Determination of Amine or Amide Nitrogen in Vegetable Oils

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ABSTRACT

A procedure is described for the determination of small amounts of amine or amide nitrogen in vegetable oils. Amines are extracted quantitatively from the oil after it is treated with aqueous HCl and steam. Nitrogen then is determined in the aqueous extract by the Kjeldahl method.

INTRODUCTION

Although there are procedures recommended for the determination of fatty amines in industrial products (1), we found no references for procedures to determine small amounts of amine or amide nitrogen in vegetable oils. In this paper, a method has been described for the determination of small amounts of amine or amide nitrogen in vegetable oils.

The method may be used as a tool in determining the amount of amine nitrogen in vegetable oils when they are extracted with different solvents. It may also be useful for detecting trace amounts remaining in oils after the addition of amines for removal of color bodies in the bleaching of oils.

The proposed procedure was tested through the use of a refined, bleached, and deodorized salad oil of commerce to which diethylene triamine was added in known amounts. Recovery of amine nitrogen was in satisfactory agreement with the amount added, e.g. the recovery of an average of 97.4% of the added amine was obtained. Several oils then were examined to determine the quantities of amine and amine nitrogen present.

METHOD

Hydrolysis of sample: Weigh 10 g vegetable oil into a 50 ml round bottom extraction flask. Add 10 ml dry 7 N hydrochloric acid in ethanol (dry hydrogen chloride was collected over concentrated sulfuric acid into absolute ethyl alcohol) and swirl to form an emulsion. Connect the flask to a condenser and reflux on a steam bath overnight. Add 10 ml aqueous 6 N hydrochloric acid, swirl, and continue to reflux for ca. 6 hr.

Transfer the mixture to a 60 ml separatory funnel and let it stand 5-10 min or until the two layers separate. Then collect the bottom layer in a 100 ml Kjeldahl flask. Return the oil layer to the same extraction flask. Wash the separatory funnel with 5 ml 6 N hydrochloric acid, and add the washing to the oil layer in the extraction flask and reflux the mixture overnight.

Then separate the two layers, as directed above, and repeat the refluxing operation of the oil layer with an additional 5 ml 6 N hydrochloric acid for ca. 6 hr. Combine all of the aqueous extractions in the Kjeldahl flask for the digestion of the sample by the conventional Kjeldahl method.

EXPERIMENTAL PROCEDURES

In establishing the procedure, diethylenetriamine was purified and mixed with a refined, bleached, deodorized, and winterized vegetable salad oil that had been prepared commercially. The amine was purified, essentially, in accordance with the procedures described by Jonassen, et al., (2) and Fargher (3). The nitrogen content was determined by the micro-Kjeldahl method, and the average of four determinations was 39.88% (theoretical 40.74%), corresponding to a 97.90% purity.

Then, samples were prepared by accurately weighing a known amount of the purified diethylenetriamine in a 10 ml volumetric flask. A commercial winterized cottonseed oil was added to the mark and mixed well by inverting the flask several times, at intervals, over a 1 hr period. The percent amine recovered was determined by the procedure described in the method. A control determination of the same oil (no amine added) was conducted simultaneously. It can be noted in Table I that an average of 97.4% of the amine added to the oil was recovered.

Amine nitrogen content was determined for four crude vegetable oils, three of which were extracted from raw seed by hexane and a commercial oil. All analyses were in duplicate. The results are recorded in Table II. They demonstrate that olive oil showed no amine nitrogen, while rape and sunflower oils showed a trace of titrable amino nitrogen. However, the crude cottonseed oil showed an appreciable amount of amine nitrogen, probably from phospholipids (4).

Rapeseed was extracted in the laboratory with three different solvents, and the amine nitrogen was determined for each. All analyses were in duplicate. The data are recorded in Table III. They indicate that the hexane extracted oil had a trace of amine nitrogen, the chloroform-methanol mixture (1:1) extracted oil had a small amount more, and the oil extracted with the hexane-acetone-water azeotrope (5) had more amine nitrogen than either of the other two oils.

DISCUSSION

A method is presented for the determination of small amounts of amine and amide nitrogen in vegetable oils. Although we tested the procedure for only four oils, it is reasonable to assume that the method can be applied to most vegetable oils.

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TABLE I

Recovery of Diethylenetriamine from a Commercial Winterized Cottonseed Oil

Sample no.	Amine added to oil (mg)	Nitrogen[a] added to oil (mg)	Nitrogen recovered (mg)	Amine[b] recovered (%)
A	53.60	21.38	20.93	97.9
B	51.64	20.60	19.97	96.9
C	52.60	20.98	20.45	97.5

[a]Based upon the formula wt of diethylenetriamine (103.16) containing 40.74% nitrogen and a purity of 97.90%.

[b]Relative standard deviation of the average is 0.4%.

TABLE II

Amine Nitrogen in Four Different Vegetable Oils

Name	Treatment	Percent
Olive oil	Commercial	0.000
Crude rapeseed oil	Hexane extracted in laboratory	0.001
Crude sunflowerseed oil	Hexane extracted in laboratory	0.001
Crude cottonseed oil	Hexane extracted in laboratory	0.012

The method may also be used as a tool in determining the amount of amine nitrogen in vegetable oils when they are extracted with different solvents and for the detection of trace amounts of amines added to oils for removal of color bodies during bleaching.

TABLE III

Amine Nitrogen in the Crude Rape Oil Extracted with Different Solvents

Treatment	Percent
Hexane extracted in laboratory	0.001
Chloroform-methanol mixture (1:1) extracted in laboratory	0.004
Hexane-acetone-water azeotrope extracted in laboratory	0.007

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