A New Spectrophotometric Method for the Determination of Uranium (VI)

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Fig. 1. Comparison of the IPT-method presented in this communication with methods tested by Ahrland: 1 Potassium cyanoferrate (II), 2 Thiocyanate in ethanol, 3 Thiocyanate in water, 4 Sodium cyanoferrate(II), 5 Basic peroxide. The dashed line is the absorbance per cm of the U(VI)-IPT-acetone-pyridine solution using air as reference.

R ecently Ahrland[1] has presented a critical examination of the three best methods for a spectrophotometric determination of U(VI). He concludes that the thiocyanate method is the most expedient one, but he points out that the absorbance is very sensitive to small variations in the thiocyanate concentration. This drawback has given us reason to look for another procedure that would be more expedient for the determination of the distribution of U(VI) between two liquid phases. A method, which is suitable for such a purpose, should (*a*) have a high sensitivity, (*b*) be independent of the solvent composition of the samples, *i.e.* be insensitive to the acidity of the two phases and to organic solvents and reagents, which in general are colorless but absorb light in the UV-region.

In an extensive investigation[2] of the extraction properties of IPT (*β*-isopropyltropolone) we observed that the U(VI) complex has an extinction coefficient of 8 000 M^{-1} cm^{-1} at 3 950 Å, and previously Dyrssen[3] showed that the U(VI) complex of tropolone has an extinction coefficient of 6 630 M^{-1} cm^{-1} at 4 000 Å in chloroform. The Fe(III)complex has also a very large extinction coefficient[2], 13 900 M^{-1} cm^{-1} at 4 100 Å. The stability constants of IPT-metal complexes are usually very large[2], so it is in general not difficult to find conditions where a final complex is formed, *i.e.* a complex with a wide stability range. With IPT as with TTA (thenoyltrifluoroacetone) and other chelating acids, U(VI) forms an adduct, a UO_2A_2HA complex. The extra HA can be replaced by solvents that contain ligand-forming atoms (*e.g.* tributyl phosphate, dibutyl sulfoxide, ketones, etc). The use of such a solvent should therefore decrease color changes due the displacement of HA in the uranyl-IPT complex by the sample solvent. A high molarity of the displacing solvent molecule should be favorable, which is more easily obtained if it has a
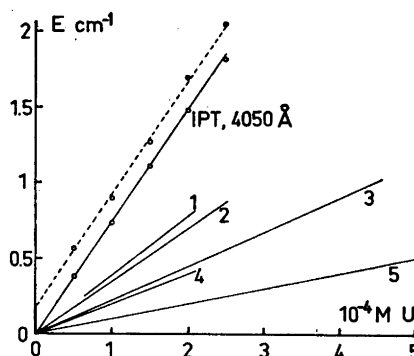
low molecular weight. IPT is a rather weak acid ($pK_a = 7.04$), so to avoid the effect of the acidity of the sample a proton acceptor must be introduced. The acceptor must have a $pK_a < 7.04$ otherwise the yellow anion of IPT (A^-) may be formed. The salt formed between the proton acceptor and the acids in the samples should be soluble in the solution that is measured. The sample, irrespective if it is an aqueous or organic solution (*e.g.* trilaurylamine in dodecane), should be soluble in the IPT reagent solution.

Considering these facts, we have found that a solution of *v* ml of a liquid sample containing U(VI) + (10−*v*) ml of 0.05 M IPT + 1 M pyridine in acetone has an extinction coefficient of 0.740 cm^{-1} per mmole of U added to the 10 ml at 405 mμ, which is independent of the solvent composition of the sample as long as *v* < 1 ml (in some cases a larger value of *v* may be used). The light absorbance per cm using the Hilger Uvispek was a linear function of the U(VI) concentration ([U_{tot}]) up to 2 (99 %) (*cf.* Fig. 1). This means that it is possible to determine [U]$_{tot}$ ≥ 10^{-4} M in a solution by this method using 1 cm cells. The sensitivity of the method is twice that of the thiocyanate in ethanol or potassium cyanoferrate(II) as demonstrated in Fig. 1.

No attempt has been made to eliminate the influence of Fe(III) as in the case of the thiocyanate method.

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1. Ahrland, S. *Svensk Kem. Tidskr.* **72** (1960) 757 (in English).
2. Dyrssen, D. *Trans. Royal Inst. Technol. Stockholm* (1962) No. 188.
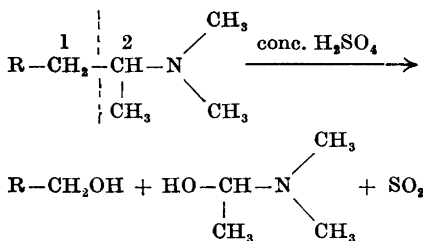3. Dyrssen, D. *Acta Chem. Scand.* **9** (1955) 1567.

Correction to "Formation of Free Radicals from Some Phenothiazine Derivatives as Studied by Electron Spin Resonance" *

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In the reaction scheme on p. 1554 the side chain of the promethazine molecule is erroneously given as 3-dimethylamino-2-methyl-propyl. This is corrected to 2-dimethylaminopropyl and the products obtained in the reaction with conc. sulphuric acid are 10-(hydroxymethyl)-phenothiazine, 1-dimethylaminoethanol and sulphur dioxide.

$$R-CH_2-CH-N\begin{matrix}CH_3\\CH_3\end{matrix} \xrightarrow{\text{conc. } H_2SO_4}$$

(1 2 on R-CH₂-CH-N, with CH₃ below)

$$R-CH_2OH + HO-CH-N\begin{matrix}CH_3\\CH_3\end{matrix} + SO_2$$

R = phenothiazine nucleus.

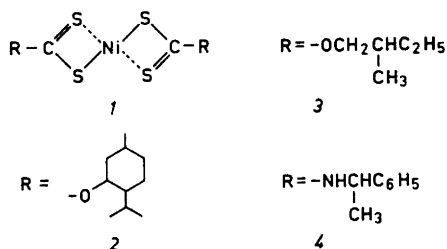* Acta Chem. Scand. **15** (1961) 1545.

Optical Rotatory Dispersion of some Nickel Complexes

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In a recent investigation [1] of xanthates it was shown that these compounds often exhibit strong Cotton effects and that the anomalous dispersion curves can be used for stereochemical correlations. However, the amplitudes and at times even the appearance of Cotton effects of xanthates are very dependent upon chemical constitution. Thus rigid compounds, like bornyl xanthates, have Cotton effects of large amplitudes whereas the methyl xanthate of 2-methylbutanol only shows a plain dispersion curve. We thought it possible to increase the interaction between the C=S chromophore and the various substituents of the pertinent molecule by complexing with a metal.

In the preparation of alkyl xanthates the appropriate alcohol is first treated with alkali and carbon disulfide and then with an alkyl halide. If nickel acetate is added instead of the alkyl halide, a coloured metal complex *1* precipitates. Drawert, Reuther and Born [2] recently investigated this type of complex of several racemic alcohols and found a series of absorption bands in the visible and ultraviolet region. The first group of bands are situated at about 480 and 420 mμ, and the extinction of the complexes seems to be fairly dependent on the structure of the alcohol. However, the ε values will generally be of the order of

R = -OCH₂CHC₂H₅
            |
           CH₃

3

R = -NHCHC₆H₅
           |
          CH₃

4