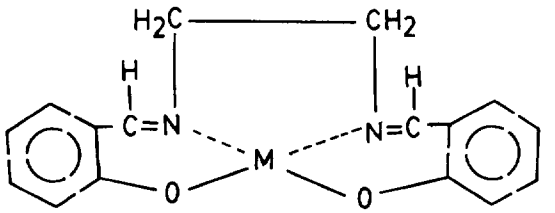

Fig. 1. Structural diagram of reagent.

used bis(quaternary ammonium hydrazones) of 2,6-diacetylpyridine for the chromatographic determination of uranium(VI), titanium(IV), iron(II) and vanadium(V). Gradient elution with aqueous acetonitrile containing formate and perchlorate was obtained with detection limits of 0.2 μM per injection. Fuping et al. [16] have studied the retention behaviour of α-hydroxyisobutyric acid complexes of thorium and uranium in reversed-phase HPLC.

N,N′-Ethylenebis(salicylaldimine) [bis(salicylaldehyde)-ethylenediimine] (H_2SA_2en) (Fig. 1) has been extensively studied as complexing reagent for copper(II), nickel(II), palladium(II), platinum(II), iron(II), iron(III), cobalt(II), cobalt(III), manganese(II), oxovanadium(IV), oxochromium(V), dioxomolybdenum(VI) and dioxouranium(VI) [17–34]. The uranyl complex of H_2SA_2en was reported as early as 1937 [32]. Pasini et al. [33] and El-Sonbati [34] have reported the nature of uranyl complex with tetradentate Schiff bases including H_2SA_2en. Uden and his coworkers used H_2SA_2en for the HPLC separation and determination of copper(II), nickel(II) and palladium(II) using normal- and reversed-phase modes [35,36] with detection limits in the low ng/injection range. The reagent can easily be prepared from simple and inexpensive laboratory chemicals in good yield (90% theoretical). It reacts with a limited number of metal ions at all concentrations. Therefore, in the present work H_2SA_2en has been used for the solvent extraction and the HPLC determination of uranium, iron, nickel and copper in real samples.

2. Experimental

The reagent H_2SA_2en and its copper(II), nickel(II) and dioxouranium(VI) complexes were prepared as reported [33]. The reagent H_2SA_2en was prepared by simple condensation of salicylaldehyde with ethylenedimine in 2:1 molar ratio in ethanol. The copper(II), nickel(II) and dioxouranium(VI) complexes were prepared by refluxing together equimolar (0.0014) solutions of H_2SA_2en and copper(II) acetate, nickel(II) acetate or dioxouranium(VI) nitrate in methanol.

2.1. Solvent extraction procedure

An aliquot of the solution (1–5 ml) containing copper(II), nickel(II), iron(II) and dioxouranium(VI) (0–200 μg) was transferred to a well stoppered test tube and the volume was adjusted to 5 ml. Sodium acetate–acetic acid buffer, pH 6 (2 ml, 0.5M) and reagent H_2SA_2en solution [2 ml 1% (w/v) in methanol] were added. The mixture was heated on a water bath for 15 min and allowed to cool at room temperature. Chloroform (2 ml) was added and the contents were mixed well (2–3 min). The layers were allowed to separate and exactly 1 ml of extract was transferred to the sample vial; the solvent was evaporated. The residue was dissolved in methanol (1 ml) and was injected on a Hypersil ODS, 3 μm column, 5 μl solution (150×4.6 mm I.D); complexes were eluted with methanol–acetonitrile–water (40:40:20, v/v/v) using a flow-rate of 0.6 ml/min and UV detection at 260 nm.

2.2. Solvent extraction recovery of metals

A portion of the solution (2 ml) containing 50, 100 or 200 μg each of copper, nickel and iron in a mixture and uranium separately were treated as in Section 2.1. The aqueous phase was separated and 65% nitric acid (0.5 ml) was added; then, it was heated to near-dryness. For the determination of copper, iron and nickel the residue was dissolved in water and final volume was adjusted to 10 ml. The metal ions were determined using air–acetylene flame atomic absorption spectrometer. In case of uranium, the residue was dissolved in 3 ml of water and determination was carried out using spectrophotometry as reported by Cheng [37] with 1-(2-pyridylazo)-2-napthol.

2.3. Analysis of mineral ore samples

To mineral ore samples 1, 2, 3, 4 and 5 (1 g each) were added 37% hydrochloric acid (60 ml) and 65% nitric acid (40 ml); the solutions were heated gently to near-dryness. A further 30 ml of 65% nitric acid was added and contents were again heated to dryness. The residue was dissolved in 0.1*M* nitric acid and was filtered. The final volume was adjusted to 50 ml. A 5-ml volume from samples 2–5 and 15 ml from sample 1 was taken, pH was adjusted to 6 and the procedure described in Section 2.1 was followed.

2.4. Analysis of phosphate rocks residues

The acidic phosphate rocks residues (fluoroapatite) sample (5 g) was added to 37% hydrochloric acid (30 ml) and 65% nitric acid (2 ml) and was heated to near-dryness. Then a further 20 ml 65% nitric acid was added and again heated to near-dryness. The residue was dissolved in 0.1*M* nitric acid and the volume was adjusted to 10 ml. A sample of solution (2 ml) was taken and pH was adjusted to 6 and procedure was followed as for Section 2.1.

The mineral ore samples (house reference standards of sand stone) were obtained from Atomic Energy Minerals Centre, Lahore, Pakistan. Phosphate rock residue (fluoroapatite) samples of Pak. Arab Fertilizer, Multan were obtained from PINSTECH, Islamabad, Pakistan. Uranyl nitrate (BDH) was used for the preparation of uranium standard solution (1 mg/ml).

HPLC studies were carried out on a Hitachi 655A (Japan) liquid chromatograph connected with variable-wavelength UV monitor, Rheodyne 7125 injector and Hitachi Chromato-integrator D2500.

Hypersil ODS, 3 μm (Shandon, USA) column A (150×4.6 mm I.D) was used. Spectrophotometric studies were carried out on Hitachi 220 (Japan) spectrophotometer. A Varian spectr AA-20 (USA) atomic absorption spectrometer with air–acetylene flame nebulizer was used.

3. Results and discussion

The reagent reacts with dioxouranium(VI) to form a coloured complex. which was extractable in chloroform, ethyl acetate and methyl isobutyl ketone. The effect of pH on the extraction of uranyl complex in chloroform was examined spectrophotometrically by measuring its maximum absorbance at 472 nm. Maximum transfer occurred within the pH range 6–8. Iron(II) and iron(III) could also be extracted in chloroform, but maximum extraction of iron(III) was observed at pH 6. At higher pH iron(III) precipitated out as hydrated iron(III) oxide and interfered with the determination. pH 6 was selected for the simultaneous extraction of dioxouranium(VI), iron(II), iron(III), copper(II) and nickel(II). The percentage transfer of metal ions in chloroform using single extraction was calculated by measuring the concentration of metal ions remaining in aqueous phase. The average percentage extraction for copper, iron, nickel and uranium was 95, 87, 90, 89% respectively with R.S.D. within 1.5–6.6% (n=3).

Uranyl complex easily eluted from the Hypersil ODS column, but an optimal separation between uranyl, iron(III), nickel(II) and copper(II) occurred when eluted isocratically with a ternary mixture of methanol–acetonitrile–water. The excess of reagent added for derivatization eluted first and did not interfere with the separation (Fig. 2). The presence of the precious metals, palladium(II) and platinum(II), did not affect the determination, and

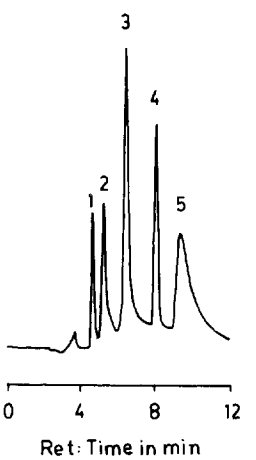

Fig. 2. HPLC separation of (1) H_2SA_2en, (2) UO_2, (3) Fe(III), (4) Ni(II), (5) Cu(II) complexes. Column: Hypersil ODS, 3 μm (150×4.6 mm). Eluent: methanol–water–acetonitrile (40:40:20, v/v/v), flow-rate 0.6 ml/min. Detection at 260 nm.

complete separation between uranyl, iron(II), palladium(II), platinum(II), nickel(II) and copper(II) was observed when eluted with a mixture of methanol–acetonitrile–water (20:60:20, v/v/v) (Fig. 3).

Calibration curves for simultaneous determinations were obtained by plotting average peak height vs. concentration, and linear relationship was obtained at the final concentration of 0–100 μg/ml of extract with coefficients of correlation (r) of 0.994, 0.998, 0.996 and 0.992 for uranium(VI), iron(II), nickel(II) and copper(II), respectively. The detection limit for the simultaneous detection of uranium, iron, nickel and copper, measured at a minimum of three times the background noise, was 2.5 μg/ml for each of the elements, corresponding to 12.5 ng/injection of 5 μl (AUFS=0.005; attenuation 4). The detection limits are based on the concentration in the extract, which involved a preconcentration factor of 2.5 and correspond to about 1 μg/ml in original solution. For determining the detection limits of individual elements, the concentration of acetonitrile could be increased in the eluent to obtain sharper peaks with a significant improvement in the detection limits.

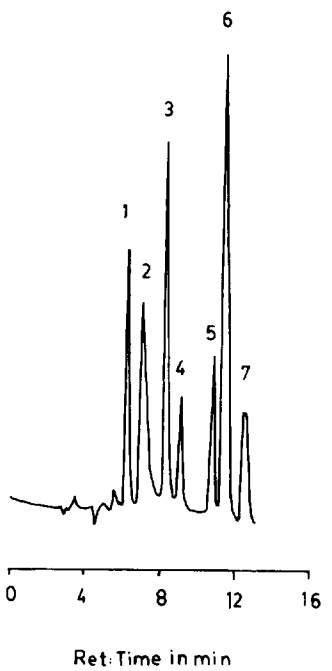

Fig. 3. HPLC separation of (1) H_2SA_2en, (2) UO_2, (3) Pt(II), (4) Fe(II), (5) Pd(II), (6) Ni(II), (7) Cu(II) complexes. Column: Hypersil ODS, 3 μm (150×4.6 mm). Eluent: methanol–water–acetonitrile (20:20:60, v/v/v), flow-rate 0.6 ml/min. Detection at 260 nm.

Table 1
Analysis of uranium in mineral ore samples and phosphate rocks residues

Sample	Amount of uranium μg/g reported[a]	Amount of uranium found by HPLC (μg/g)[b]
1	106.0	100(4.8)
2	423.0	396(3.6)
3	626.0	584(6.4)
4	1273.7	1190(5.1)
5	1718	1600(2.8)
6		48(5.8)
7		52(4.6)

[a] Values given by the supplier.
[b] In parentheses are R.S.D values (%), $n=3$.

Test solutions of uranium were analysed using the extraction procedure as in Section 2.1 in triplicate and amounts in unknown solutions were evaluated from the calibration curve. The percent relative error was within ±0–4%. Citrate, tartrate, phosphate and fluoride, when added at ten times the concentration of metal ions, did not interfere. The method was applied for the determination of uranium, iron, nickel and copper contents in mineral ore samples and phosphate rock residues. The results are summarized in Table 1 and Table 2. The samples were also analysed for the contents of copper, iron and nickel using atomic absorption. The results in Table 1 for uranium contents indicate R.S.D. within 2.8–6.4%, but the observed values are about 6.4 to 6.9% lower than the reported values for mineral ore samples. This may be due to low dissolution efficiency of uranium from sandstone samples in hydrochloric–nitric acid. Similar results have been reported elsewhere [38]. However, there is a reasonable correlation between the results obtained by HPLC for copper, iron and nickel and atomic absorption. The R.S.D. on HPLC was within 2.6–7.2% as compared to 0.8–3.8% on atomic absorption (Table 2).

4. Conclusion

A simple complexing reagent H_2SA_2en has been developed for the extraction of uranium from mineral ore samples and phosphate rock residues, together with copper, iron and nickel. The solvent extraction

Table 2
Analysis of copper, nickel and iron in mineral ore samples and phosphate rocks residue

Sample	Amount found by HPLC (μg/g)			Amount found by atomic absorption (μg/g)		
	Copper	Nickel	Iron	Copper	Nickel	Iron
1	36.8	35.0	10800	38.0	42.0	10620
	(3.8)	(5.6)	(2.6)	(0.8)	(1.8)	(2.8)
2	44.0	45.0	60250	48.0	48.6	60620
	(6.6)	(4.2)	(3.6)	(1.1)	(1.6)	(0.6)
3	22.0	48.0	16670	26.0	52.0	16870
	(5.2)	(3.7)	(3.2)	(2.5)	(1.3)	(0.8)
4	34.0	43.0	18330	36.0	48.0	18120
	(4.4)	(5.1)	(4.8)	(1.4)	(2.1)	(1.1)
5	26.0	42.0	49200	23.0	46.0	49370
	(6.1)	(5.8)	(7.2)	(3.6)	(2.8)	(1.8)
6	21	11.0	188	26.0	9.0	196
	(6.5)	(4.8)	(3.4)	(1.6)	(2.6)	(1.4)
7	17	13.0	186	22.0	10	192
	(5.2)	(3.9)	(4.4)	(2.1)	(2.3)	(3.8)

In parentheses are R.S.D. values (%), $n=3$.

procedure combined with HPLC determination enabled their quantitative evaluations. The detection limits are at the ng/injection level for each of the elements. The simultaneous determination of uranium, copper, iron and nickel is completed in about 10 min with solvent consumption of 5 ml for each determination.

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