



New validated method for determination of acrylamide in potato chips by planar chromatography



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Introduction

A new planar chromatographic method was developed to monitor the acrylamide content in potato chips. Due to the dynamic minimization principle the current "signal levels" of acrylamide in concerned food like french-fries, roasted coffee or cereals are ranged between 180 and 1000 $\mu\text{g}/\text{kg}$ [1]. The latter value is listed among others for potato chips.

HPTLC method

Application: 6 x 3 mm areas by ATS 4 (CAMAG)
4 μL dansyl hydrazine, 20 μL sample

Stationary phase HPTLC glass plate silica gel 60
20 x 10 cm (Merck, Art. No. 1.05641)

Derivatization: 20 min at 190 °C on TLC Plate Heater 3 (CAMAG)

Mobile phase: Ethyl acetate

Development: TTC (CAMAG); migration distance 80 mm

Detection: Fluorescence measurement at 366/>400 nm by TLC Scanner 3 (CAMAG) after fluorescence stabilization with PPG 2000

Online MS: By ChromeXtract (ChromAn) coupled with HP 1100 pump (Agilent) and Q-MS VG platform II (Micromass); extraction solvent: methanol - ammonium formiate buffer (0.01 M, pH 4.0 + 2 % MeOH) 95:5 (v/v)

Results and discussion

The high water solubility of acrylamide (AA), its high reactivity and the lack of a chromophor group are demanding for analysis. Thus, potato chips were extracted with acetonitrile by accelerated solvent extraction (ASE) to streamline the analysis (short extraction times, low solvent use). Then, an in situ pre-chromatographic derivatization (overspotting) of the AA starting zones with dansyl hydrazine was performed to increase the selectivity and sensitivity of detection, followed by a heating step.

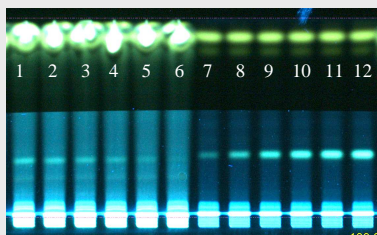
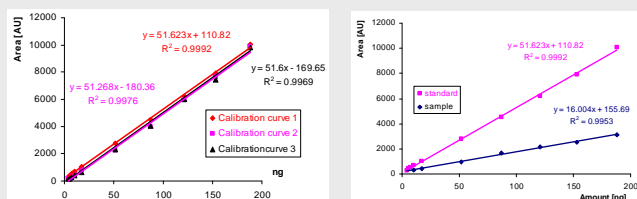


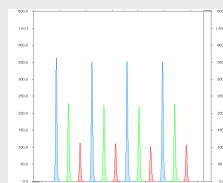
Plate image (UV 366 nm) of extracts from potato chips (track 1-6) spiked in the working range between 100 and 1880 $\mu\text{g}/\text{kg}$ and the respective standard calibration (track 7-12)

The limit of detection (LOD, S/N 3) was 6 ng/zone and in matrix 55 $\mu\text{g}/\text{kg}$; the limit of quantification (LOQ, S/N 9) was 10 ng/zone and in matrix 104 $\mu\text{g}/\text{kg}$. The external calibration - also on different plates - was excellent, however, a systematic error was evident if the external calibrations with and without matrix were compared. The derivatization yield was reduced by matrix and hence a calibration with matrix is generally recommended.



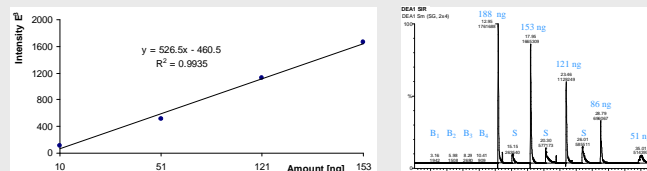
Comparison of calibration curves (left) obtained on different plates and (right) without matrix (pink) and with matrix (blue) in the working range 100-1880 $\mu\text{g}/\text{kg}$.

The repeatabilities of the analysis of the same potato chips sample (RSD, $n=4$, peak area) were $\pm 1.4\%$ (1884 $\mu\text{g}/\text{kg}$), $\pm 1.2\%$ (1211 $\mu\text{g}/\text{kg}$) and $\pm 2.0\%$ (518 $\mu\text{g}/\text{kg}$). The repeatabilities (RSD, $n=4$) of the analysis of different potato chips samples were $\pm 8.8\%$ (1884 $\mu\text{g}/\text{kg}$), $\pm 6.6\%$ (1211 $\mu\text{g}/\text{kg}$) and $\pm 10.2\%$ (518 $\mu\text{g}/\text{kg}$).



Repeatabilities (RSD) of the in-situ derivatization of the same potato chips sample: $\pm 1.4\%$ at 1884 $\mu\text{g}/\text{kg}$ (blue), $\pm 1.2\%$ at 1211 $\mu\text{g}/\text{kg}$ (green) and $\pm 2.0\%$ at 518 $\mu\text{g}/\text{kg}$ (red)

Positive findings in a potato chips samples were confirmed by HPTLC/ESI-MS. The HPTLC/ESI⁺ mass spectra of dansyl ethyl amide (DEA) were recorded in the SIM mode at m/z 329 [M+Na]⁺.



HPTLC/ESI-MS of DEA in the SIM mode at m/z 329 [M+Na]⁺ (left) calibration; (right) confirmation of positive findings (standards of different amount, blanks B and samples S)

Conclusion

The new HPTLC/FLD-MS method offers a more selective determination and a cost-effective usage of the MS system.

[1] BVL, "Acrylamid in Lebensmitteln", October 2005, www.bvl.bund.de/acrylamid (last access 20.06.2006)

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