Communications to the Editor

Chem. Pharm. Bull.
32(6)2468—2470(1984)

A NEW METHOD FOR THE SPECTROPHOTOMETRIC DETERMINATION OF ALIPHATIC AMINES WITH A "CROWNED" DINITROPHENYLAZOPHENOL – Ba(II) COMPLEX

Kenichiro Nakashima,[a] Noriko Mochizuki,[a] Shin'ichi Nakatsuji,[a] Shuzo Akiyama,*,[a]
Takahiro Kaneda,[b] and Soichi Misumi*,[b]
Faculty of Pharmaceutical Sciences, Nagasaki University,[a]
1 – 14 Bunkyo-machi, Nagasaki 852, Japan and
The Institute of Scientific and Industrial Research, Osaka University,[b]
Mihogaoka, Ibaraki, Osaka 567, Japan

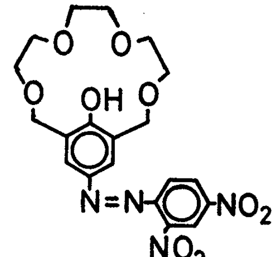
A new sensitive and simple method for the spectrophotometric determination of triethylamine with a "crowned" dinitrophenylazophenol – Ba(II) complex in MeOH is developed. This procedure is successfully applied to the determination of various aliphatic amines with a range of 0.2 to 4 μg/ml.

KEYWORDS ——— amine determination; colorimetry; crown ether; crowned dinitrophenylazophenol; triethylamine; aliphatic amine

A number of colorimetric methods have been reported for the determination of aliphatic amines,1) *e.g.*, 2,5-diethoxytetrahydrofuran – *p*-dimethylaminobenzaldehyde,2) sodium 1,2-naphthoquinone-4-sulfonate – 2,4-dinitrophenylhydrazine,3) and phenol – hypochlorate methods.4)

However, these methods are not always convenient. Moreover, one of the major problems seems to be the lack of color stability.

We have recently reported the application of "crowned" dinitrophenylazophenol (CDPA, I) as an analytical reagent for the sensitive colorimetric determination of alkali and alkaline earth metal ions.5,6) In the above studies it was found that the CDPA – Ba(II) complex reacted with a trace amount of triethylamine (TEA) in $CHCl_3$ – MeOH to develop sensitively a red color.7,8)



I

Now, this reaction has been fully examined in MeOH, and a simple, rapid, and sensitive colorimetric determination method for TEA has been developed. Furthermore, this method was successfully applied to the determination of various aliphatic amines.

To our knowledge this is the first report that a crown ether has been used as an analytical reagent for the determination of amines.

A standard procedure is as follows. To a solution of $BaCl_2$ in MeOH (0.5 ml,

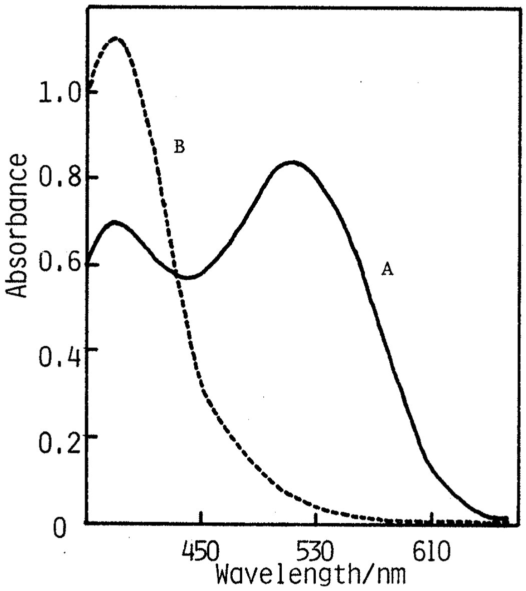


Fig. 1. Absorption curve of I—Ba(II) complex

A: I—Ba(II) complex against MeOH (TEA, 2.8 ppm).
B: Reagent blank against MeOH.

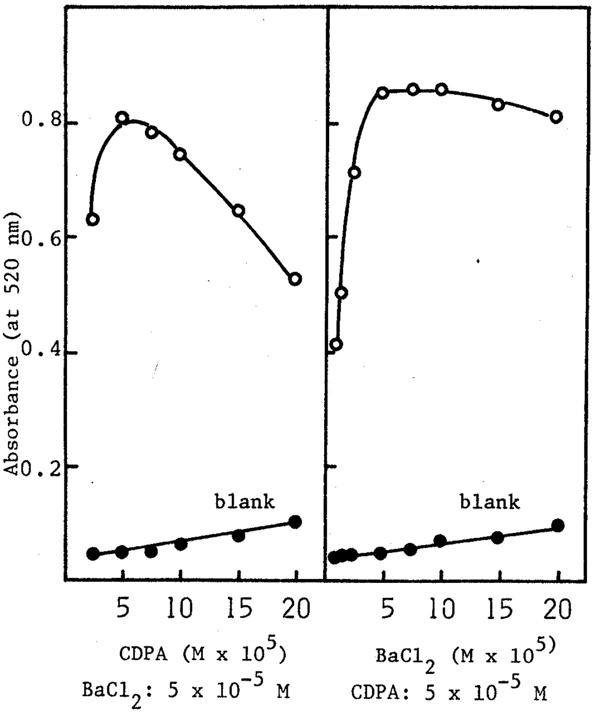


Fig. 2. Effect of CDPA and BaCl$_2$ Concentration (TEA: 2.9 x 10^{-5} M)

1.0 x 10^{-3} M, 1 M = 1 mol·dm^{-3}) and CDPA in MeOH (0.5 ml, 1.0 x 10^{-3} M) in a 10 ml volumetric flask is added a solution of TEA ($\leqq$ 40 μg) in the same solvent. The whole is adjusted to 10 ml with MeOH, mixed well, and then the absorbance is measured at 520 nm against the reagent blank. The absorption spectra obtained in this manner are shown in Fig. 1. The effect of the BaCl$_2$ and CDPA concentrations was examined at a constant concentration of TEA (2.9 μg/ml). As shown in Fig. 2, the color development was maximal at (5 – 10) x 10^{-5} M BaCl$_2$ and 5 x 10^{-5} M CDPA concentrations. The red coloration appeared rapidly and its absorbance was unchanged for periods up to 90 min. The influence of water on the stability of the resulting color was checked. The absorbance was almost unaffected by the water content up to 1%(v/v). The calibration curve through the origin was linear from 0.2 to 4.0 μg/ml of TEA. The apparent molar absorption coefficient (ε_{app}) of the chromogen as estimated from the calibration curve was 2.7 x 10^4 dm^3·mol^{-1}·cm^{-1}. The coefficient of variation for the five replicated experiments was 1.3% (TEA, 1.5 μg/ml). By the method described above, other aliphatic amines were determined as illustrated in Table 1.

The important feature of the method is that it is carried out in a nonaqueous solvent (MeOH) and is very simple and rapid. Various aliphatic amines including volatile ones can be determined sensitively.

The application of this method to the determination of total volatile aliphatic amines in biological samples is under investigation.

Table 1. Range of Determination Limit of Amines[a)]

Amine	Range (ppm)	$\varepsilon_{app} \times 10^{-4}$ f)
Triethylamine	0.2 – 4.0	2.7
Diethylamine	0.5 – 2.4	2.9
Ethylamine[b)]	0.3 – 1.5	2.4
Trimethylamine[c)]	0.4 – 2.0	3.4
Dimethylamine[d)]	0.4 – 1.8	2.6
Methylamine[e)]	0.3 – 1.6	2.5
Propylamine	0.2 – 2.1	2.6
Isopropylamine	0.3 – 2.7	2.5
Pyrrolidine	0.4 – 4.3	3.0
Piperidine	0.3 – 4.3	3.1
N-Methylpiperidine	0.3 – 3.9	3.0
N-Methylpyrrolidine	0.3 – 3.6	2.8

a) Obtained from the corresponding calibration curve at 520 nm.

b) 70; c) 28; d) 50; e) 40%.

f) Unit: $dm^3 \cdot mol^{-1} \cdot cm^{-1}$.

ACKNOWLEDGEMENT This work was partly supported by a Grant-in-Aid for Scientific Research (Nos. 58470031 and 58350050) from the Ministry of Education, Science and Culture of Japan, which is gratefully acknowledged.

REFERENCES AND NOTES

1) M. Pesez and J. Bartos, "Colorimetric and Fluorimetric Analysis of Organic Compounds and Drugs," Marcel Dekker, Inc., New York, pp. 115 – 186 (1974).
2) E. Sawicki and H. Johnson, Chemist-Analyst, 55, 101 (1966).
3) J. Bartos and M. Pesez, Bull. Soc. Chim. Fr., 1970, 1627.
4) E. J. Poziomek, E. V. Crabtree, and J. W. Mullin, Anal. Lett., 14, 825 (1981).
5) a) K. Nakashima, S. Nakatsuji, S. Akiyama, T. Kaneda, and S. Misumi, Chem. Lett., 1982, 1781; b) T. Kaneda, K. Sugihara, H. Kamiya, and S. Misumi, Tetrahedron Lett., 22, 4407 (1981); c) K. Sugihara, T. Kaneda, and S. Misumi, Heterocycles, 18, 57 (1982).
6) K. Nakashima, Y. Yamawaki, S. Nakatsuji, S. Akiyama, T. Kaneda, and S. Misumi, Chem. Lett., 1983, 1415.
7) The coloration mechanism of CDPA – M^{n+} (M = alkali or alkaline earth metal) complexes in the presence of bases was already inferred, see Ref. 5a and 5b.
8) With respect to the structure of the resulting complex it was found that the maximal absorbance is obtained when the molar proportion of TEA, Ba(II), and CDPA is 1 : 1 : 1.

(Received April 23, 1984)