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DETERMINATION OF FREE DIETHANOLAMINE CONTENT

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Abstract

Quantification of alkanolamines is imperative for health and chemical safety risk reasons. A fast method that requires less equipment has been developed for the determination of free diethanolamine in different types of additives. Repeatability tests were carried out. The free diethanolamine content of commercially available additives has been determined. We have recommended industrial applicability.

Keywords*: DEA, additives, method, development.*

1. Introduction

Today, an effective method for quantifying alkanol and alkylamines is essential due to their potential health and chemical safety risks. Diethyl and triethylamine are used as reagents in the preparation of many pharmaceutical ingredients, such as oxybutynin hydrochloride or trazodone hydrochloride [1]. The amount of diethanolamine found in cosmetics and personal care products is limited, whereas residues of diethanolamine can react with other specific ingredients forming nitrosodiethanolamine which has strong carcinogenic properties [2]. Consequently, qualitative and quantitative determination of that components is an essential task. Among the available methods for analyzing alkanolamines, gas chromatography or liquid chromatography techniques are the most prominent. The most up-to-date methods combine the chromatographic separation with mass spectroscopy. In order to improve chromatographic separation and detection, derivatization of alkanolamines is carried out to convert the analyte into a more suitable form for analysis [2].

The best means of derivatization is to use a reagent that can react with a specific functional group of analytes forming derivatives. There are two ways to derivatize in the matter of analytical applications by liquid chromatography; either pre-column or post-column derivatization (PCD) [3]. The GC-MS method is quick and easy for determination of diethanolamine content, however for reliable quantification, the sample should have minimum DEA content of 1000 mg/kg [2]. For the quantification of DEA (diethanolamine) and TEA (triethanolamine), it is necessary to dissolve it in dimethyl sulfoxide after addition of sodium hydroxide to the sample. Because ionic bonding is not possible in the solution, DEA and TEA can be readily recovered and quantified by headspace gas chromatography [1].

Reviewing the literature, only multistep instrumental analytical methods are available tfor the determination of DEA content. Our purpose was to develop a method that is simple, fast and requires less equipment.

Table 1. *Properties of materials*

	DEA	PEG-300
Molecular weight g/mol	105.14	285-315
Boiling point °C	268	>220 decompose
Freezing point °C	28	between -15 and -8
Density g/cm^3	1.09	1.125

Table 2. *Properties of DEA reaction fatty acids*

	Coco-DEA	Coco-DEA	Fatty acid DEA
Manufacturer	Alpha Chemical	Kelemen és Társa	(MOL Lub Kft.)
pH	5.5-7.5	5.6-7.5	6-8
Color	pale yellow	pale yellow	pale yellow
Free fatty acid, w%	max 1.5	max 1.0	max 1.0
Solubility in water, at 20°C	complete, pH 9.0-10.5	complete, pH 9.0-10.5	-

Table 3. *Results of repeatability tests*

	Free amine content
Coco-DEA product 1	14.2
Coco-DEA product 2	14.1
Coco-DEA product 3	14.1
Coco-DEA product 4	13.9
Coco-DEA product 5	14.0
Avarage	14.1
Deviation	0.14
RSD%	0.98

2. Materials

In our investigation, DEA and PEG (polyethylene glycol) as well coconut fatty acid reaction products were used.

DEA and PEG-300 were found to be suitable for the experiment based on their properties.

The properties of the investigated fatty acid DEA reaction products have changed in a narrow range.

3. Method development

A new, simple and fast experimental method was developed in our investigation which can be used to determine the free amine content of various additives and preparations. Conversion of raw materials can be characterized by that method. In the case of free amine content, the quality control of the preparations can be more extensive [4]. The standard ITM-40-006 was the starting point for the development of the method [5].

Execution of the test

– ~ measuring 1 g of the substance;
– dissolving the mixture in 10 ml of methanol;
– adding 100 ml of IPA/water to the solution;
– titration of the resulting mixture with 0.1 M HCL.

Preparation of 1 l IPA/water

– weighing 7.5 g of potassium chloride;
– dissolving the weighed potassium chloride in 330 ml distilled water;
– adding 670 ml of isopropyl alcohol to the solution.

Titration

– weighing the mixture into an Erlenmeyer flask;
– Adding a drop of methyl red indicator;
– Titration until titration endpoint.

The equation used to determine the free amine content is as follows:

$$wt\% = \frac{V_f * f * K * C_{HCl}}{m} \quad (1)$$

where:

V_f – consumption of 0.1 M hydrochloric acid in cm^3
f – factor of hydrochoric acid (value is 1, because it was titrated with dedicated hydrochloric acid)
K – titer number
C_{HCl} – concentration of hydrochoric acid
m – mass of the sample taken in g.

The repeatability of the method was investigated, Table 3 summarizes the results.

Based on the repeatability tests (RSD value less than 5 %) it was found that the developed method can be reliably repeated. Based on this, further investigations were carried out by the method.

4. Results

The tests were started by determination of free amine content of DEA/PEG300 mixture in various ratios. The results are shown in Table 4.

It was found that the free DEA content determined by the new method correlates well with the measurement data as shown Figure 1.

Examinations were continued to determine free amine content of products containing DEA produced by various manufacturers. The results are shown in Table 5.

We conclude that the free DEA content determined by the new method correlates well with the data provided by manufacturer as illustrated in Figure 2.

Our measurements are a good reflection of the fact that the method presented can accurately determne the DEA content, both checked by weighing, as well as compared to the data provided by manufacturer.

5. Conclusions

Our experiment leads us to the following deductions:

- a fast and less device requiring method has been developed;
- the method has proved to be reliable;
- the developed method is suitable for determining the DEA content of products.

This method can be applied due to its simplicity on site during production of DEA containing products.

Table 4. *Examination of products with various DEA content*

Number of sample	1.	2.	3.	4.	5.	6.	7.
DEA content according weighing w%	1.00	5.20	9.9	15.10	20.15	25.05	50.10
DEA content according titriometric method w%	1.11	4.98	10.05	15.08	20.12	24.99	49.91

Table 5. *DEA content of commercial surfactants*

Signal of sample	DEA content according titriometric method w%	DEA content according to manufacturer w%
Coco DEA (Alpha Chemical)	14.05	14.20
Coco DEA (Kelemen & Társa Kft.)	12.80	12.80
Fatty acid DEA (MOL Lub Kft.)	14.45	14.50

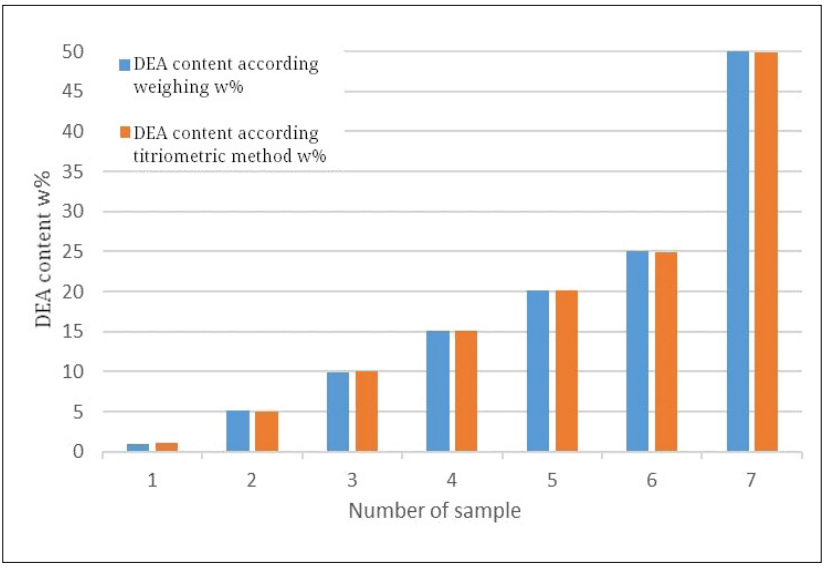

Figure 1. *Examination of various DEA-containing products*

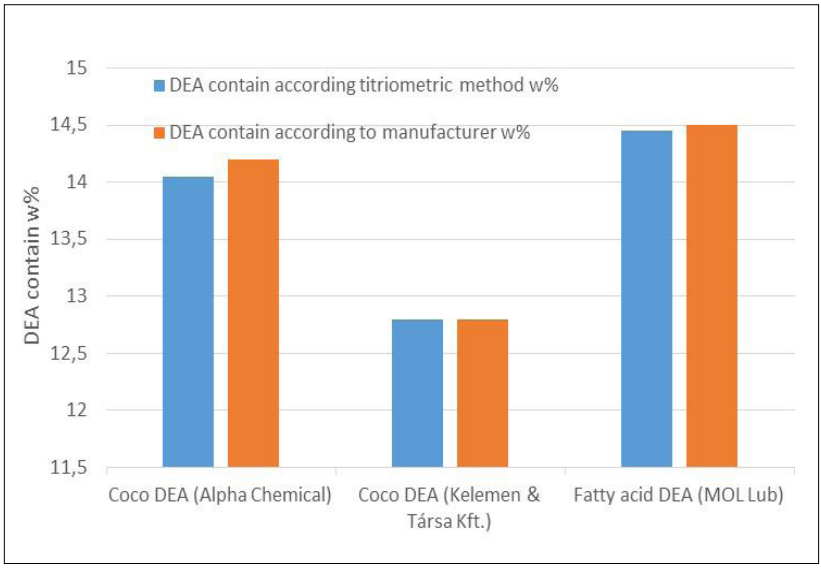

Figure 2. *Examination of DEA containing additives from different manufacturers.*

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