



## Assessment of Silymarin Content in Plant Material and Extracts Using HPLC and Raman spectroscopy

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Silymarin is a mixture of flavonolignans from the plant *Silybum marianum* (L.) Gaerth., which derives mainly from its fruits. *S. marianum* has been found to exhibit antioxidant, lipid-lowering, antihypertensive, antidiabetic, antiatherosclerotic, anti-obesity, and hepatoprotective effects. In modern therapy, standardized silymarin products are used. According to the European Pharmacopoeia (Ph. Eur. 11.0), the nominal silymarin content in the dried seeds is not less than 1.5% w/w, while in the refined and quantified milk thistle dry extract, it is within the range of 30-65%.

Therefore, this research work aimed to estimate the silymarin content in wild and cultivated milk thistle fruits as well as in commercially available dry extracts according to the monograph in Ph. Eur. 11.0 and to speed up the analysis by applying rapid quantification methods such as Raman spectroscopy. The Ph. Eur. 11.0 method involves very long and complex sample preparation followed by extensive HPLC analysis.

The obtained HPLC results of the samples of cultivated milk thistle fruits collected throughout several years showed that silymarin content varied within 0.3–1.8% w/w. The same extracts were analyzed using a portable Raman spectrometer, and the collected spectra were assigned and used for building a partial least-squares (PLS) model for quantification, where HPLC was used as a reference technique. The extracts from the wild-growing plants were quantified with the developed model, and the content in all samples was found to be above 1.5% w/w. Furthermore, the dietary supplements containing silymarin-rich dry extract (35% w/w) were quantified both with HPLC and the Raman method, and the obtained results were complementary and met the Pharmacopoeial requirements for silymarin content.

**Keywords:** *Silybum marianum*, quantification, PLS model, chromatography, spectrometry.