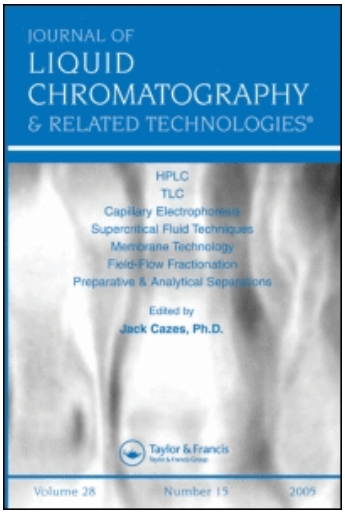

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Quantification of Solid Sorbent-Sampled Airborne Aliphatic Polyamines on HPLC using a Common Calibration Standard -Application of the Concept of Isolation of a Selected n-System of a Derivative for Specific Detection

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QUANTIFICATION OF SOLID SORBENT-SAMPLED AIRBORNE ALIPHATIC POLYAMINES ON HPLC USING A COMMON CALIBRATION STANDARD – APPLICATION OF THE CONCEPT OF ISOLATION OF A SELECTED π-SYSTEM OF A DERIVATIVE FOR SPECIFIC DETECTION

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ABSTRACT

Quantification of five aliphatic polyamines was performed on a reversed-phase HPLC equipped with a fluorescence detector after dervatizing with 1-naphthyl acetic anhydride (NAAn). The NAAn-derivatized diisopropyl amine (DIPA-NAAn) was the only calibration standard used for quantifying. A model study for the simulation of air sampling was conducted using a Test Atmosphere Generation System for ethylene diamine (EDA) which has the highest vapour pressure amongst the five amines investigated. The collection of EDA in the dynamically generated atmosphere was carried out on NAAn-coated Tenax tubes.

INTRODUCTION

Since the molecules of aliphatic polymines contain no chromophore, their quantification at microgram levels using high performance liquid chromatograph (HPLC) relies on making suitable derivatives. Although there are many derivatization methods for analyzing aliphatic amines, only a few have involved derivatization of airborne aliphatic amines on solid sorbents (1-6), in particular, the derivatization of a wide range of aliphatic polyamines. Levin et. al. developed a personal sampler for collecting airborne aliphatic polyamines through use of 1-naphthyl thioisocyanate coated on XAD-2 resin(3). Derivatives are desorbed from resin and subsquently quantified by HPLC equipped with a UV detector. However, the UV detection lacks sensitivity at submicrogram levels. In addition, 1-naphthyl thioisocyanate may not be an ideal electrophile since the derivatization site is directly conjugated with the aromatic group and the thioisocyanato (NCS) is not a good electron-withdrawing group compared to its isocyanato (NCO) analog (1,7). For these reasons, we searched for a derivatizing reagent which can improve sensitivity and selectivity of the detection, as well as the reactivity of derivatization. It is also crucial that the reagent is capable of being coated on a solid sorbent for solid phase derivatization for the convenience of performing personal sampling.

It is well-known that the organic anhydrides are very reactive towards amines. Anhydrides having direct conjugation of aromatic ring with the carbonyl group display less reactivity than aliphatic anhydrides. On the other hand, anhydrides which contain a fluorophore are desirable since the fluorescence detection is both more selective and sensitive compared to UV detection. We have, therefore, synthesized 1-naphthyl acetic

anhydride (NAAn) as the derivatizing reagent which possesses the required characterestics for analyzing aliphatic polyamines. In comparison to the derivatization with 1-naphthyl isothiocyanate, reactions of aliphatic polyamines with NAAn were fast. Also, the NAAn derivatives showed high sensitivity by at least one logarithmic unit.

The accuracy of chromatographic quantification depends on the purity of the synthesized calibration standard of the analyte. However, we found that synthesizing pure aliphatic polyamine derivatives of NAAn, especially for those with higher molecular weights, was not an easy task. Purification by recrystallization was hindered by the solubility problem of the derivatives and by the difficulty of removing substantial amounts of the by-product, 1-naphthyl acetic acid, from derivatives. A practical solution for solving the calibration standards problem may be possible by avoiding the use of standards with ambiguous purity. This approach has become feasible since the concept of the isolation of a π-system of a derivative for specific HPLC detection (8) was proposed by us. The application of this concept was successful for analyzing various isocyanates by HPLC using only one calibration standard synthesized with known high purity (9-11). Having secured the confidence of calibrations for quantification, we have continued the investigation on using reagent-coated solid sorbent tubes for sampling vapours of aliphatic polyamines. Two common types of resins, Tenax and XAD were investigated; the former resin is commonly applied to trap amines. Both sorbents were found unsuitable for sampling without being reagent-coated. However, the NAAn-coated Tenax clearly demonstrated the superiority to XAD. In this paper, we are reporting the analysis of five aliphatic polyamines, i.e., ethylene diamine (EDA), diethylene

triamine (DETA), triethylene tetramine (TETA), tetramethylene diamine (TMDA), and hexamethylene diamine (HMDA). Quantifications were performed on a reversed-phase HPLC equipped with a fluorescence detector using only N,N-diisopropyl-1-naphthyl acetamide as the calibration standard. Although the spiking recoveries from NAAn-coated sampling tubes were conducted on all five amines, the simulation of air sampling was performed on a Test Atmosphere Generation System (11,12) by employing ethylene diamine as a model compound since it is the most volatile aliphatic polyamine.

EXPERIMENTAL

Sources of chemicals and operating conditions of instruments can be referred to in the previous publication (8). Tenax resin was obtained from the corresponding sampling tubes manufactured by SKC (Cat. No. 226-35-03, Eight Four, PA, USA). The 'Amberlite' XAD was purchased from BDH (Toronto, Ontario, Canada).

High-performance liquid chromatograph

The HPLC system consisted of a ESA 420 solvent delivery pump and a Hewlett-Packard HP 1046 A fluorescence detector with excitation wavelength set at 216 nm and the emission wavelength set at 360 nm. A 5 um CSC-Hypersil-ODS column (25 cm x 4.6 mm i.d.) from Chromatography Sciences Co. Inc. (Montreal, Quebec, Canada) was used. The injection volume was 20 μl. The mobile phase was acetonitrile and 0.6% aqueous ammonium acetate in a ratio of normally 60% to 40%. However, the ratio was adjusted to 50% for each in order to resolve the separation of NAAn-derivatized EDA and TMDA. The flow-rate of the mobile phase was set at 0.8 ml min^{-1} throughout all runs.

Preparation of 1-naphthyl acetic anhydride

The synthetic method of Rinderknect and Gutenstein (13) was adapted for preparing 1-naphthyl acetic anhydride (NAAn, m.p. 118 -122°C, IR of carbonyl group at 1810 cm^{-1}) by the reaction of 1-naphthyl acetic acid and thionyl chloride in the presence of triethyl amine. The 1-naphthyl acetic acid at about 0.03 mole level was used for each batch of the reaction.

Synthesis of N,N -diisopropyl-1-naphthyl acetamide

Dry benzene solution containing NAAn was reacted slowly with the corresponding amount of diisopropyl amine (DIPA). The solid product, obtained after the extraction with alkaline water, was recrystallized from methanol (m.p. 86-88 °C, IR of the carbonyl group at 1630 cm^{-1}). This NAAn-derivatized DIPA (DIPA-NAAn) was used as the calibration standard for quantifying all NAAn-derivatized aliphatic polyamines studied in this paper.

Preparation of NAAn-coated sold sorbent sampler

A batch of NAAN-coated solid sorbent enough for packing a minimum of ten sampling tubes should be prepared in order to minimize the variation of packed content between individual samplers. The coating procedure was carried out in a round-bottomed flask by dissolving pre-determined amounts of NAAn in acetonitrile, mixing with the required amounts of solid sorbent based on packing to a height of 2.5 cm in a 5 mm i.d. x 4 cm tube for each sampler. Acetonitrile was continuously removed on a rotary evaporator at 30-40°C temperature under water aspiration.

Recoveries of spiked aliphatic polyamines in aerated samplers

Acetonitrile solutions of various individual aliphatic polymines in micro gram levels were spiked with a 10 μl syringe into both uncoated and NAAn-coated Tenax and XAD samplers. Spiked

samplers were immediately aerated for several hours at the air flow rate of 0.1 l min^{-1}. To treat each sampler for HPLC injection, the solid content (including glass wool for packing) were emptied into a glass vial containing 3 ml acetonitrile and left for 1 hr. The solution was then made to 10 ml. To 1 ml of this solution, 50 μl water was added to deplete the excess NAAn. The final volumn was made to 10 ml for HPLC quantification. While relative recovery was calculated against identically spiked samples with no aeration, the actual recovery was calibrated against the DIPA-NAAn standard directly.

Simulation of air sampling

Most of the aliphatic polyamines have very low vapour pressure and are not easy to vapourize. Simulated air sampling by the generation of polyamine vapours was, therefore, conducted using EDA as a model. This study was carried out on a Test Atmosphere Generation System in which uniform concentrations of airborne EDA were generated and simultaneously collected at up to twelve sampling outlets. The sampling rate of air flow was 0.1 l min^{-1}. Quantification of NAAn-derivatized EDA was done against synthesized DIPA-NAAn standard

RESULTS AND DISCUSSION

Recoveries of individual aliphatic polyamines at the level of up to approximately 10 μg, spiked on both NAAn-coated Tenax and XAD-2 samplers (Tables 1-5) showed that although both samplers had good relative recoveries, the absolute recoveries were, however, satisfactory for only Tenax samplers.

The losses of spiked amines from NAAn-coated XAD-2 were subsartial whether air was passed through the spiked tubes or not.

TABLE 1. Recoveries of Spiked EDA From Aerated Samplers

Sample Number	Type of Absorbent[A]	Air Volume Aerated, l	Amount of EDA Recovered, μg	Relative Recovery,%[B]
Ref-1	Solution	0	10.9[C]	-
Ref-2	Tenax	0	11.6	100
1-F[D]	Tenax	2.8	11.7	101
1-B[E]	Tenax	2.8	0	0
2-F	Tenax	5.6	11.4	98.1
2-B	Tenax	5.6	0	0
3-F	Tenax	8.6	11.8	102
3-B	Tenax	8.6	0	0
4-F	Tenax	10.4	11.0	95.3
4-B	Tenax	10.4	0	0
Ref-3	XAD-2	0	8.4	100
1-F'	XAD-2	2.8	8.9	108
1-B'	XAD-2	2.8	0	0
2-F'	XAD-2	5.5	8.9	108
2-B'	XAD-2	5.5	0	0
3-F'	XAD-2	8.5	8.6	102
3-B'	XAD-2	8.5	0	0
4-F'	XAD-2	10.3	8.4	100
4-B'	XAD-2	10.3	0	0

A: Coating amount of 0.5 mg NAAn for each sampler
B: Parallel spiking samplers with no aeration assigned as reference (100 %) for comparison for each set of samplers having similar absorbent
C: Amount of EDA spiked in each sampler
D,E: Front and back samplers (in series) respectively

The NAAn-coated Tenax tubes showed satisfactory recoveries of all polyamines on these tubes. By increasing the amount of NAAn coating ten-fold to 5 mg per tube, the amount of polyamines capable of being retained and recovered satisfatorily was also increased ten-fold as shown by the data in Table 6.

Spiking recoveries from uncoated Tenax were conducted only on DETA and TETA as illustrative examples. Table 7 shows that the rates of depletion of both amines were dependent on the volume of air aerated following first-order reaction kinetics (Fig. 1).

TABLE 2. Recoveries of Spiked DETA From Aerated Samplers

Sample Number	Type of Absorbent[A]	Air Volume Aerated, l	Amount of DETA Recovered, μg	Relative Recovery,%[B]
Ref-1	Solution	0	8.3[C]	-
Ref-2	Tenax	0	8.2	100
1	Tenax	11.1	7.8	95.1
2	Tenax	11.0	7.8	95.1
3	Tenax	11.8	7.8	95.1
4	Tenax	11.6	7.5	91.4
5	Tenax	10.8	7.3	89.0
Ref-3	XAD-2	0	2.6	100
6	XAD-2	11.2	2.5	96.2
7	XAD-2	11.4	2.3	88.5
8	XAD-2	10.3	2.9	112
9	XAD-2	11.3	2.9	112
10	XAD-2	11.7	2.6	100

A, B, C: Similar designations as referred in Table 1.

TABLE 3. Recoveries of Spiked TETA From Aerated Samplers

Sample Number	Type of Absorbent[A]	Air Volume Aerated, l	Amount of TETA Recovered, μg	Relative Recovery,%[B]
Ref-1	Solution	0	5.6[C]	-
Ref-2	Tenax	0	4.7	100
1	Tenax	11.0	4.9	104
2	Tenax	11.7	5.0	106
3	Tenax	11.7	4.7	100
4	Tenax	11.5	4.9	104
5	Tenax	10.7	4.6	97.9
Ref-3	XAD-2	0	3.2	100
6	XAD-2	11.1	2.8	87.5
7	XAD-2	11.3	2.6	81.2
8	XAD-2	10.3	2.1	65.6
9	XAD-2	11.2	2.5	78.1
10	XAD-2	11.7	2.3	71.9

A, B, C: Similar designations as referred in Table 1.

TABLE 4. Recoveries of Spiked TMDA From Aerated SAmplers

Sample Number	Type of Absorbent[A]	Air Volume Aerated, l	Amount of TMDA Recovered, μg	Relative Recovery,%[B]
Ref-1	Solution	0	10.7[C]	-
Ref-2	Tenax	0	10.5	100
1	Tenax	13.0	9.2	87.6
2	Tenax	13.7	9.9	94.3
3	Tenax	15.1	10.3	98.1
4	Tenax	14.8	9.9	94.3
5	Tenax	14.6	10.9	103.8
Ref-3	XAD-2	0	1.1	-
6	XAD-2	14.2	1.0	90.9
7	XAD-2	14.1	0.9	81.8
8	XAD-2	15.1	1.0	90.9
9	XAD-2	14.1	1.0	90.9
10	XAD-2	14.3	1.2	109

A, B, C: Similar designations as referred in Table 1.

TABLE 5. Recoveries of Spiked HMDA From Aerated Samplers

Sample Number	Type of Absorbent[A]	Air Volume Aerated, l	Amount of HMDA Recovered, μg	Relative Recovery,%[B]
Ref-1	Solution	0	7.7[C]	-
Ref-2	Tenax	0	7.6	100
1	Tenax	14.6	7.2	94.7
2	Tenax	15.1	7.1	93.4
3	Tenax	15.3	7.6	100
4	Tenax	14.4	7.0	92.1
Ref-3	XAD-2	0	4.3	100
5	XAD-2	13.4	4.4	102
6	XAD-2	13.4	4.3	100
7	XAD-2	15.4	4.5	105
8	XAD-2	15.4	4.4	102
9	XAD-2	15.2	4.8	112

A, B, C: Similar designations as referred in Table 1.

TABLE 6. Recoveries of Aliphatic Polyamines Spiked at Higher Levels on NAAn-coated Tenax.

Type of Amine Spiked	Amount of Amine Spiked,ug	Air Volumn Aerated, l+	Amount of Amine Recovered, μg
EDA	109	11.5 ± 0.4	100 ± 2.3 (n=5)
DETA	83.4	11.8 ± 0.4	76.4 ± 2.0 (n=5)
TETA	56.2	11.3 ± 0.3	51.3 ± 1.5 (n=5)
TMDA	107	12.9 ± 0.2	99.7 ± 4.1 (n=5)
HMDA	77.5	11.3 ± 0.3	73.8 ± 4.2 (n=5)

+ Aeration rate of 0.1 ml min^{-1}

TABLE 7. Depletion of TETA ana DETA spiked on Uncoated Tenax Tubes During Aeration

Type of Amines	Air Volume Aerated, l	Relative Recovery,% (C_t)	log [C_o/C_t]
TETA	0	100, C_o+	—
TETA	3.9	92.6	0.0333
TETA	7.7	80.0	0.0969
TETA	11.7	63.7	0.1960
TETA	19.7	50.2	0.2990
DETA	0	100, C_o+	—
DETA	4.1	48.4	0.3152
DETA	7.2	36.8	0.4342
DETA	11.4	24.1	0.6180
DETA	14.7	14.7	0.8327

+ Intial amount of amines approximately 10 μg in each tube

Depletion rate constants for DETA and TETA were calculated as 10.5 x 10^{-2} l^{-1} and 2.99 x 10^{-2} l^{-1} respectively which reflected 11% and 3% depletion per liter air passage for these two amines.

Results of simulated air sampling for EDA using a Test Atmosphere Generation System are shown in Table 8. Vapourized EDA was collected into three sets of NAAn-coated Tenax tubes after

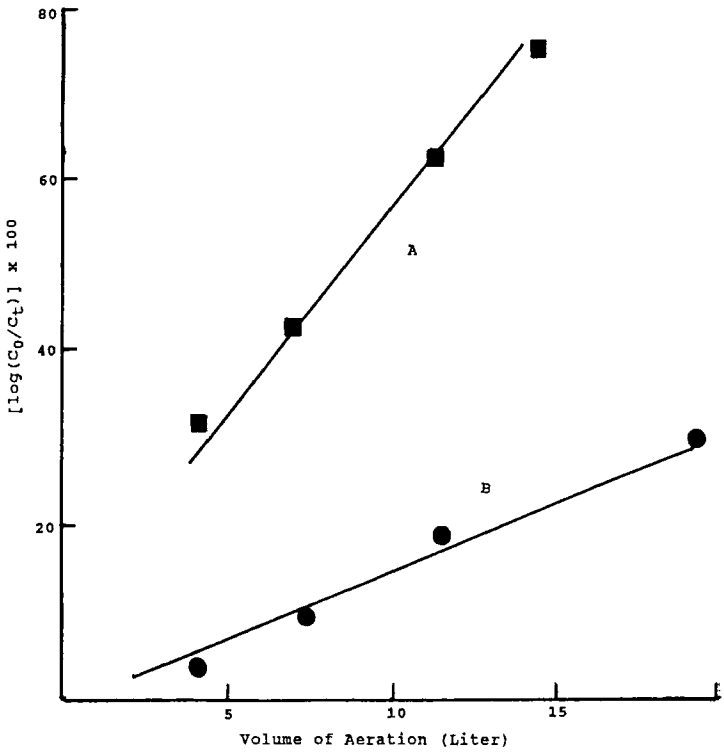

Figure 1. Depletion curves for DETA (A) and TETA (B).

various sampling periods. Each tube had a back-up tube in series to capture EDA escaping from the front tube. The break-through amount of EDA (coated with 2 mg NAAn) was about 120 μg. Experiments also showed that the Tenax tube coated with 5 mg NAAn can retain approximately 250 μg EDA without any break-through.

The selection of coating amount of NAAn for each Tenax tube would depend on the need of the individual laboratory. In our case, two tubes in series with each containing 5 mg NAAn were sufficient for sampling most of the aliphatic polyamines.

TABLE 8. Recoveries of EDA from Simulated Air Sampling Using Test Atmosphere Generation System

Set #	Amount of NAAn Coating,ug	Approx. Sampling Time,hr+	Amount of EDA Found in Sampler,μg Front	Back	Total Amount of EDA found,μg
1	2	1	122	0	122
			102	0	102
			123	0	123
			127	0	127
2	2	1.5	107	55	162
			108	66	174
			117	43	160
			121	35	156
3	2	2	103	102	205
			105	99	204
			103	102	205
			104	107	211
4	5	2	224	0	224
			260	0	260
			255	0	255
			245	0	245

+ Aeration rate of 0.1 ml min^{-1}

The theoretical background of using DIPA-NAAn as the calibration standard to quantify all NAAn-derivatized polyamines separated on HPLC was established in the earlier publications (8-11). The retention times of the individual derivatives can be established based on the relative retention times using DIPA-NAAn as the reference. However, retention times of amine derivatives can always be re-established by injecting the instantly prepared solutions which contain NAAn and crude amines.

It is obvious that the fluorescence of all polyamine derivatives was only from the introduced 1-naphthyl groups. The linearity of fluorescence detection of 1-naphthyl group of

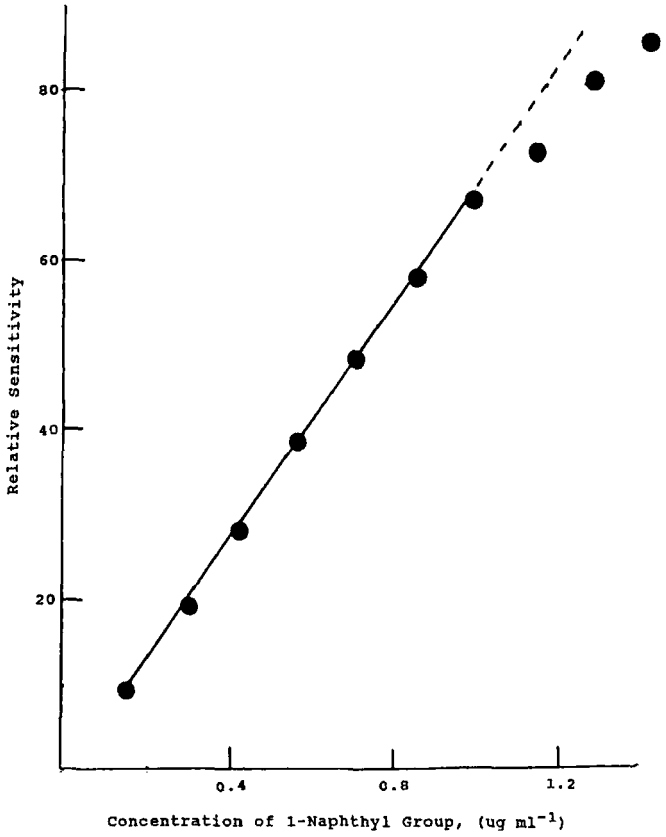

Figure 2. Linearity of fluorescence detection for 1-naphthyl group of NAAn derivatized DIPA

DIPA-NAAn was approximately up to 1 μg ml^{-1} (Fig. 2). Table 9 gives the conversion factors between 1-naphthyl and various polyamines. The lower detectable concentration of individual polyamines can easily reach 0.005 μg ml^{-1}. With the dilution factor of 100 before HPLC analysis in our procedure, this amount represents a detection level of approximately 0.08 mg m^{-3} air

TABLE 9. Molecular Weight Conversion for 1-Naphthyl and Amine of the NAAn Derivatives

Type of Amine Derivatized	Conversion Factor For 1 Unit of Amine	For 1 Unit of 1-Naphthyl
DIPA	1.351	0.740
EDA	4.232	0.236
DETA	4.915	0.203
TETA	3.462	0.289
TMDA	3.839	0.261
HMDA	2.972	0.336

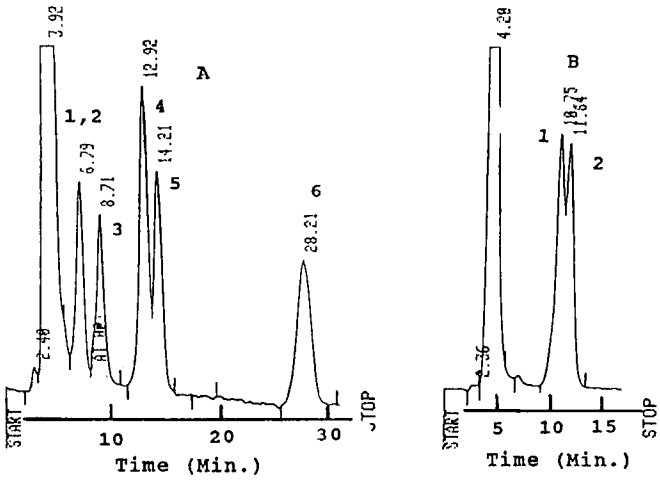

Figure 3. Chromatograms of NAAn derivatized Aliphatic Polyamines. **A**: eluted with CH_3CN - 0.6% NH_4Ac (60+40), no separation for peaks 1 and 2 (6.8 min.) representing 2.8 and 6.1 ng for EDA and TMDA respectively; **3**: 8.7 min., 4.7 ng HDA; **4**: 12.9 min., 12.9 ng DETA; **5**: 14.2 min., 15.9 ng DIPA; **6**: 28.2 min., 11.3 ng TETA, **B**: CH_3CN - 0.6% NH_4Ac (50+50), **1**: 10.7 min., 14.8 ng DEA; **2**: 11.6 min., 14.1 ng TMDA.

concentration for various polyamines, based on a sampling volume of 6 liters.

It is generally not required to analyze all of the described five aliphatic polyamines on HPLC in one sample. By using a mobile phase containing 60% : 40% of acetonitrile and 0.6% NH_4Ac, EDA-NAAn and TMDA-NAAn co-eluted. Satisfactory separation was feasible by using acetonitrile and 0.6% NH_4Ac in equal ratio (Fig.3).

Although NAAn is sensitive towards nucleophilic reagents, it showed amazing stability on storage. In a capped vial at room temperature, NAAn has been stable for over two years with no signs of deterioration.

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