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# A New Sensitive Reagent for Uranium

## 1-(2-Thiazolylazo)-*m*-dimethylaminophenol (TAM). Application to the Assay of Rocks and Solutions Low in Uranium

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A simple analytical method for uranium is presented. It is based on the extraction of uranyl nitrate with methyl *iso*butyl ketone from a sample solution saturated with aluminium nitrate. An intensely coloured complex is formed *in situ* by addition of the reagent 1-(2-thiazolylazo)-*m*-dimethylaminophenol. The uranium content can be determined spectrophotometrically with a sensitivity of about 0.1 μg.

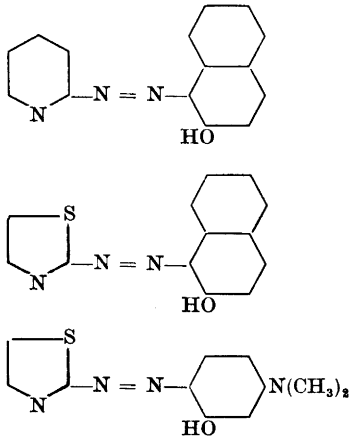
During the investigation of uranium-bearing rocks from southern Greenland the search for easy-handled, sensitive analytical methods was a major point.

A considerable work has been done with a modification of the dibenzoylmethane method by Booman, Maeck, Elliott and Rein [1]. Its principle is that uranyl nitrate is extracted into methyl *iso*butyl ketone (hexone) from a solution saturated with aluminium nitrate. Colour development is made *in situ* by the addition of dibenzoylmethane in pyridine. The lower level of detection is 0.5 μg of uranium. The new method takes its origin in a paper by Spinner and Miller [2]. These authors have determined uranium in thorium process solutions by means of 1-(2-pyridylazo)-2-naphthol (PAN) which forms an intensely coloured uranium complex.

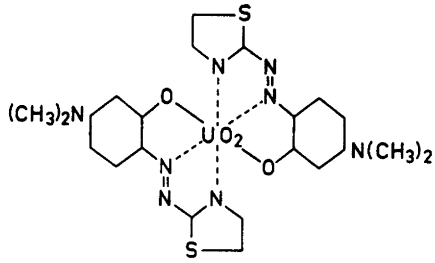
In this laboratory Skytte Jensen has for other purposes prepared a series of dyes on the basis of 2-aminothiazol [3]. Among these the compound 1-(2-thiazolylazo)-2-naphthol (TAN) has been tried as a reagent for uranium and proved useful. However, previous experience suggested that the introduction of a dimethylamino-group in the molecule would intensify the colour. This led to the synthesis of 1-(2-thiazolylazo)-*m*-dimethylaminophenol (TAM). As shown in Fig. 1, the TAM-uranium chelate has an optical density about 100 % higher than that of the corresponding TAN-compound. Therefore TAM was chosen for the further development of this method.

## CHELATE FORMATION

The three dyes mentioned have the formulas



The chelate of TAM with the uranyl ion may be written



The dye is slightly soluble in water, the uncharged chelate, however, is nearly insoluble. Both are readily dissolved in a variety of organic solvents, *e.g.* hexone.

The colour depends on the composition of the solvent used. To obtain reproduceable results it is recommended to equilibrate the hexone solution with an aqueous buffer. At low pH the chelate will dissociate, and at high pH the uncomplexed dye assumes a colour much like that of the uranium chelate. Thus a pH optimum must exist for the colorimetric measurement of the chelate against a reagent blank. This optimum has been experimentally obtained by using a buffer containing pyridine — pyridinium chloride in the proportion 7 : 1.

## EXPERIMENTAL

*Reagents:* Ammonium hydroxide 12 M. $Al(NO_3)_3$, $9H_2O$, salting agent. $Al(NO_3)_3$-$KIO_3$ scrub solution. Methyl *iso*butyl ketone (Shell Chemicals). Dye solution: $0.5 \times 10^{-3}$ M TAM, 4 M pyridine, 0.5 M HCl in $H_2O$.

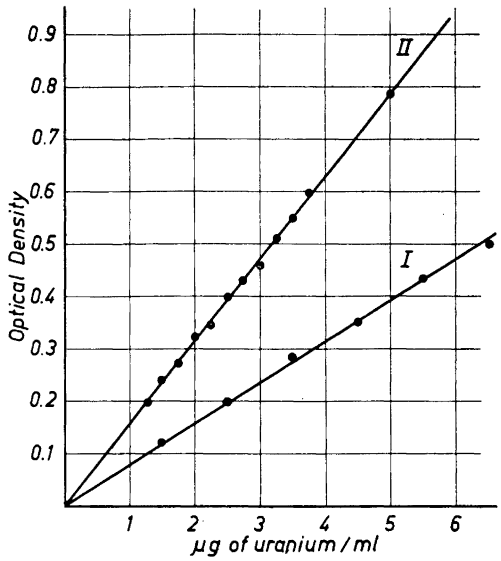



*Fig. 1.* Standard uranium-optical density curve.

I TAN complex, $\lambda$ — 585 m$\mu$
II TAM complex, $\lambda$ — 575 m$\mu$

Aluminium nitrate salting agent: 1 kg of $Al(NO_3)_3$, 9 $H_2O$ (Merck, purum) + 100 ml of $H_2O$ is molten in a beaker and stored in a 1 l two-necked flask. The flask is kept heated on an infrared bath at a temperature just sufficient to prevent crystallization (*ca.* 100°C). One neck is provided with a reflux condenser. The other, allowing for pipetting, is closed with a glass stopper.

$Al(NO_3)_3$-$KIO_3$-scrub solution. 5.4 g of $KIO_3$ and 350 g of $Al(NO_3)_3$, $9H_2O$ are dissolved in 250 ml of $H_2O$. After cooling the specific mass is adjusted to 1.33 g/ml by addition of $H_2O$ or $Al(NO_3)_3$.

Dye solution: 31 mg of TAM are dissolved in 80 ml of pyridine in a 250 ml volumetric flask. About 150 ml of water are added. The mixture is allowed to cool. Then 10.4 ml of conc. HCl are added and the volume is adjusted to the mark with $H_2O$.

Where not specified, the chemicals used are analytical grade.

## Method

*Uraniferous rock.* In most cases fuming with HF and $HClO_4$ is sufficient to bring the sample in solution. If necessary the fuming may be followed by melting with $NaHSO_4$ without interfering with the extraction procedure. The dissolved sample is oxidized with 2 drops of 6 % $H_2O_2$ and is neutralized with $NH_3$ to incipient hydroxide precipitation. Further 0.025 ml of 12 M ammonium hydroxide and 2 ml of salting agent are added per ml of sample solution. After being homogenized by gentle agitation the sample is ready for extraction with hexone of which an amount is taken corresponding to 0.3—1 ml per $\mu$g of uranium expected.

It is preferable to carry out the extraction in two stages, proceeding in the following manner: Add exactly half of the hexone to be used, and shake vigorously for 2 min. Centrifuge. Separate in a funnel taking care that the aqueous phase is free from hexone drops. Repeat the operation using the other half of the hexone. Equal volumes from the two extracts are combined and shaken with the scrub solution for 2 min. After complete separation of the phases about 2.5 ml of the organic layer and exactly the same volume of the dye solution are transferred to a small tube with a special pipet arrangement (Fig. 2). They are mixed by gentle agitation for 5 min. (Glass stoppers are used in all

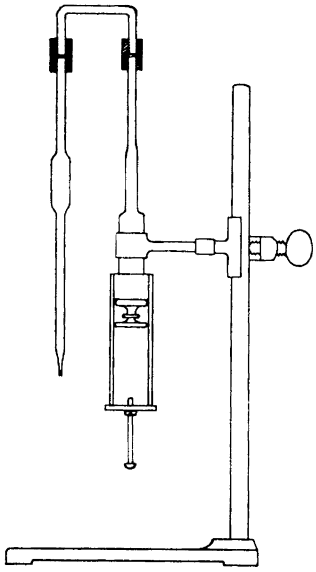


*Fig. 2.* Syringe with exchangeable pipet.

operations where hexone is involved.) After centrifuging the organic layer is transferred to a 1 cm colorimetric cell and the absorbance is measured at 575 mμ against a reagent blank. The uranium content is read from a standard calibration curve (Fig. 1).

*Uranium pregnant liquor.* In case of a uranium pregnant liquor the method will be especially applicable for routine work, as the extraction may be carried out in one stage and the scrubbing omitted.

## DISCUSSION

The hexone extraction as described here is rather selective for uranium. The most common interfering ions are $Ce^{+4}$, $Fe^{+++}$ and $Th^{+4}$. $Ce^{+4}$ is reduced by the $H_2O_2$-treatment to $Ce^{+++}$, which is not extracted. $Fe^{+++}$ has a low distribution coefficient but is often present in large concentrations. It is effectively removed by the scrubbing procedure. $Th(NO_3)_4$ is extracted to a considerable extent. However the $IO_3^-$-scrubbing ensures a sufficient low level given by the solubility product of thorium iodate.

Further the two-phase system of chelate formation has an inherent selectivity, as it has been found that only chelates of dipositive metal ions show a definite tendency to be extracted by organic solvents. The calibration curve is a straight line all over the range covered by the spectrophotometer.

The standard deviation of a reading has been estimated to 0.025 μg of uranium per ml.

## REFERENCES

1. Booman, G. L., Maeck, W. I., Elliott, M. C. and Rein, I. E. *IDO-14437.*
2. Spinner, I. H. and Miller, F. C. *AECL-789.*
3. Skytte Jensen, B. *Acta Chem. Scand.* **14** (1960) 927.

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