WHICH ANALYTICAL TECHNIQUES CAN REDUCE MATRIX EFFECTS IN LC-MS ANALYSIS

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ABSTRACT

Matrix effects might exert a detrimental impact on important method parameters (analytical limits, linearity, accuracy, and precision). Ion suppression or enhancement appears as a kind of matrix effect specifically linked to mass spectrometry that probably represents one of the main sources of pitfalls in LC–MS. The negative influence of matrix effects from the testing material influences significantly the sensitivity and the selectivity of the measurements. Hence, matrix effects need to be evaluated and examined during method validation in order to achieve a consistent quantification. In this survey various analytical techniques are applied to investigate ways of eliminating these disturbing matrix effects.

Applying different analytical techniques resulted in some cases to an improvement of the signal to noise ratio and selectivity retrieving the performance of the LC–MS and reducing the negative effects of these phenomena.

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INTRODUCTION

Matrix effects (ME) are responsible for poor and inaccurate data in quantitative analysis causing significant effects to reproducibility, linearity, and accuracy of the method. In the recent years, rapid developments in the introduction of new mass spectrometers and in the advancement and augmentation of the technology (ion detection and mass analyzers) have offered more capabilities in solving challenging analytical tasks.

Our aim in the present work was to apply different analytical techniques in order to evaluate the occurrence of ME in LC-MS methods for the analysis of:

- coccidiostats in compound feed
- β-agonists in bovine hair
- & phenylbutazone in equine muscle.

Mass analyzers of high resolution mass spectrometry (HRMS), such as, Orbitrap technology and low resolution, such as, triple stage quadrupole together with ion mobility spectrometry (IMS) were the main analytical platforms used for this experimental design.

MATERIALS AND METHODS

The selection of the compounds and matrices analysed was based on already observed variation in the analysis. Sample preparation and LC conditions remain the same in order to compare the data mainly based only on the different detection technique of each instrument. The detection techniques applied were:

- QTRAP 6500 in MS/MS (Q2 MS^2)
- QTRAP 6500 in MS^3 (Q2 MS^3)
- QTRAP 6500 with Selexion Differential Ion Mobility (SI) with and without modifier
- Q-Exactive in full scan (FS) accurate mass at different resolutions (17.5K, 35K, 70K and 140K)
- Q-Exactive (Qexa) in MS/MS (TMS^2) at different resolutions (17.5K, 35K, 70K and 140K) &
- Exactive in FS at resolution of 50K
- TQS in MS/MS (TQS MS^2).

Replicates of 10 different samples were analysed as such and including fortification with the analytes before and after the extraction. Based on these results the matrix effects (ME), recovery (RE), signal to noise ratio (S/N), response factor (RF) and ion ratio (R) were evaluated if applicable.

RESULTS

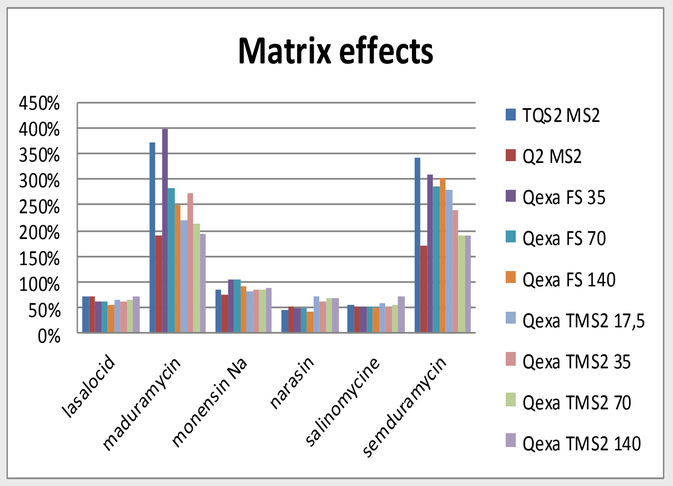

Figure 1. ME for the analysis of coccidiostats in feed.

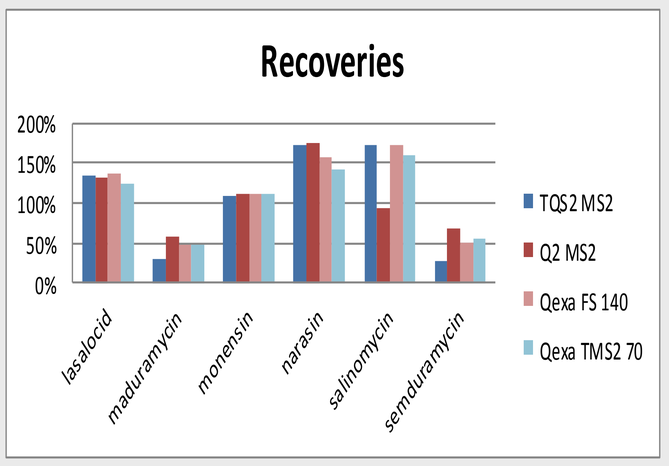

Figure 2. RE for the analysis of of coccidiostats in feed.

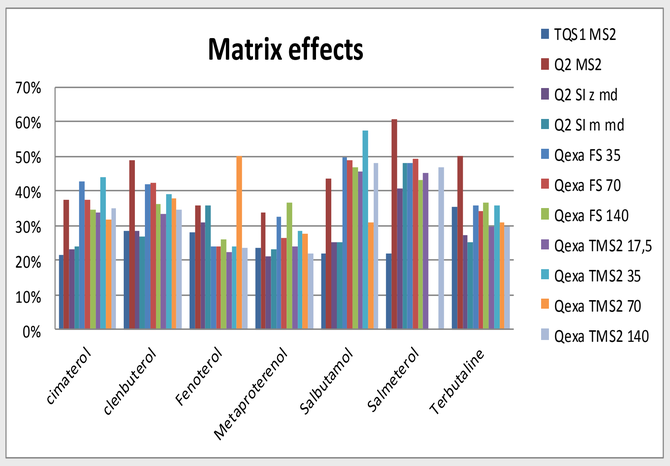

Figure 3. ME for the analysis of β-agonists in hair.

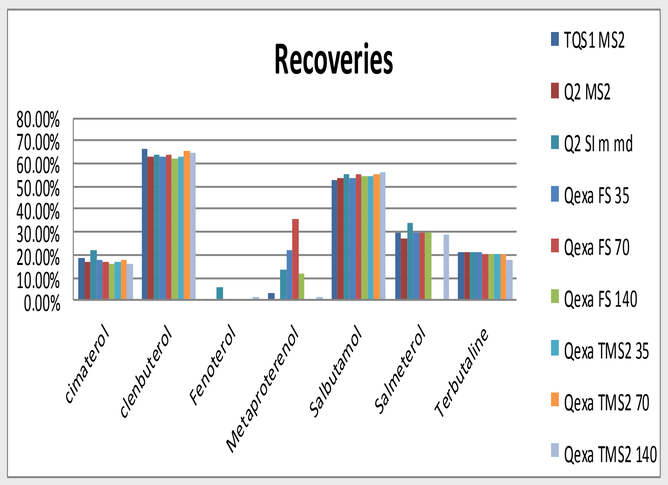

Figure 4. RE for the analysis of β-agonists in hair.

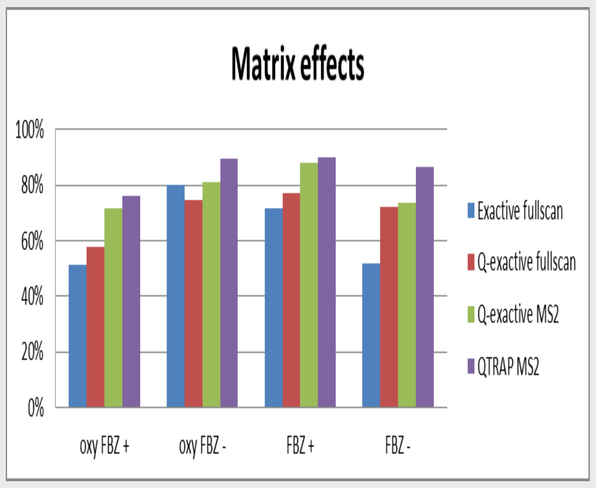

Figure 5. ME for the analysis of phenylbutazone in muscle.

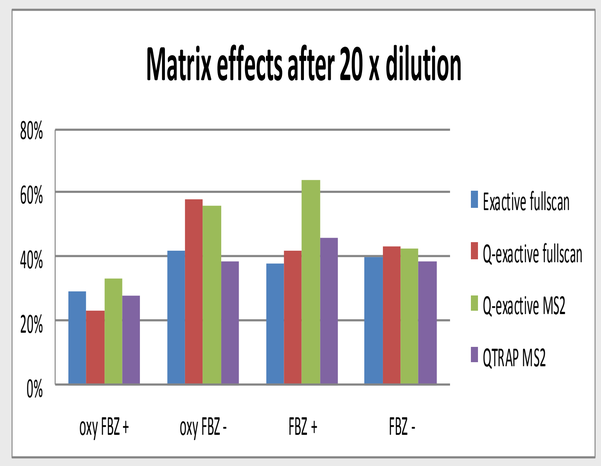

Figure 6. ME for the 20 times diluted extracts.

CONCLUSIONS

Matrix effect is a very frequent issue in multi-analyte LC-MS based analysis and the magnitude is essential to be minimized. Thus, the application of different analytical techniques was evaluated.

- It seems that there is no exclusive analytical technique that can eliminate the matrix effects.
- Generally more improved results appear by conducting the analysis in MS^2 mode and HRMS MS^2.
- Dilution steps and changing ionization modes can have an effective impact.
- A strategy in order to avoid matrix effects is not straightforward and there is a strong correlation between the group of analytes and type of matrix selected for the analysis.

REFERENCES

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