Atmospheric pressure photo-Ionization as a useful ion source for LC-MS of photoinitiators used in UV-curable inks

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Introduction

UV-curable inks are more and more important for printing food packaging. UV curing has several advantages compared with the conventional thermal curing. The possible absence of solvents reduces the release of volatile organic compounds (VOC). Additionally the use of UV radiators at ambient temperatures reduces the energy consumption significantly. Hence, due to the lack of photoactive moieties of most of the useable monomers, photoinitiators need to be used. Most of these substances are not incorporated into the polymer chain during curing process. Thus, they have a migration potential even in fully cured ink layers. The normally used photoinitiators are generally not sufficient toxicologically evaluated. Therefore migration into food should not occur and none of the substances should be detectable at a detection limit of 10 µg kg^{-1} food. To achieve this low detection limit, sensitive analysis methods are needed. Because of the low thermal and UV stability of the substances gas chromatography can not be used. Also, the "classical" Ionization techniques like Electrospray Ionization (ESI) and Atmospheric Pressure Chemical Ionization (APCI) are not applicable for LC-MS. Within this a new sensitive method for the determination of several photoinitiators in different food matrices and food simulants using the atmospheric pressure photolonization technique for LC-MS was developed.

Method

Sausage was filled into a casing printed with UV-curable inks. The samples were stored for 10 days and 60 days, respectively, at 5 °C. Subsequently the samples were extracted with a mixture of acetonitrile and methylenchloride (1:1, v:v). Aliquotes of the extracts were evaporated under a nitrogen flow to dryness and transferred into 95% ethanol: The 95% ethanol solutions were analyzed using a Synergy Fusion RP 80 HPLC column (20 x 2 mm, 2.5 µm) in combination with a Thermo Finnigan TSQ Quantum Ultra mass spectrometer in SRM-Mode. HPLC-Conditions: Solvent A: Methanol; Solvent B: 5 mM NH_4Ac; SRM-Conditions: Substance Transition: Irgacure 379 381.1 -> 190.1, TPO-L 317.0 -> 147.0, CPTX305.0 -> 263.0.

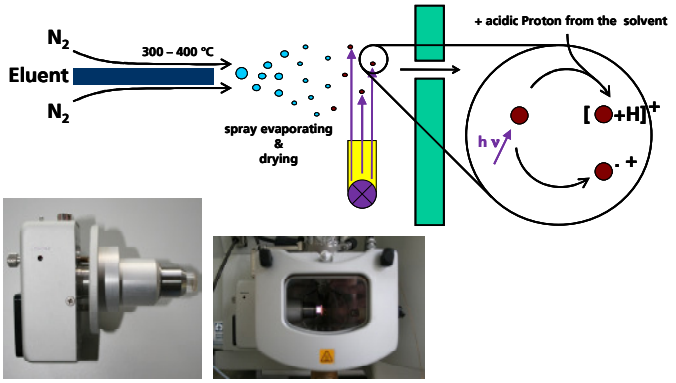

Figure 1: APPI - Ionization mechanism

Results

The ionization principle of the APPI is shown in Figure 1. APPI is using a hollow-cathode lamp instead of a corona discharge needle (APCI) or a charged capillary (ESI) before spray evaporation. Due to the fact, that the wavelength of the applied UV light is near to the absorption maximum of photoactive substances, only the photoinitiators will be ionized. This increases the sensitivity of the APPI detection method towards photoinitiators significantly in comparison to APCI or ESI. Figure 2 shows a comparison between standard calibration curves for the photoinitiators Irgacure 379, TPO-L and CPTX for APCI and APPI. In the case of APPI, the calibration curves for neat stock solutions as well as spiked sausage show a better linear behavior than for APCI. Signal to noise ratios for Irgacure 379 and TPO-L at concentration levels of 5 ppb are shown in Figure 3.
In practice, only hard UV sources (<170 nm) with 10 & 10.6 eV are available. Therefore the ionization of clusters of ethanol, methanol, toluene or acetone (if used as dopand) is possible. Hence, a significant enhancement of sensitivity can be observed for photoactive substances.

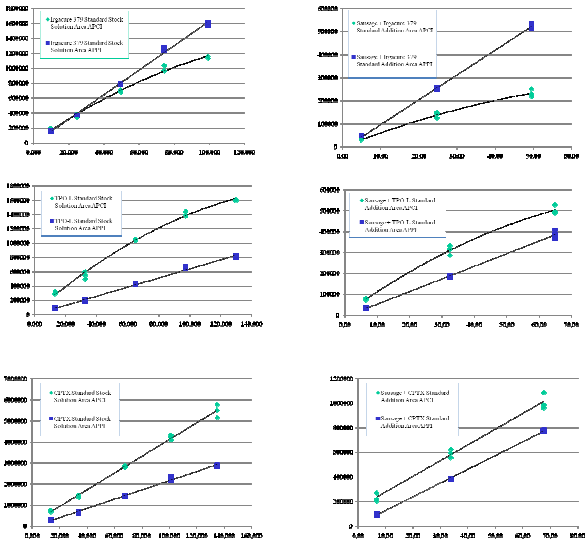

Figure 2: Comparison of standard calibration curves for APPI vs. APCI

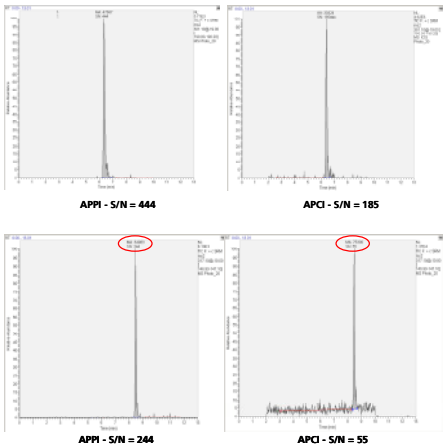

Figure 3: Signal to noise ratios for Irgacure 379 (top) and TPO-L (bottom) at a concentration of 5 ppb

Conclusions

The APPI shows a significant improvement in the signal to noise ratio in comparison to APCI, which results in a significantly lower detection limit even if the peaks have lower peak areas. In addition, the linearity is better compared to APCI. As a consequence, with applied APPI detection method, detection limits of 1 µg kg^{-1} can be achieved. Change of the hollow-cathode lamp can improve the sensitivity.

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