

Determination of Vinyl Chloride Monomer in Food Contact Materials by Solid Phase Microextraction Coupled with Gas Chromatography/Mass Spectrometry

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Abstract

JORDÁKOVÁ I., DOBIÁŠ J., VOLDŘICH M., POUSTKA J. (2003): **Determination of vinyl chloride monomer in food contact materials by solid phase microextraction coupled with gas chromatography/mass spectrometry.** Czech J. Food Sci., 21: 13–17.

The present study concerns the optimisation of the headspace solid phase microextraction (HS/SPME) combined with gas chromatography/mass spectrometry (GC/MS) for the vinyl chloride monomer determination. Samples of PVC materials were analysed using the Carboxen/Polydimethylsiloxane (CX/PDMS) 75 µm fibre. For this fibre, the achieved limit of detection was 0.05 µg/kg, and that of quantification 0.17 µg/kg, respectively, with RSD 5%. The levels of VCM found ranged from 0.29 to 0.44 mg/kg, in the case of foil, the VCM content determined was 3.65 mg/kg which means that the maximal limit allowed was exceeded.

Keywords: migration; solid phase microextraction (SPME); vinyl chloride monomer

PVC materials can be used for many applications, for example for the production of various industrial products (floorings or plastic parts of food processing machines), and also for safety tools (gloves), transport materials as well as toys. The major problem is the migration of vinyl chloride monomer (VCM) into food which can cause a significant food contamination.

In the Czech Republic, there is a directive which establishes the maximal residual amount allowed of VCM at 1 mg/kg of the PVC material. As regards the specific migration limit any amount must not be detected by recommended method (Decree No. 38/2001, Collection of Law of the Czech Republic). This directive complies fully with European legislation (90/128/EEC 1990). Vinyl chloride monomer is a carcinogenic compound. An occupational exposure to VCM is associated with an increased incidence of angiosarcoma of the liver and other malignant tumours, circulatory disturbance, and impaired liver function (ATSDR 1997). When VCM is combusted, it may produce toxic gases (such as phosgene, hydrogen chloride, and carbon monox-

ide). At ambient temperature, VCM is a colourless flammable gas (boiling point – 13.5°C) and therefore it is stored and transported as a liquefied material under high pressure (CHARVET *et al.* 2000).

The conventional headspace method was applied for the determination of VCM migrated into various food-simulating solvents (KONTOMINAS *et al.* 1985). The aim of this work was to use the solid phase microextraction for determination of VCM in food contact materials. The solid phase microextraction (SPME) was developed by Pawliszyn and co-workers (ARTHUR & PAWLISZYN 1990). It appeared as an alternative technique for the isolation of volatile compounds – it is a rapid and solvent-free method (ZHANG & PAWLISZYN 1996; GORECKI & PAWLISZYN 1997). As concerns the SPME analyses of plastics, only few papers were published on this subject. The principle is partitioning between an aqueous phase (direct SPME) or a gas phase (headspace SPME) and a polymeric organic phase (a stationary phase). SPME procedure consists of two steps – the first one is sorption and the second one is desorption. The sorption is realised by the fused

silica fibre coated with the stationary phase through immersion into the liquid (direct SPME) or into the gas phase (headspace SPME) where the analytes are adsorbed on the fibre. The direct SPME is used for less volatile analytes in clean matrices, headspace SPME is used for volatile analytes and/or for dirty samples which can contain substances able to damage the fibre coating. For the desorption, either the thermo desorption is used (in the injection chamber of the gas chromatograph), or desorption with solvents using the special interphase for HPLC (PAWLISZYN 1997). CHARVET *et al.* (2000) analysed vinyl chloride monomer in aqueous samples using SPME/GC/MS with the limits of detection and quantification of 0.05 µg/kg and 0.10 µg/kg, respectively.

This study was focused on the optimisation of headspace SPME for VCM analysis. The parameters tested were: fibre stationary phase type, sorption time, sorption temperature, and desorption time. Further, an analytical method for the GC/MS determination was developed.

MATERIALS AND METHODS

Vinyl chloride monomer (99.5%) and N,N-dimethylacetamide (99.5%) were obtained from Fluka (Switzerland). Stock solution of VCM in N,N-dimethylacetamide was prepared in the concentration of 1 µg/ml and was used for the preparation of the testing solutions (for method optimisation) in the range from 0.05 to 0.5 µg/ml in 16ml vials. Because of the VCM boiling point, all operations had to be carried out in the freezer (temperature approximately –18°C). Amount of VCM in the case of stock solution preparation was verified by weighting. After the introduction of the spiking solution, the vials were immediately sealed with the PTFE faced septum. The spiked solution was heated at the temperature of 60°C in

the water bath for 2 h. Then the SPME fibre was introduced in the headspace of the vial for the sampling of the analyte. The fibre with the analyte was analysed using GC.

During the experiments, various kinds of PVC samples were analysed: feeders, lid seals, parts of toys etc. The materials tested are commonly used in the food industry or are intended for the contact with food. They were investigated because of the legislation requirements.

In the case of real samples, 0.3 g of the PVC material tested was put into the vial and an appropriate amount of the stock VCM solution was added to reach contents 0.5 to 5 mg of VCM added per 1 kg of PVC material. Total volume was then made up to 3 ml. The next procedure was the same as in the case of the standard solutions. For each sample, two parallel determinations were carried out. Results calculation was based on the standard addition technique.

The fibres with five different stationary phases were obtained from Supelco (USA). The optimisation of the SPME method was investigated. Conditions are summarised in Table 1.

GC/MS system consisted of Hewlett Packard 5890 Series II gas chromatograph (Hewlett Packard, USA) with the mass spectrometric detector 5972 Series (Hewlett Packard, USA). DB 5-MS (30 m × 0.32 mm i.d. with 0.25 µm film thickness), fused silica capillary column (J&W Scientific, USA) was used for the chromatographic separation. GC conditions were as follows: the initial oven temperature 35°C, the initial time 1.0 min, the oven temperature increase rate from 35°C to 90°C at 10°C/min, then from 90°C to 260°C at 25°C/min. The carrier gas (helium) flow rate was held constant at 1.1 ml/min. The injector temperature was 250°C and the detector temperature was 280°C. For the quantification, ions were used with the following m/z values: 62 and 64.

Table 1. Tested conditions for optimisation of SPME method for the determination of VCM

Fibre type	Carbowax/Divinylbenzene (CWX/DVB) 65 µm, Carboxen/Polydimethylsiloxane (CX/PDMS) 75 µm, Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) 65 µm, Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CX/PDMS) 50/30 µm, Polyacrylate (PA) 85 µm
Sorption time (min)	0.5, 1.0, 2.0, 5.0, 10.0, 20.0, 30.0
Sorption temperature (°C)	25, 30, 40, 50, 60, 80
Desorption time (min)	0.5, 1.0, 1.5, 2.0, 5.0

RESULTS AND DISCUSSION

Comparison of fibres. Five fibres were tested with 0.1 µg/ml vinyl chloride monomer solution to estimate the highest intensity of adsorption under the conditions tested (Figure 1). With each fibre type, 10 runs were realised. The highest adsorption intensity was obtained with the Carboxen/Polydimethylsiloxane fibre with the film thickness of 75 µm which showed the best affinity to VCM.

Sorption time. The next experiment was focused on the influence of the sorption time on the extracted amounts of VCM (Figure 2). This experiment was carried out with 0.1 µg/ml vinyl chloride monomer solution, and with the Carboxen/Polydimethylsiloxane fibre (film thickness 75 µm). In the range of shorter sorption times (0.5–10.0 min),

the amount of VCM absorbed was steeply increasing. The absorbed amount was practically constant in the range of 10 to 30 min, as the optimal time the period of 10 min was determined.

Sorption temperature. The extraction of the 0.1 µg per ml vinyl chloride monomer solution was tested at different sorption temperatures in the range from 25°C to 80°C (Figure 3). The experiments were performed using the Carboxen/Polydimethylsiloxane fibre (film thickness 75 µm) with the sorption time of 10 min. Maximum amount of VCM extracted was found at the temperature of 60°C.

Desorption time. Five different desorption times were studied to estimate the best separation and results of the 0.1 µg/ml vinyl chloride monomer solution under the following conditions: the Carboxen/Polydimethylsiloxane fibre (film thickness 75 µm),

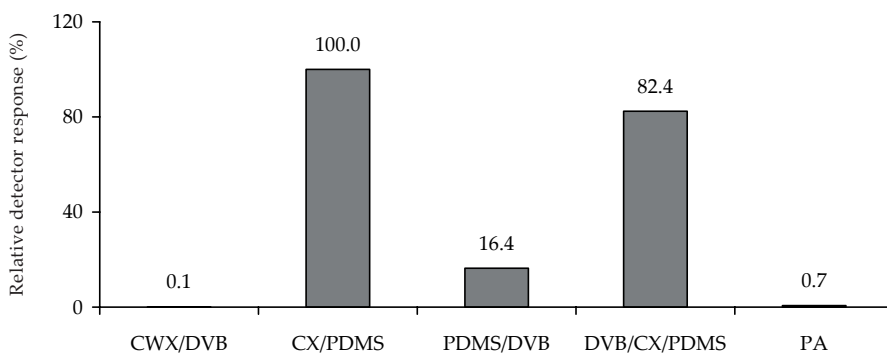


Figure 1. Comparison of relative detector responses for the different fibre coatings (sorption time 10 min, desorption time 1 min, sorption temperature 60°C)

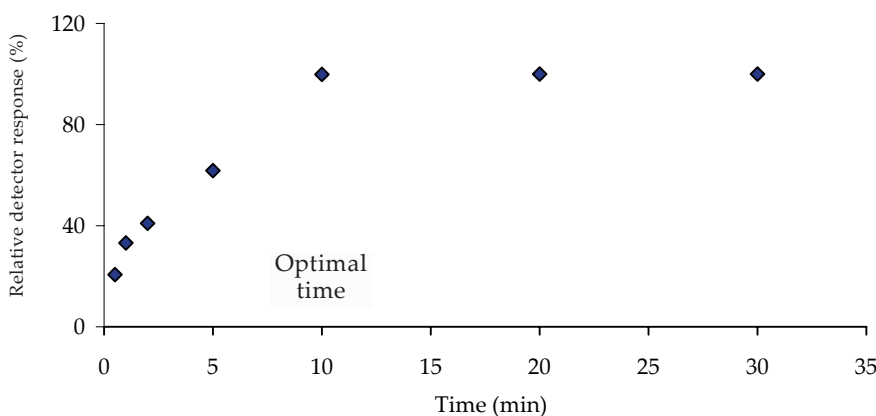


Figure 2. Comparison of relative detector responses for the different sorption times (CX/PDMS, desorption time 1 min, sorption temperature 60°C)

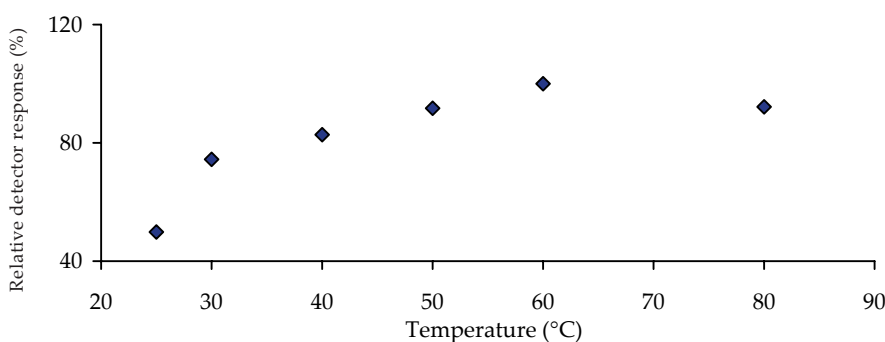


Figure 3. Profile of the relative detector response of vinyl chloride monomer extraction depending on extraction temperature (CX/PDMS, sorption time 10 min, desorption time 1 min)

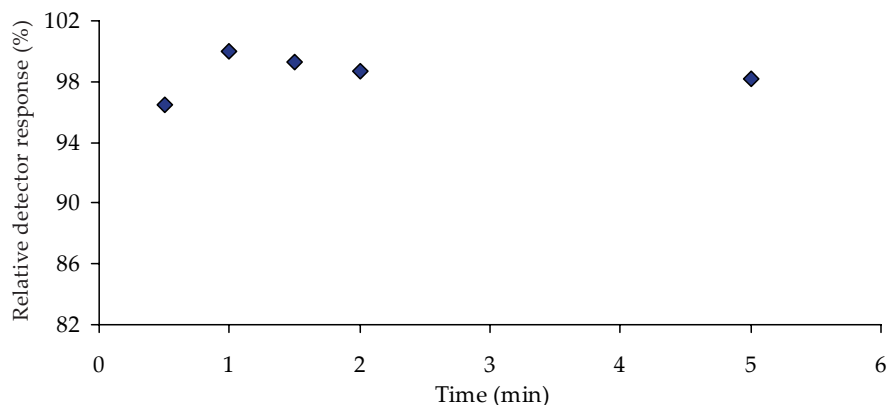


Figure 4. Comparison of the relative detector response of vinyl chloride monomer depending on desorption time (CX/PDMS, sorption time 10 min, sorption temperature 60°C)

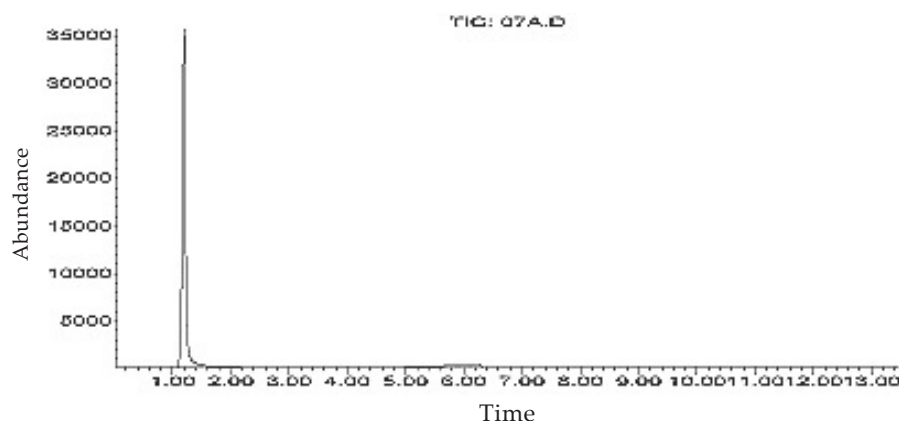


Figure 5. GC/MS chromatogram of a standard solution of vinyl chloride monomer at the level 0.1 µg/ml

Table 2. Determined levels of VCM in various packaging materials (mg/kg)

Sample	VCM content
Feeder	0.29
Foil	3.65
Gloves	0.44
Lid seal	0.44
Plastic part of toy	0.36

sorption time 10 min, sorption temperature 60°C (Figure 4). The best result was obtained for the desorption time one minute.

Optimised method. The following conditions for the VCM determination were found as optimal: Carboxen/Polydimethylsiloxane fibre with film thickness 75 µm, sorption time 10 min, sorption temperature 60°C, and desorption time 1 min (Figure 5).

Limit of detection (LOD) limit of quantification (LOQ), method repeatability. RSD was measured for ten replicates at the concentration level of

0.1 mg/kg. The RSD value was 4.8%, it indicated a good repeatability. LOD and LOQ were determined as 0.05 µg/kg and 0.17 µg/kg, respectively.

Levels determined in packaging materials. Table 2 summarises the results obtained for various kinds of PVC materials. The contents of VCM found were in the range from 0.29 to 0.44 mg/kg, in the case of foil the VCM content determined was 3.65 mg/kg which means that the maximal limit allowed was exceeded.

CONCLUSION

Validation of the headspace SPME technique proved its suitability for the analysis of the vinyl chloride monomer in plastic materials which is documented by means of the performance characteristics determined. In the case of its application in routine laboratory practice, it is necessary to compare SPME method with the conventional headspace method which is recommended in Decree No. 38/2001, the Collection of Laws of the Czech Republic.

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Souhrn

JORDÁKOVÁ I., DOBIÁŠ J., VOLDŘICH M., POUSTKA J. (2003): **Stanovení monomeru vinylchloridu v materiálech přicházejících do styku s potravinami pomocí SPME/GC/MS**. *Czech J. Food Sci.*, **21**: 13–17.

Práce je zaměřena na optimalizaci headspace mikroextrakce na pevnou fázi (HS/SPME) ve spojení s plynovou chromatografií s hmotnostní detekcí (GC/MS) pro analýzu monomeru vinylchloridu. Vzorčky PVC materiálů byly analyzovány pomocí vlákna se stacionární fází Carboxen/Polydimethylsiloxan s tloušťkou filmu 75 µm. Toto vlákno umožňuje stanovení monomeru vinylchloridu s mezí detekce 0,05 µg/kg a mezí stanovitelnosti 0,17 µg/kg polymeru (RSD = 5 %). Nalezené hladiny monomeru vinylchloridu se pohybovaly v rozmezí od 0,29 do 0,44 mg/kg, v případě fólie byl obsah monomeru vinylchloridu stanoven na 3,65 mg/kg, což znamená, že maximální přípustné množství dané vyhláškou bylo překročeno.

Klíčová slova: migrace; mikroextrakce na tuhou fázi (SPME); monomer vinylchloridu

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