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Extraction of Inorganic Ions with Organic Solvents. I. Continuous Extraction of Uranyl Nitrate with Tetrahydrosylvane and Tetrahydropyrane*

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The extraction of uranyl nitrate with tetrahydrosylvane and tetrahydropyrane was investigated and compared with that of ethylacetate and diethylether. The effect of ammonium nitrate and nitric acid was shown and the influence of sulfate, chloride, and phosphate anions as well as calcium nitrate and ferric nitrate was examined.

In the course of our work on separation of uranium from solutions of very low concentration we have used the extraction of uranyl nitrate with organic solvents. According to many authors[1], best results are obtained with extraction media containing oxygen bound in ether-, keto- or esther-form. The influence of nitric acid, nitrates and other ions on the extraction of uranium with ethyl ether has been described[2]. Following chromatographic data[3], we investigated the extraction of uranyl nitrate with tetrahydrosylvane (THS) and tetrahydropyrane (THP). The results of these experiments are briefly described in this paper and compared with those obtained using ethyl ether and ethyl acetate.

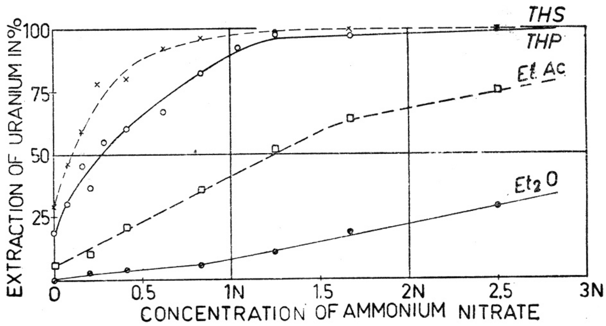

Fig. 1. The extraction data of uranyl nitrate (%) plotted against the concentration (*N*) of ammonium nitrate in the aqueous phase, Solvents: tetrahydrosylvane (THS), tetrahydropyrane (THP), ethylacetate (EtAC) and diethylether (Et_2O). The amount of uranyl nitrate 1mg.U/12ml., the concentration of nitric acid 0.25 *N*, and the extraction time 70 minutes.

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Fig. 1. shows how the extraction of uranium with tetrahydrosylvane (THS), tetrahydropyrane (THP), ethyl acetate (EtAc) and diethyl ether (Et_2O) depends on the concentration of ammonium nitrate in the aqueous phase; the extraction time (70 min.) and the concentrations of nitric acid (0.25 *N*) and of uranyl nitrate (1 mg. U/12 ml.) were kept constant.

The best extraction medium seems to be the THS. The salting out effect of ammonium nitrate is less pronounced with ethyl acetate and diethyl ether; 100 percent extraction was obtained with THS and THP at 0.8 *N* and 1.2 *N* ammonium nitrate respectively.

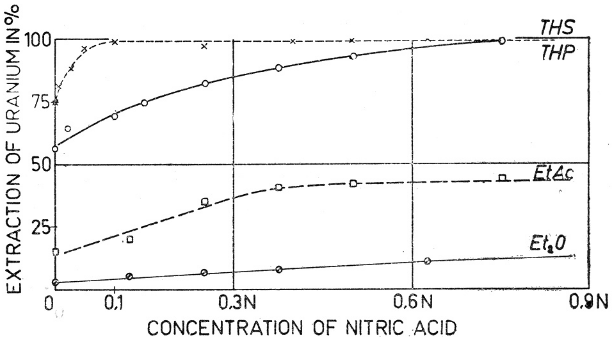

Fig. 2. The extraction data of uranyl nitrate (%) plotted against the concentration (*N*) of nitric acid in the aqueous phase. Solvents: tetrahydrosylvane (THS), tetrahydropyrane (THP), ethylacetate (EtAc) and diethylether (Et_2O). The amount of uranyl nitrate 1mg.U/12 ml., the concentration of ammonium nitrate 0,8 *N*, the extraction time 70 minutes.

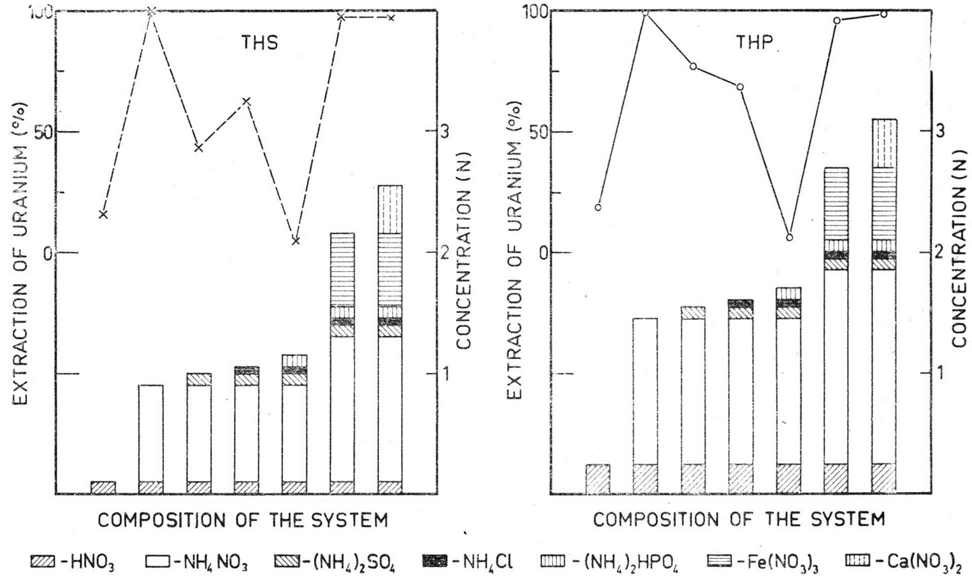

Fig. 3. and 4. The extraction data of uranyl nitrate (%) for different compositions of the aqueous phase. Solvents: tetrahydrosylvane (THS in Fig. 3.) and tetrahydropyrane (THP in Fig. 4.). The amount of uranyl nitrate was 1mg.U/12 ml., the extraction 70 minutes.

The change of the extractibility of uranyl nitrate by THS, THP, EtAc and Et_2O, with the concentration of nitric acid is given in Fig. 2. The concentrations of ammonium nitrate (0.8 *N*) and uranyl nitrate (1 mg. U/12 ml.), and the extraction time (70 min.) being constant. It seems that a complete extraction of uranyl nitrate with EtAc and Et_2O is impossible under these conditions.

To obtain a 100 percent extraction of uranyl nitrate (in 70 min.) — in the concentration range from 12 μg. to 180 mg, of uranium per 12 ml. — it is thus necessary to perform the extraction with THS in presence of 0.8 *N* ammonium nitrate and 0.1 *N* nitric acid, or with THP in presence of 1.2 *N* ammonium nitrate and 0.25 *N* nitric acid.

The influence of various impurities in the aqueous phase on the extraction of uranyl nitrate with THS and THP is shown diagramatically in Figs. 3. and 4. The inhibitory effect of phosphate ions is very pronounced; the chlorides and sulfates act in the same way but their effect is weaker. To remove inhibitory effect of these ions we added calcium- and ferric- nitrate. Calcium nitrate was without effect, while ferric nitrate enabled the extraction of uranyl nitrate in presence of phosphate- chloride- and sulfate- ions.

The precipitate of uranyl nitrate with phosphate-ions is soluble in ferric nitrate solution, whereas calcium nitrate itself was precipitated with phosphate-ions. The mixture of ammoniumphosphate (0.1 *N*), -chloride (0.05 *N*) and -sulfate (0.1 *N*), with uranyl nitrate (1 mg. U/12 ml.), ferric nitrate (0.6 *N*) and calcium nitrate (0.4 *N*) is a clear solution, from which uranyl nitrate can be easily extracted.

EXPERIMENTAL

An automatic microextractor[4] was used for continuous extraction of uranyl nitrate. There were always 12 ml. of aqueous phase in the contacting vessels (the vessels were 12 cm. high and 1.4 cm. in diameter); the organic solvent layer was 1 cm. high. The circulation rate of the solvent was about 1 ml./min. (2.6—3.5 drops/sec.) for THS and THP; it was much greater for EtAc and Et_2O; the heating conditions were always the same. For each extraction 6—8 ml. of solvent were used.

After the extraction was finished and the solvent evaporated, the residue (probably a polymerisate of THS or THP), was destroyed by heating on an air-bath; 2 × 0.5 ml. of redistilled nitric acid (15 *N*) were carefully added, followed by 2—3 × 1 ml. 30% H_2O_2, and evaporated nearly to dryness each time. Finally 0.5 ml. perchloric acid (70%) were added to remove nitrate-ions and change uranium into six-valent state.

The residue was dissolved in the supporting electrolyte (0.16% salicylic acid, 0.009% thymol and 0.4% v/v sulphuric acid) and uranium determined polarographically[5].

Cambridge Pen-recording Type polarograph was used; the results are given percentages (the ratio of the diffusion currents of the sample to that of the standard).

Tetrahydrosylvane and tetrahydropyrane were synthesized in the Institute for Industrial Research, Zagreb. Ethyl acetate and nitric acid were redistilled. All other chemicals were of analytical grade purity.

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REFERENCES

1. H. N. Irving, *Quart. Revs. (London)* **5** (1951) 200.
2. A. Noström and L. G. Sillen, *Svensk Kem. Tidskr.* **60** (1948) 227; C. J. Roden, *Anal. Chem. of Manhattan Project,* New York 1950.
3. T. V. Arden, F. H. Burstall and R. P. Linstead, *J. Chem. Soc.* **1949** (Suppl. Issue, No. 2.) S 311.
4. M. Branica, *Arhiv kem.* **26** (1954) 119.
5. V. B. Vouk, M. Branica and O. A. Weber, *Arhiv kem.* **25** (1953) 225.

IZVOD

Ekstrakcija anorganskih iona organskim otapalima. I. Kontinuirana ekstrakcija uranil nitrata tetrahidrosilvanom i tetrahidropiranom

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Ispitivana je ekstrakcija uranil nitrata, tetrahidrosilvanom (THS) i tetrahidropiranom (THP) u usporedbi prema etilacetatu (EtAc.) i dietileteru (Et_2O), u automatskom mikroekstraktoru[4]. Istraživan je utjecaj amoniumnitrata i dušične kiseline na ekstrakciju uranilnitrata, nepovoljan utjecaj amonium-sulfata, -klorida i -fosfata kao i sprečavanje tih pojava kalcium i feri nitratom. Uz umjerene uvjete potrebno je 70 minuta za postizavanje kvantitativne ekstrakcije uranilnitrata (od 12 μg do 180 mg urana/12 ml) tetrahidrosilvanom i tetrahidropiranom, dok se to ne može postići etilacetatom i dietileterom. Određivanja urana vršena su polarografskom metodom[5].

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