Matrix enhancement effect: A blessing or curse for gas chromatography?

Jae-Han Shim[a*], Md. Musfiqur Rahman[a], A. M. Abd El-Aty[a,b]
[a]*Natural Products Chemistry Laboratory, Biotechnology Research Institute, Chonnam National University, 300 Yongbong-dong, Buk-gu, Gwangju 500-757, Republic of Korea*
[b]*Department of Pharmacology, Faculty of Veterinary Medicine, Cairo University, 12211-Giza, Egypt*

E.F.A.B.R
Environment–Friendly Agricultural Bio–Material Research Team

Abstract

The matrix enhancement effect in gas chromatography (GC) has been a problem for the last decade and results in unexpected high recovery. Most efforts, including the use of different types of injectors/matrix simplification procedures, and further clean-up associated with removing this effect has focused on equalizing the response of the standard in the solvent and matrix. However, after eliminating the matrix enhancement effect, the sensitivity of GC remained unchanged. But, GC sensitivity can be increased by utilizing this matrix effect originating from a matrix matched standard. Very few studies have highlighted utilizing the matrix effect but have rather advocated eliminating it. Analyte protectants (3-ethoxy-1, 2-propanediol, gulonolactone and sorbitol) have been introduced as an alternative for GC-mass spectroscopy (GC-MS) (not examined for other GC detectors), as they equalize the response without removing the matrix effect, and, hence, increase sensitivity. Versatile applications of analyte protectants are not observed in practice. The European guidelines recommend the use of matrix-matched standard calibration for residue measurements. As a result, numerous applications are available for matrix-matched standards that compensate for the matrix effect. Moreover, the matrices (among them pepper leaf matrix) act as a protectant for thermolabile analytes in some cases. A lower detection limit should be achieved to comply with the maximum residue limits. Therefore, the matrix enhancement effect, which is considered a problem, can play an important role in lowering the detection limit by increasing the transfer of analyte from the injection port to the detector.

Keywords: Gas chromatography, matrix effect, sensitivity, analyte protectants, signal enhancement, thermal protection.

Introduction

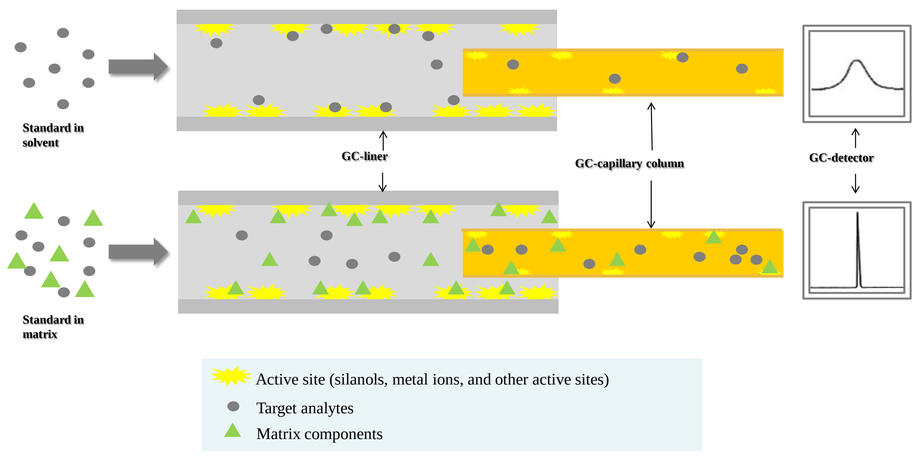


Fig. 1. Schematic flow for the matrix enhancement effect.

- Matrix enhancement effect (MEE) provided unexpected high recovery in GC analysis.
- Eliminating the MEE does not improve the sensitivity of GC analysis.
- The sensitivity of gas chromatography can be increased using matrix-matched standard.
- Some matrices could act as a protectant for thermolabile analytes.
- We propose that pepper leaf matrix could be a promising natural analyte protectant.

Objectives

The aim of this review was to investigate the common problems in gas chromatography, utilization of matrix enhancement effect for more sensitive gas chromatography analysis, and introduce pepper leaf matrix as a promising natural analyte protectant for thermolabile analytes

Problems in gas chromatography

✓ **GC system (Injection port, capillary column, and detector)**

- **Not inert**
- **Have many active sites**

✓ **Causes**

- **Loss of analytes** → Unacceptable recovery percentage
- **Peak alteration** → Difficult to identify and integrate
- **Poor peak shape & peak tailing** → Higher detection limit
- **Standard decomposition** → Impossible to detect

Loss of analyte

❖ **Unacceptable recovery percentage (>120%) when compared with solvent calibration due to loss of analyte**

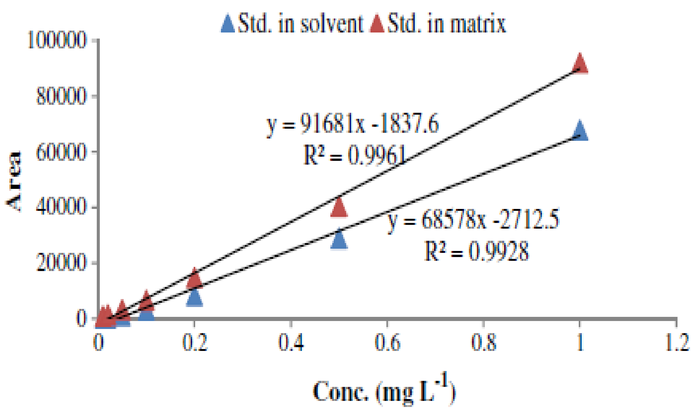
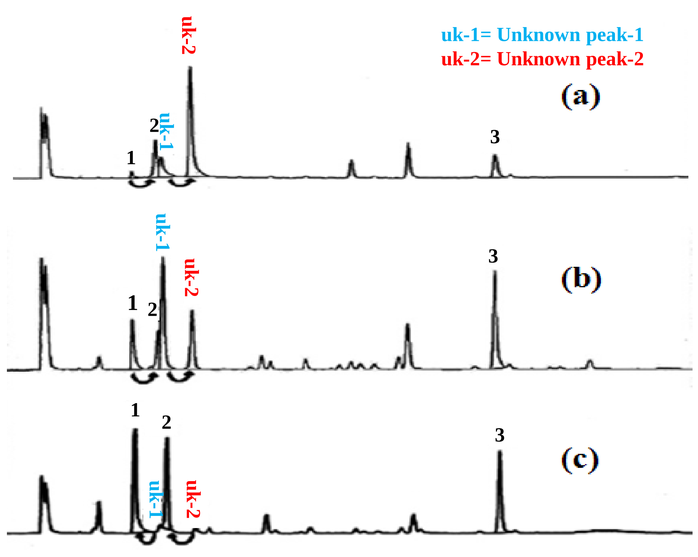


Fig. 2. Comparison between solvent and matrix calibration

Peak alteration



1: terbufoxon sulfoxide, 2: terbufos sulfoxide, 3: terbufoxon sulfone

Fig. 3. Terbufos metabolites mixture (5 ppm) in a) solvent; b) pepper matrix; and c) pepper leaf matrix.

Poor peak shape & tailing

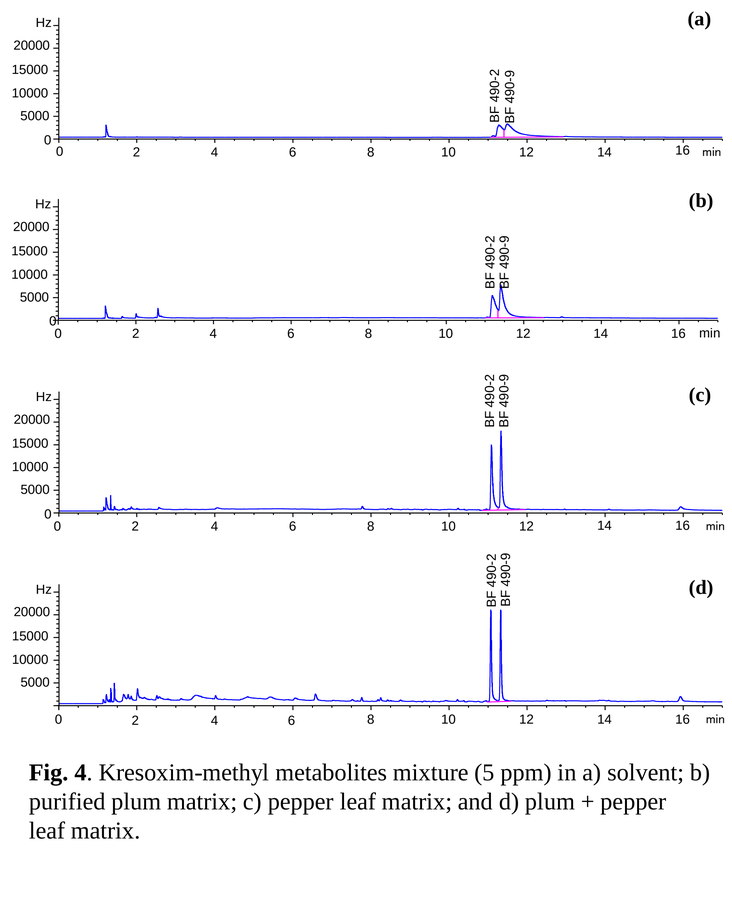


Fig. 4. Kresoxim-methyl metabolites mixture (5 ppm) in a) solvent; b) purified plum matrix; c) pepper leaf matrix; and d) plum + pepper leaf matrix.

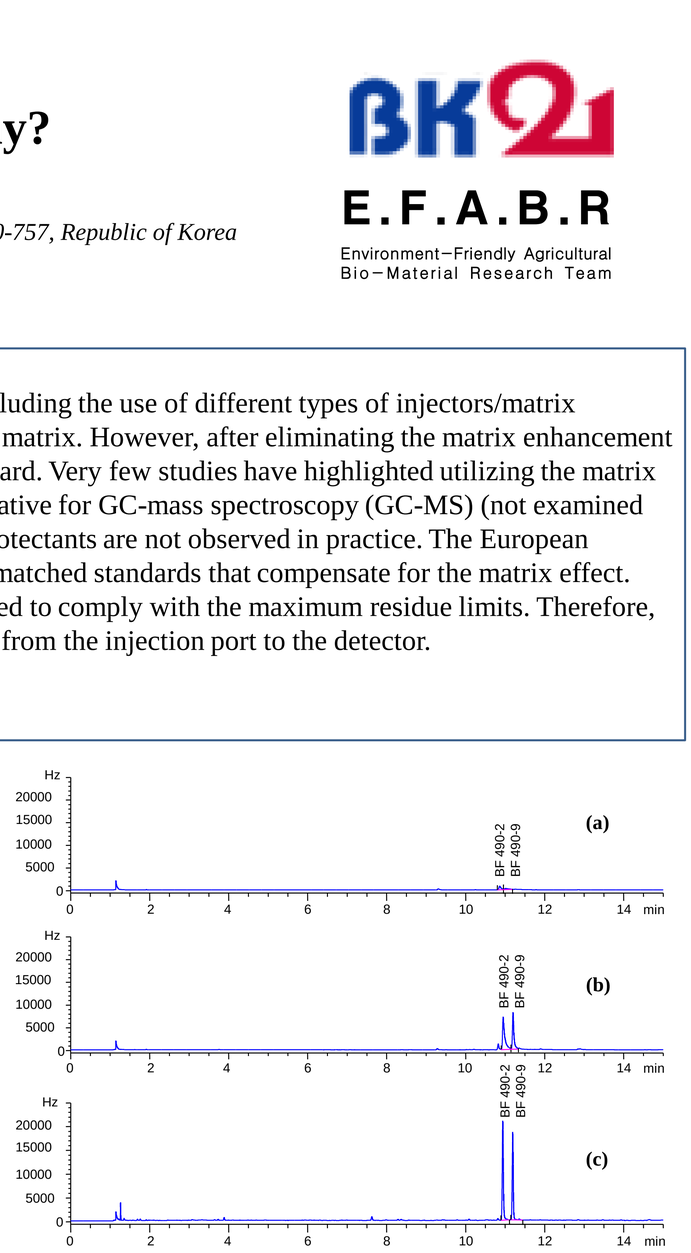


Fig. 5. GC-μECD chromatograms of BF 490-2 (9 ppm) and BF 490-9 (5 ppm) std. mixture in (a) solvent; (b) pear matrix, and (c) pear and pepper leaf matrix.

Standard decomposition

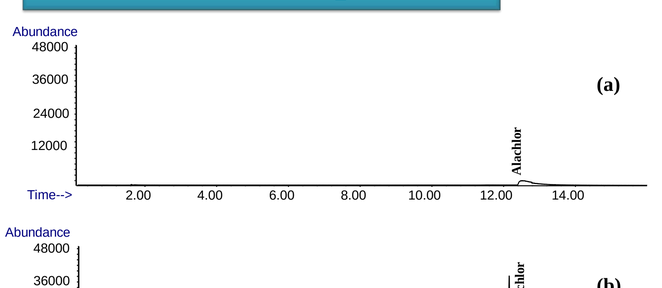


Fig. 6. GC/MS chromatograms of alachlor (5 ppm) in (a) solvent; and (b) pepper leaf matrix.

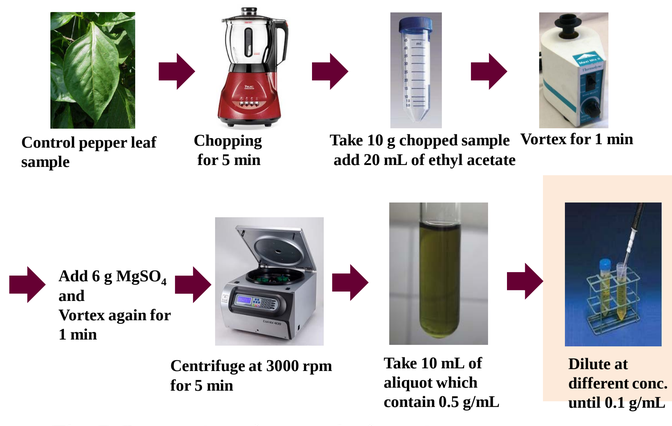


Fig. 7. Preparation of pepper leaf matrix

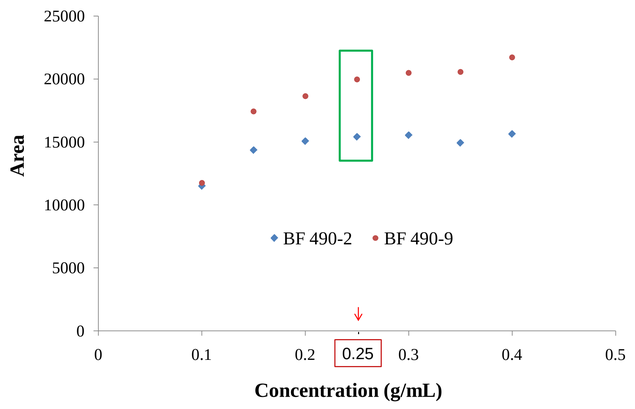


Fig. 8. Responses of BF490-2 and BF490-9 with different concentration of pepper leaf matrix.

Conclusions

A sharp, narrow, and sensitive peak is a pre-condition for a sensitive GC analysis. Therefore, a protectant is needed to protect the analyte from any type of distortion for integration and to prevent overestimation. Existing solutions do not overcome these problems completely due to limitations. As the matrix enhancement problem originated from matrix components, its solution should come from similar components. Finally, the matrix enhancement effect will be a blessing for GC only when types and concentration of matrix can be optimized for a particular pesticide so that it can act as a natural analyte protectant.

Homepage: http://altair.chonnam.ac.kr/~jhshim Email: jhshim@jnu.ac.kr