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A NEW METHOD FOR THE SPECTROPHOTOMETRIC DETERMINATION OF Li(I) WITH A "CROWNED" DINITROPHENYLAZOPHENOL

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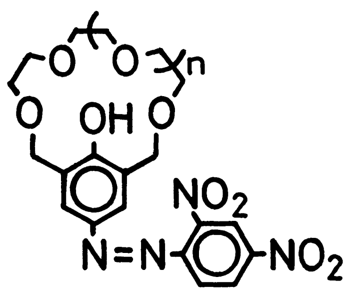
A new method for the spectrophotometric determination of Li(I) with a "crowned" dinitrophenylazophenol is proposed, with a range between 25 and 250 ppb of Li(I) in chloroform-dimethylsulfoxide-triethylamine. The method shows both an excellent sensitivity and a fairly good selectivity, and is applied satisfactorily for the analysis of commercial preparations, *e.g.*, lithium carbonate (tablet).

A "crowned" dinitrophenylazophenol(1_n, n = 1 and 2) was synthesized and 1_1 showed a characteristic coloration only with lithium of alkali metal ions.[1] We now report on a sensitive and selective spectrophotometric method for the determination of Li(I) with 1_1. This is the first example of the determination of Li(I) using a crown ether. After a coloration reaction of 1_1 for the determination of Li(I) was fully examined in a number of solvent systems it was clear that the 1_1-Li complex formed easily in $CHCl_3$-dimethylsulfoxide(DMSO) (95:5 v/v) and changed rapidly from yellow(400 nm) to reddish purple (565 nm) by adding triethylamine(TEA).[2] Then, we use the phenomenon to the determination of Li(I).[3]



1_n, n = 1 and 2

A recommended procedure is as follows. To a solution of LiCl(≦ 2.5 μg as Li) in DMSO(0.5 ml) in a 10 ml volumetric flask, a solution of 1_1 in $CHCl_3$ (2×10^{-4}M, 2.5 ml) is added, and the whole is diluted to *ca.* 9 ml with $CHCl_3$. To the mixed solution is added TEA(0.05 ml) and the whole is adjusted finally to 10 ml with $CHCl_3$. This solution is mixed and allowed to stand for 10 min, then the absorbance is measured at 565 nm against the reagent blank. The absorption spectra obtained by the method are shown in Fig. 1. After examination of the influence of the concentration on the absorbance, 5 v/v%, 0.5 v/v%, and 5×10^{-5}M were estimated advantageously for DMSO, TEA, and 1_1, respectively.[4] The resulting color was very stable and the unchanged absorbance was observed during 10 - 90 min after the coloration reaction. The calibration curve for Li(I) was linear from 25 - 250 ppb. The apparent molar absorptivity coefficient of the Li(I)-1_1 complex as estimated from the calibration curve was 4.3×10^4 l $mol^{-1}cm^{-1}$.[5] Na(I) did not interfer, but K(I), Rb(I), Ca(II), Sr(II), Ba(II), and Mg(II) interfered with the determination by a similar coloration. Therefore, these disturbing ions should be removed before this method is practically applied.

The determination of commercial preparation, *e.g.*, Li_2CO_3(tablet) could be carried out satisfactorily under the same condition even though the pretreatment was necessary. A commercial tablet containing Li_2CO_3(200 mg) was dissolved in concd. HCl, diluted with water, and the resulting solution was filtered. The sample solution was prepared by diluting the filtrate with a definite volume of water. from which 1 ml was picked up and evaporated *in vacuo*. After drying up overnight(0.2 mmHg) the residue obtained was dissolved by adding DMSO(1 ml) and 0.5 ml of this solution was used for the determination of Li(I) according to the recommended procedure.6) The sensitivity and the selectivity of the proposed method are superior to those of the colorimetry based on thorin-Li(I) complex formation7) and the recent spectrofluorometry based on 1,8-dihydroxyanthraquinone-Li(I) reaction.8) The efforts on the improvement of the selectivity for Li(I) are now in progress.

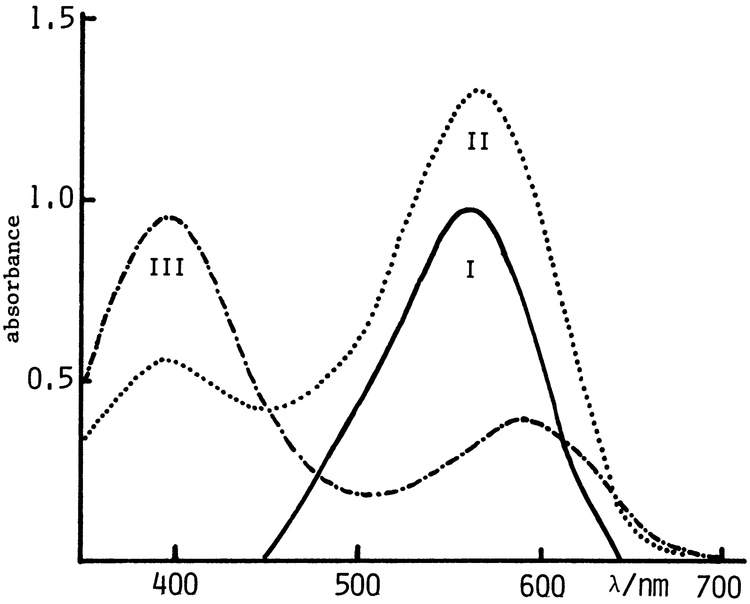


Fig. 1 Absorption curves of l_1-Li(I) complex

I: l_1-Li(I) complex against reagent blank.
II: l_1-Li(I) complex against chloroform.
III: Reagent blank against chloroform.

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References

1) T. Kaneda, K.Sugihara, H.Kamiya, and S.Misumi, Tetrahedron Lett.,22, 4407(1981).
2) This color change seemed to happen with the elimination of a proton. The mechanism of the complexation and the succeeding coloration indicated in $CHCl_3$-pyridine system could be applied also to this system($CHCl_3$-DMSO-TEA), see, ref. 1).
3) The original method1) could not be applied directly for the determination because of taking a long time for a complete dissolution even a small amount of Li salt. The above modified solvent system($CHCl_3$-DMSO-TEA) was slightly inferior in the selectivity for Li(I) but was superior in the reproducibility to the original one.
4) Consant absorbances were obtained in the range of 4 - 6 v/v% of DMSO and 0.3 - 0.6 v/v% of TEA, respectively. A maximum absorbance was given between 2×10^{-5} and 7×10^{-5}M of l_1 to Li(I)(1.44×10^{-5}M, 100 ppb).
5) The coefficient of variation for the five replicated experiments was 2.25%.
6) The recovery yield and coefficient of variation were 99.5% and 4.25%(n = 5), respectively.
7) P. F. Thomason, Anal. Chem., 28, 1527(1956).
8) M. R. Ceba, A. Fernandez-Gutierrez, and M. C. Mahedero, Anal. Lett., 14, 1579 (1981).

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