



Determination of methacrylic acid in food simulants by pyrolytic butylation-gas chromatography



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ABSTRACT

An on-line pyrolytic butylation approach was proposed to determine methacrylic acid (MA) in food simulants by gas chromatography (GC) without an expensive pyrolyzer. MA in food simulants was converted into butyl methacrylate in the presence of tetrabutylammonium hydroxide (TBAH) without any pretreatment at 330 °C in the injection-port, contributing to high GC signal response. The derivatizing conditions for the proposed method were optimized, namely the injection-port temperature, type and amount of the organic alkaline used for derivatization. A series of standard solutions of MA in the range of 1.0–50 mg/kg were analyzed with correlation coefficient $r \geq 0.9975$. The limits of detection (LODs) were less than 0.15 mg/kg for MA in four matrix simulants (distilled water, 3% w/v acetic acid, 10% v/v ethanol, and isooctane). Relative standard deviations (RSDs) for retention time, peak height and peak area were all less than 3.88%. The technique was successfully applied to the analysis of MA migrating from plastic cup samples, with recoveries of added MA in the range of 96.5–123.0%. Direct injection of the simulants into the GC system after migration tests, without any pretreatment step, makes the developed method of great value for rapid screening analysis of samples in bulks.

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1. Introduction

Plastics are widely used as food packaging materials for their outstanding advantages such as lightweight, high tensile strength, easy processing and storage, and low cost. However, low-molecular-mass substances such as residual monomers [1,2], oligomers [3,4] or additives [5–8] can migrate from the packaging materials into foods. Therefore, potential threats to food safety have to be emphasized when these plastic materials contact with foods directly.

Acrylic ester monomers are exploited for the manufacture of polymers, for polymer dispersions or other specialty resins [9]. Several acrylic ester polymers are applied in food contact materials, such as polymethylmethacrylate (PMMA), polyethylmethacrylate (PEMA) and polybutylacrylate (PBA). Methacrylic acid (MA) monomer is used as additive for the manufacture of various food contact materials, such as PMMA, polyethylene terephthalate (PET), polyamide (PA), and polycarbonate (PC). Both acrylic ester monomers and MA monomer can migrate from the

packaging materials into foods. Conventionally, most concerns are focused on the evaluation of migration of acrylic ester monomers from the polymer into the contact medium. However, little attention is paid to the determination of MA monomers, due to its low content and high polarity. MA is readily absorbed through mucous membranes of the lungs, the gastrointestinal tract, and the skin; and is distributed to all major tissues. Oral LD₅₀ values for rats ranged from 277 to 2260 mg/kg [10]. According to the directive 2002/72/EEC [11] mainly implemented on plastic materials, the specific migration limit (SML) for MA is 6.0 mg/kg in food simulants, when no methyl methacrylate exists.

Instead of real food, the quality control of packaging materials is usually carried out with food simulants, for higher analytical simplicity and better interlaboratory comparison purposes. Food simulants consist of liquids with simple chemical composition such as water, aqueous ethanol, aqueous acetic acid or olive oil to imitate the behaviour of foodstuffs. In addition, except olive oil, substitute media for migration tests were also defined for fatty simulant; namely, isooctane, 50% and 95% aqueous ethanol, and modified polyphenylene oxide (MPPO) [12]. Several methods have been reported to analyze MA in the literature. MA in aqueous samples was determined using isotachopheresis by Okkerse et al. [13], capillary zone electrophoresis by Ridder

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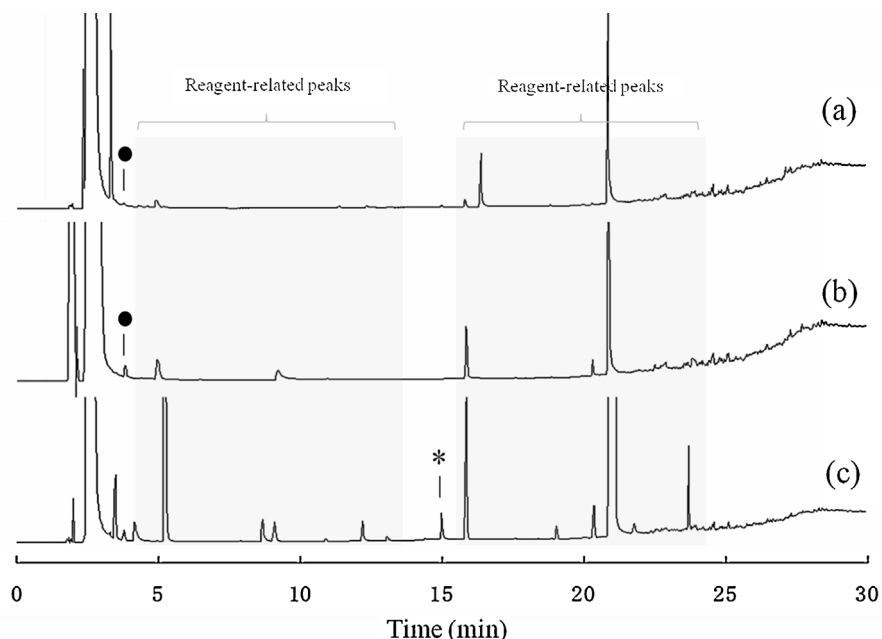


Fig. 1. Chromatograms of a standard methanol solution of 200 mg/L methacrylic acid obtained by a GC/MS at 330 °C in the presence of: (a) TMSH (0.2 mol/L), (b) TMAH (25 wt.%) and (c) TBAH (40 wt.%). Peaks: (●) methyl methacrylate; (*) butyl methacrylate.

et al. [14] and micellar electrokinetic capillary electrophoresis by Butler–Roberts and Eash [15]. Sollinger et al. [16] determined MA in ambient air after derivatization with methyl formate by gas chromatography–mass spectrometry (GC/MS). Pyrolysis-trapping technique coupled with gas chromatography or high–performance liquid chromatography was employed to determinate residual MA monomer in polymer samples [17]. Moreover, MA was also analyzed by high–performance liquid chromatography (HPLC) after extraction [18] or isotope derivatization [19]. However, there are few studies about the determination of MA in food simulants. Recently, Lai et al. [20] proposed a GC/MS method combined with purging and trapping sampling for the determination of migra-

tion amounts of 16 monomers including acrylates and styrenes in food contact materials. Unfortunately, the method was not applicable for the determination of MA in aqueous food simulants due to its high polarity. Furthermore, the above methods are not only time–wasting with laborious procedures but also solvent–consuming, thus they are not suitable for the rapid screening analysis of samples in bulks. Therefore, a rapid and effective method to determine MA in food simulants is highly desirable.

Pyrolytic methylation–gas chromatography technique was proposed by Robb and Westbrook [21] for direct methylation of organic compounds containing acidic protons in a hot injector block of GC using tetramethylammonium hydroxide (TMAH) and further

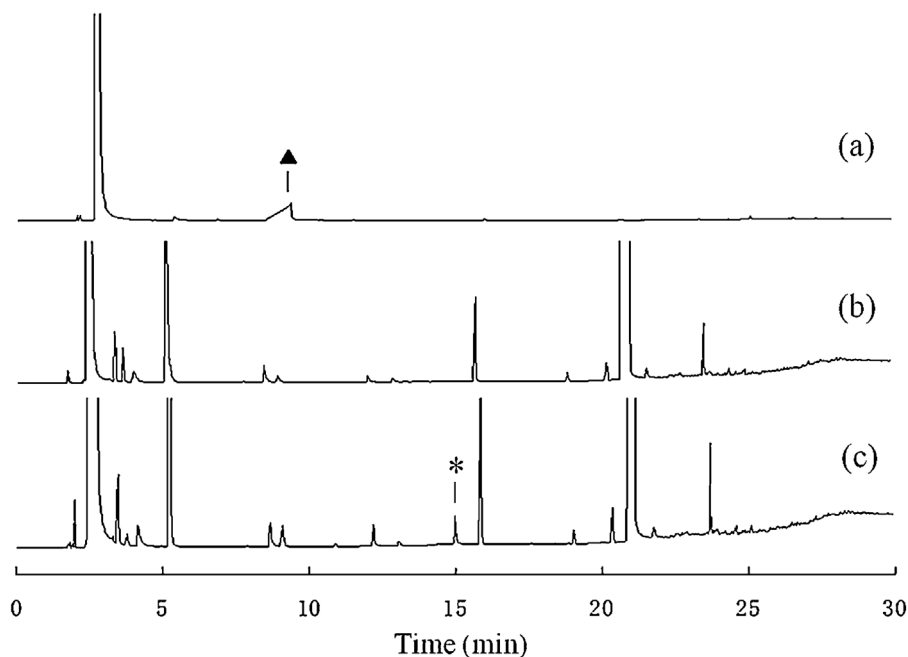


Fig. 2. Chromatograms of standard methanol solutions of methacrylic acid obtained by a GC/MS at 330 °C: (a) without addition of TBAH (40 wt.%), (b) individual TBAH (40 wt.%), and (c) in the presence of TBAH (40 wt.%). Peaks: (▲) methacrylic acid; (*) butyl methacrylate.

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