Measurement uncertainty is a quantitative indicator of the confidence in the analytical data and describes the range around a reported or experimental result within which the true value can be expected to lie within a defined probability. Several approaches can be used to estimate the measurement uncertainty associated to the analysis of pesticide residues: a) top-down approach where the estimation can be based on default values, the main ways include the Horwitz equation or fit-for-purpose relative standard deviation (FFP-SD); b) bottom - up approach where the estimation is function of the uncertainty sources. As regards bottom - up approach, we have investigated the following contributions: weight of sample, calibration solutions, final volume of sample and intermediate repeatability studies. The commodity/residue combination selected in this study was celery / tau-fluvalinate pesticide.

The tau-fluvalinate is a broad-spectrum insecticide in the pyrethroid class of pesticides. The Maximum Residue Limit (MRL) of tau-fluvalinate in celery has been set at 0.01 mg/kg (Reg. n. 39672005 of the European Parliament and Commission Reg. n. 149/2008). The presented work compares the uncertainty estimated by experimental data using repeated analysis (n = 12) of a real sample and a spiked sample. We have analysed samples of celery containing residues of the pesticide tau-fluvalinate at about 0.1 – 0.5 mg/kg; another sample of celery found free (at 0.01 mg/kg) from residues of the investigated pesticide was fortified at a concentration level (0.1 mg/kg) near the value found in the incurred samples and analysed in 12 replicates. The quantification of tau-fluvalinate residues in celery was performed by QuEChERS method (acetaminophen extraction/partitioning and dispersive SPE cleanup) followed by GC-MS/MS (QQQ) determination.

**Results and Discussion**

The sources of uncertainty for the method were identified by constructing a cause-and-effect diagram. The “effect” is the result of the analysis, the “causes” is the main parameters controlling the result. The relationship between the result (or the “measured”) and the parameters (or the “input quantities”) are shown in Eq. (1) and the cause-and-effect diagram is shown in Fig. (1).

\[
C = \frac{A}{A_i} C_v \frac{V}{T} \quad \text{(Eq. 1)}
\]

where
- \( C \) is the concentration of the pesticide in the sample (mg/kg)
- \( A_i \) is the peak Area of the sample extract
- \( A \) is the peak Area of the reference standard
- \( C_v \) is the mass concentration of the reference standard (mg/ml)
- \( V \) is the volume of the sample (ml)
- \( W \) is the weight of the sample (kg)

The uncertainties associated with these parameters will contribute to the overall uncertainty in the final result (C) in accordance with law of propagation of uncertainty (Eq. 2):

\[
\delta C = \sqrt{\left(\frac{\delta A}{A_i} C_v \frac{V}{T}\right)^2 + \left(\frac{\delta A}{A} C_v \frac{V}{T}\right)^2 + \left(\frac{\delta C_v}{C_v} \frac{V}{T}\right)^2 + \left(\frac{\delta V}{V}\right)^2 + \left(\frac{\delta W}{W}\right)^2} \quad \text{(Eq. 2)}
\]

Since the Eq. 1 involve only products and quotients, the solution of Eq. 2 is simplified in Eq. 3:

\[
\delta C = \left|\frac{A}{A_i} \frac{C_v}{C_v} \frac{V}{T}\right| \delta C + \left|\frac{A}{A} \frac{C_v}{C_v} \frac{V}{T}\right| \delta C + \left|\frac{C_v}{C_v} \frac{V}{T}\right| \delta C + \left|\frac{V}{V}\right| \delta V + \left|\frac{W}{W}\right| \delta W \quad \text{(Eq. 3)}
\]