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DETERMINATION OF ACRYLONITRILE IN MATERIALS IN CONTACT WITH FOODSTUFFS

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SUMMARY

Monitoring of the content of free acrylonitrile in plastics used for the preparation of viands is necessary due to its negative effect on human health. A content of 20 ppb is the maximal value of free acrylonitrile in such samples. In this case, head-space gas chromatography is most favourable analytical method when combined with the standard addition method together with a mass-spectrometry detector because of a very low concentration of the analyte. In samples taken for analysis, the content of free acrylonitrile was found to be within 5.1 and 10.3 ppb (µg/kg).

Key words: acrylonitrile, foodstuff, head-space gas chromatography

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INTRODUCTION

Acrylonitrile is a suspect carcinogen and belongs among substances of medium toxicity. Persons exposed to effects of acrylics such as acrylonitrile, methyl acrylate, ethyl acrylate, butyl acrylate etc. often suffer from stinging of eyes, throat, intermittent fits of coughing, headaches, sickness, dizziness, skin problems etc. The team (1) also investigated tumour markers with regard to carcinogenicity of substances to whose effects the workers were exposed: no significant differences were observed between the exposed group and a control group. On the contrary, the results of studies on the occurrence of malignant illnesses in persons professionally exposed to acrylonitrile recently published (2, 3, 4) document a lower occurrence of malignancies as compared with the amount expected.

With regard to unfavourable effects of acrylonitrile on man's health it is necessary to know the content of free acrylonitrile in plastics (5) that are used in preparation of foodstuffs (food processors, juicers, pans of scales, food dishes etc.). The maximum allowed content of free acrylonitrile in such products is 20 ppb (6).

The composition of plastics can be investigated with help of a pyrolyser (7) connected with gas chromatograph (8). Another possibility consists in application of the head-space technique (9) combined with gas chromatography. There exist two modification of head-space: dynamic and static, the former being usually referred to as purge and trap. In this arrangement, inert gas is bubbled through the sample, and the substances to be determined are mostly trapped on a sorbent. A quantitative determination necessitates that all the analysed substance should be transferred on the sorbent. The static head-space technique makes use of the equilibrium established between the condensed and gaseous phases in a closed system. The amount of substances is determined indirectly from the composition of gaseous phase. The most frequently applied method is that of standard addition.

Considering the very low concentrations of the substance followed, it is necessary to adopt a very sensitive and specific detector, the mass detector (10) representing the best choice. If the determination of free acrylonitrile (i.e. that which is not bound in the polymer) is required, then the head-space technique is more advantageous, since the pyrolysis technique damages the whole polymer structure. The head-space method can be used after dissolving the sample investigated in a suitable solvent (11).

EXPERIMENTAL

The present paper describes the determination of content of free acrylonitrile in samples of vessels used in food processing or designed for food storage. Therefore the method chosen was the static head-space technique combined with gas chromatography--mass spectrometry (GC/MS). Four samples were examined: two juicer dishes, a bread container, and a pan of kitchen scales.

Preparation of Sample for Analysis

Before the analysis proper sample had to be disintegrated. After crushing to smaller pieces the sample was ground in a ball mill in liquid nitrogen medium for 15 min. Then about 0.25 g sample was weighed and placed in 22-ml vessel and dissolved in 2.5 ml N,N-diethylacetamide using ultrasonic stirring.

Head-Space Analysis

For the determination of the title compound we chose the static head-space with standard addition. A stock solution was prepared by weighing 111.3 mg acrylonitrile and making up with N,N-diethylacetamide to 10 ml. By subsequent dilution we prepared the standard solution of 11 μg/kg (i.e. ppb) acrylonitrile concentration. One analysis involved two vessels with dissolved sample. The first one was measured without any modification, while the second was mixed with 150 μl standard solution. Both vessels were kept at a constant temperature of 90 °C in the thermostat of automatic dosing device CombiPal (CTC analytics, Switzerland) for 45 min, whereupon 1 ml of the gas phase above the sample was dosed into the gas chromatograph. Each sample was analysed 5 times.

GC/MS Analysis

The gas phase was analysed by means of a gas chromatograph GC 17A with a mass detector QP 5050A (Shimadzu, Japan). The separation was achieved on a capillary column DB 35-MS of 30 m length, 0.25 mm inner diameter, and 0.25 μm film thickness. The inlet and the detector temperatures were 180 and 230 °C, respectively. The helium flow rate was kept at the value of 0.7 ml/min with a pressure of 28.7 kPa at the column head. The sample was introduced without a flow divider, and the analysis was isothermal at 60 °C. For obtaining the highest sensitivity, the SIM mode was used, and on the basis of the mass spectrum presented in Fig. 1 the value of m/z 53 was chosen with micro-scan 0.2. This value corresponds to the molecular ion of the compound analysed. This spectrum is a part of the commercial library of spectra supplied under the name of NIST62.

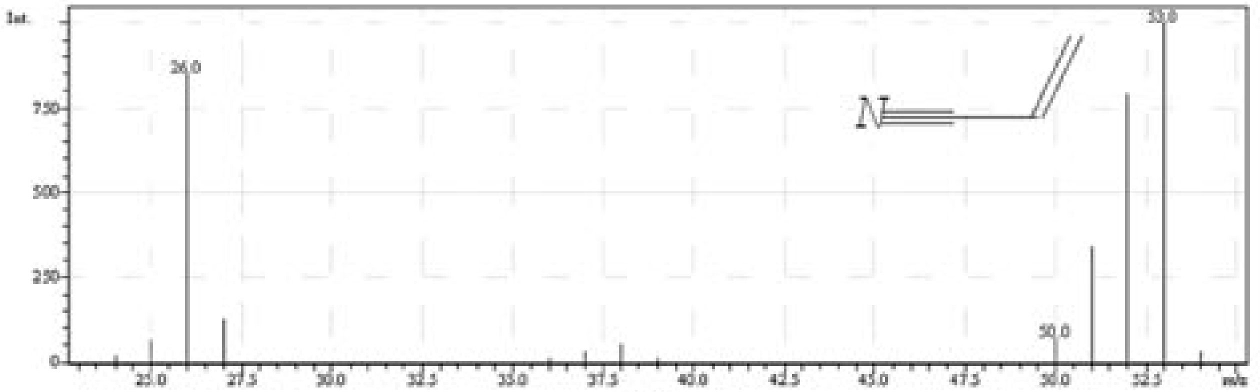

***Fig. 1**. Mass spectrum of acrylonitrile.*

RESULTS AND DISCUSSION

Four samples of plastic containers used in food processing or storage were tested: two juicer dishes, a pan of kitchen scales, and a container for bread. In these samples the content of free acrylonitrile was determined.

First the conditions of GC analyses were optimised using a specially prepared standard. A typical chromatogram obtained under the conditions given in Experimental is presented in Fig. 2. The ionisation was switched off at the retention time of 3.5 min (i.e. the elution time of solvent N,N-diethylacetamide). After finding suitable chromatographic conditions, we tested standard samples in SIM mode as mentioned above; the value m/z 53 was chosen on the basis of the mass spectrum.

After the series of test analyses of standards we followed with the analyses of the samples examined, which were prepared by the procedures given in Experimental and then submitted to the head-space analysis in combination with GC/MS. One of the chromatograms obtained is presented in Fig. 3. The content of acrylonitrile in samples was calculated from the peak areas, and the results are given in Table 1.

CONCLUSION

From the results given it follows that the method chosen, i.e. head-space combined with GC/MS, is a suitable technique for determination of the content of free acrylonitrile in plastics. It has been found that the samples examined meet the requirements of Public Notice No. 38/2001 Collect. of Laws, issued by the Ministry of Health of the Czech Republic on January 19, 2001.

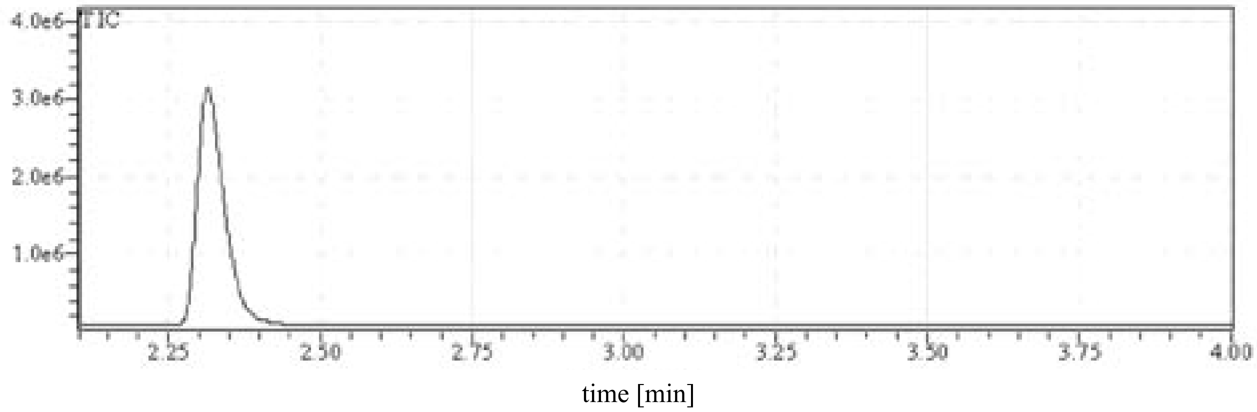

Fig. 2. *Chromatogram of standard solution (11 µg/kg).*

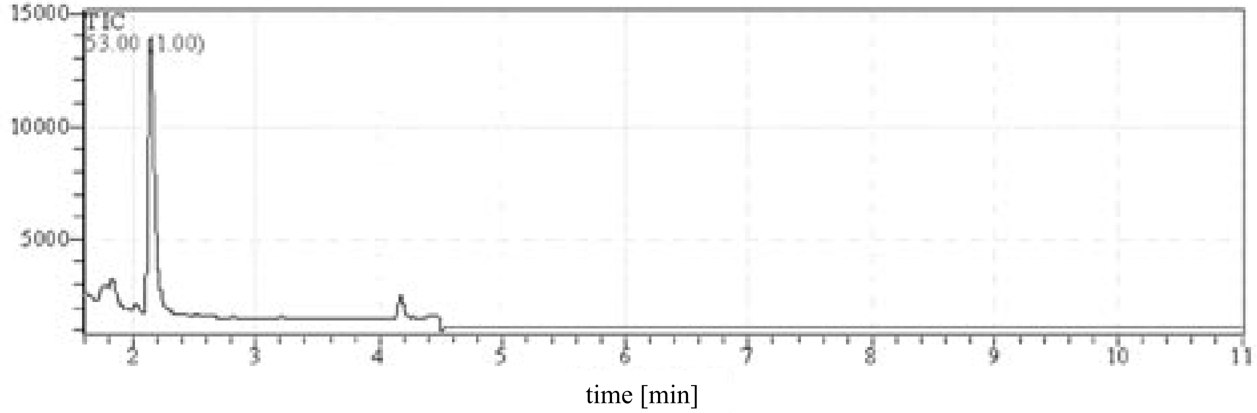

Fig. 3. *Chromatogram of sample pan of scales.*

Table 1. *Acrylonitrile content in individual samples*

Sample	Concentration* [µg/kg, i.e. ppb]
Juicer 1	5.1 ±1.2
Juicer 2	10.3 ±1.4
Pan of scales	7.5 ±1.1
Container for bread	8.2 ±1.2

*mean value from 5 analyses

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