Matrix effects on analysis of multi-pesticide residues in tobacco by LC-MS/MS and GC-MS

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Background

* Study of multi-pesticide residues analytical method based on LC-MS/MS and GC-MS

* QuEChERS method for sample preparation

* API 4000/ESI$^+$ for LC-MS/MS

* 3 types of tobacco matrixes

* 73 analytes covered by LC-MS/MS

* Calibration following matrix matched standard solutions *vs* standard solutions in acetonitrile

Contents

* **Contributions of different tobacco types to matrix effects**

* **Influences from dilution times to responses of matrix matched standard solution**
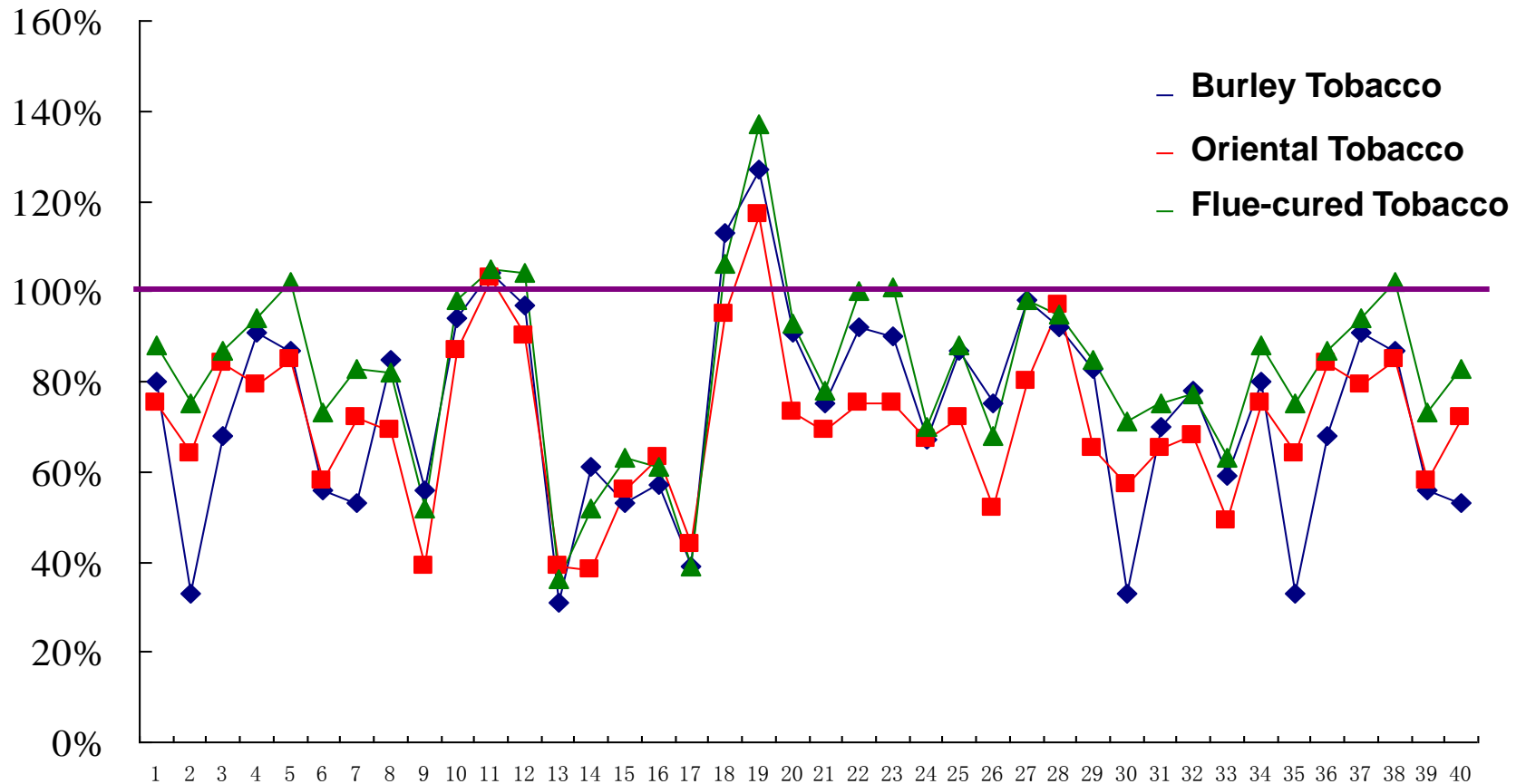
* **Moisture content of the sample and matrix effects**

Contributions of different tobacco types to matrix effects

Experimental

* 40 pesticides

* Matrix Matched Standard Solution in different tobacco types

* Standard Solution in acetonitrile with same concentrations

* Compare the responses in same detection conditions

Contributions of different tobacco types to matrix effects

Relative intensities with standard solution from different tobacco types

Contributions of different tobacco types to matrix effects

Conclusion

* Matrix effects cause responses of most analytes decrease

* For some analytes, matrix effects also cause increase

* Trends of effects from different matrixes to a pesticide are same, but the extents different

* Effects from the same matrix to different analytes are different significantly

* Application of internal standard only to decrease matrix effects is unreasonable

* Application of internal standard combined with matrix matched standard solution should be better than matrix matched standard solution only

Influences from dilution times to responses of matrix matched standard solution

Experimental

* Matrix extract solution diluted with standard solution to acquired different concentrations

* Dilution time=1.67: 6 mL Matrix extract solution + 4 mL standard solution

* Dilution time=2.5: 4 mL Matrix extract solution + 6 mL standard solution

* Dilution time=5: 2 mL Matrix extract solution + 8 mL standard solution

* Concentrations of standard solutions or matrix matched standards are all 1, 2, 10, 20, 50, 100 ppb respectively.

* Responses of standard solutions were set as 1

* Relative responses of diluted matrix solutions were acquired by compared with standard solutions

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Influences from dilution times to responses of matrix matched standard solution

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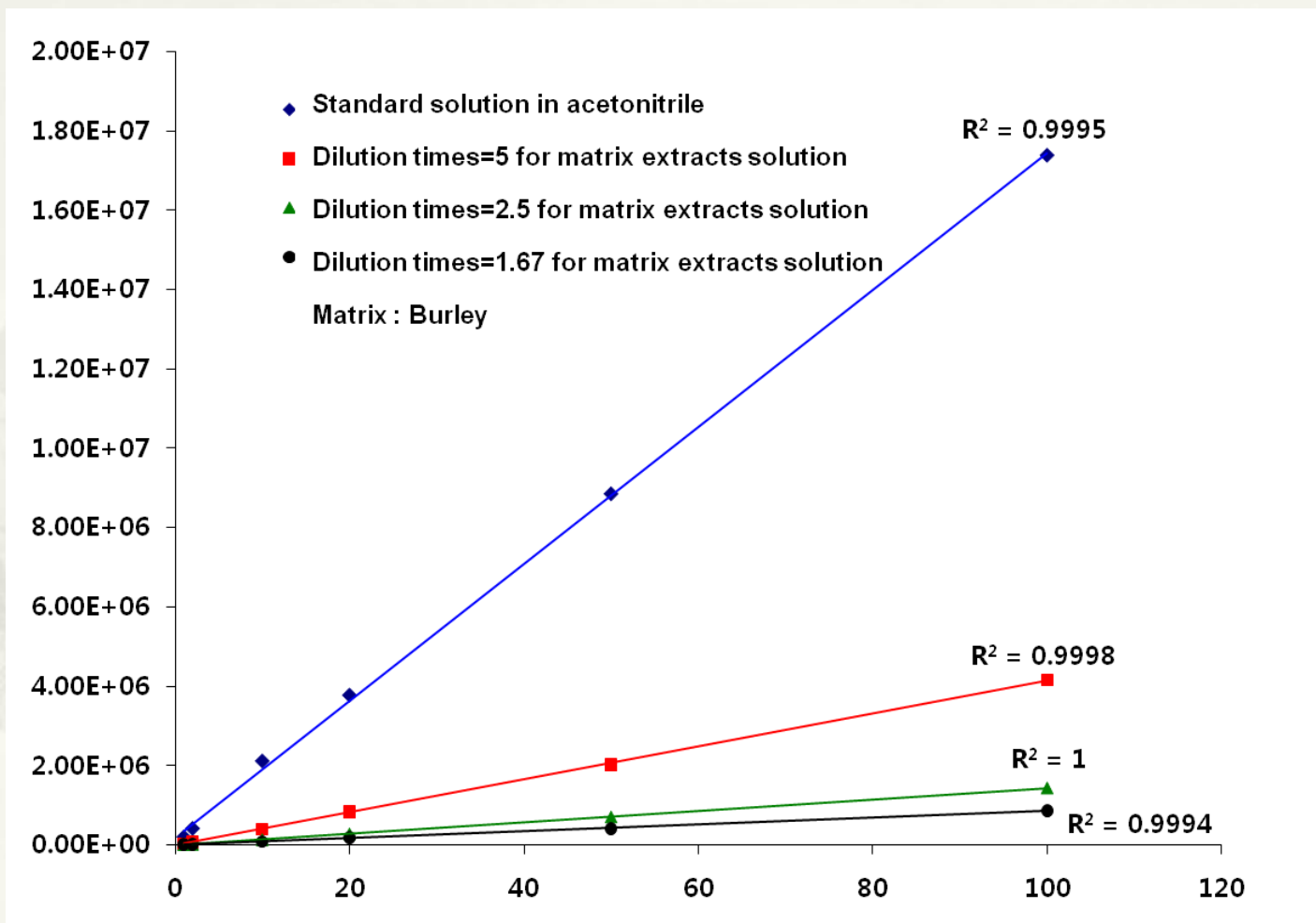
Influences from dilution times to responses of matrix matched standard solution: Burley matrix

C(ppb)	Relative responses compared with standard solution			
	Standard solution	5 times dilution	2.5 times dilution	1.67 times dilution
1	1.00	0.25	0.11	0.09
2	1.00	0.22	0.09	0.06
10	1.00	0.20	0.07	0.04
20	1.00	0.22	0.08	0.05
50	1.00	0.23	0.08	0.05
100	1.00	0.24	0.08	0.05

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Influences from dilution times to responses of matrix matched standard solution: Flue-cured matrix

C(ppb)	Relative responses compared with standard solution			
	Standard solution	5 times dilution	2.5 times dilution	1.67 times dilution
1	1.00	0.43	0.12	0.17
2	1.00	0.33	0.02	0.11
10	1.00	0.28	0.08	0.07
20	1.00	0.31	0.10	0.09
50	1.00	0.32	0.11	0.09
100	1.00	0.33	0.11	0.10

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Influences from dilution times to responses of matrix matched standard solution

Conclusion

* Dilution times of matrix influences the responses significantly.

* Dilution times of matrix influent the linear coefficient hardly

* Decrease of matrix effects by dilution is limited

* Appropriate dilution times should be helpful for both decreasing matrix effects and maintaining enough response intensity
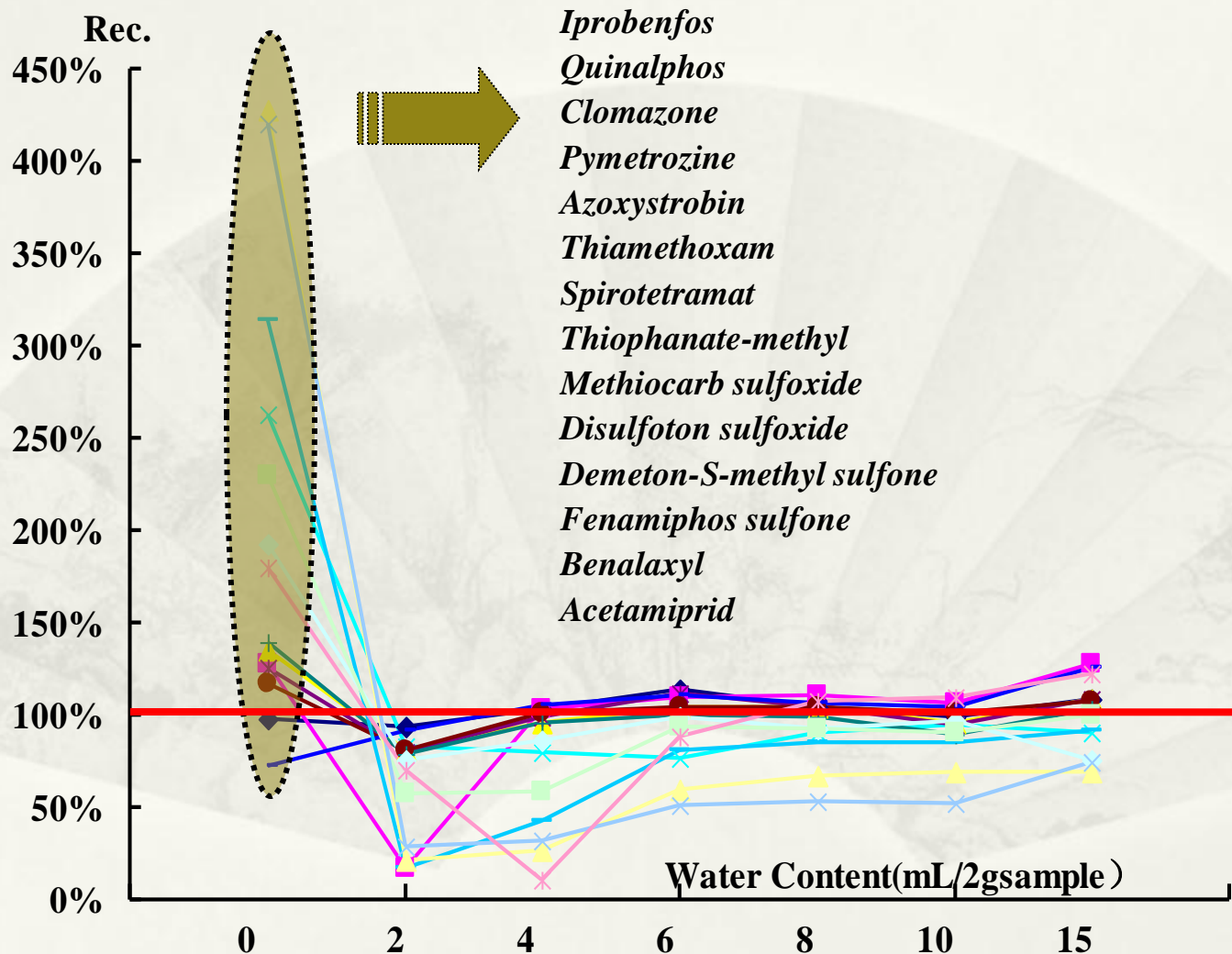
Moisture content of the sample and matrix effects

Experimental

* Blank sample type: flue–cured tobacco (40 mesh)
* Original moisture content: ~11%
* Levels of water addition: 0, 2, 4, 6 ,8, 10, 15 (g/2g sample)
* 14 analytes

   Acetamiprid, Azoxystrobin, Benalaxyl, Clomazone,Demeton-S-methyl sulfone, Disulfoton sulfoxide, Fenamiphos sulfone, Iprobenfos, Methiocarb sulfoxide, Pymetrozine, Quinalphos, Spirotetramat, Thiamethoxam,Thiophanate-methyl

* Sample preparation: homogeneization and the extraction processed below 4 degree
* Sample preparation: QuEChERS method
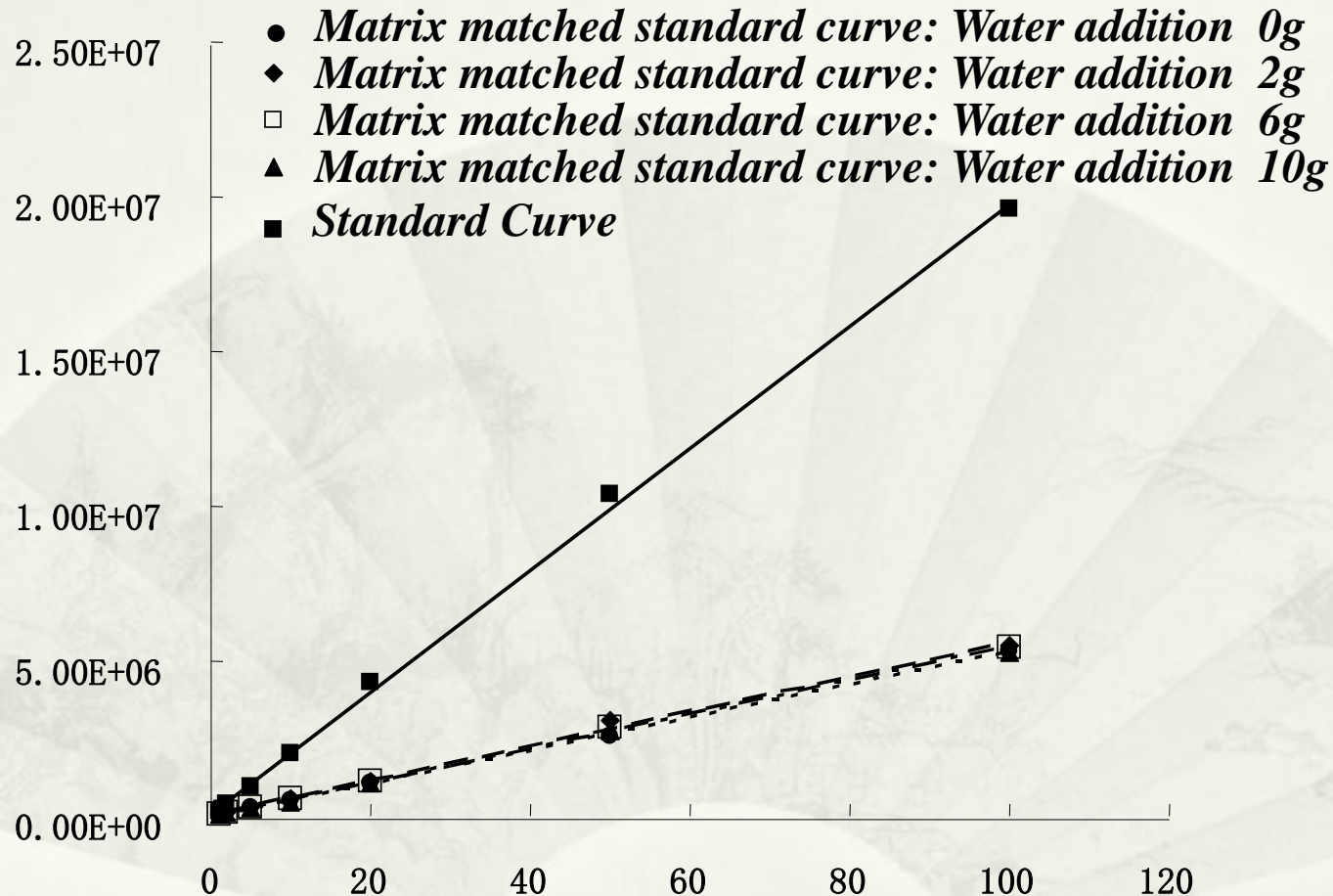* Calibration: Standard solution and matrix matched standard solutions with different moisture contents

Moisture content of the sample and matrix effects

Recoveries of 14 pesticides in tobacco samples with different water contents

Iprobenfos
Quinalphos
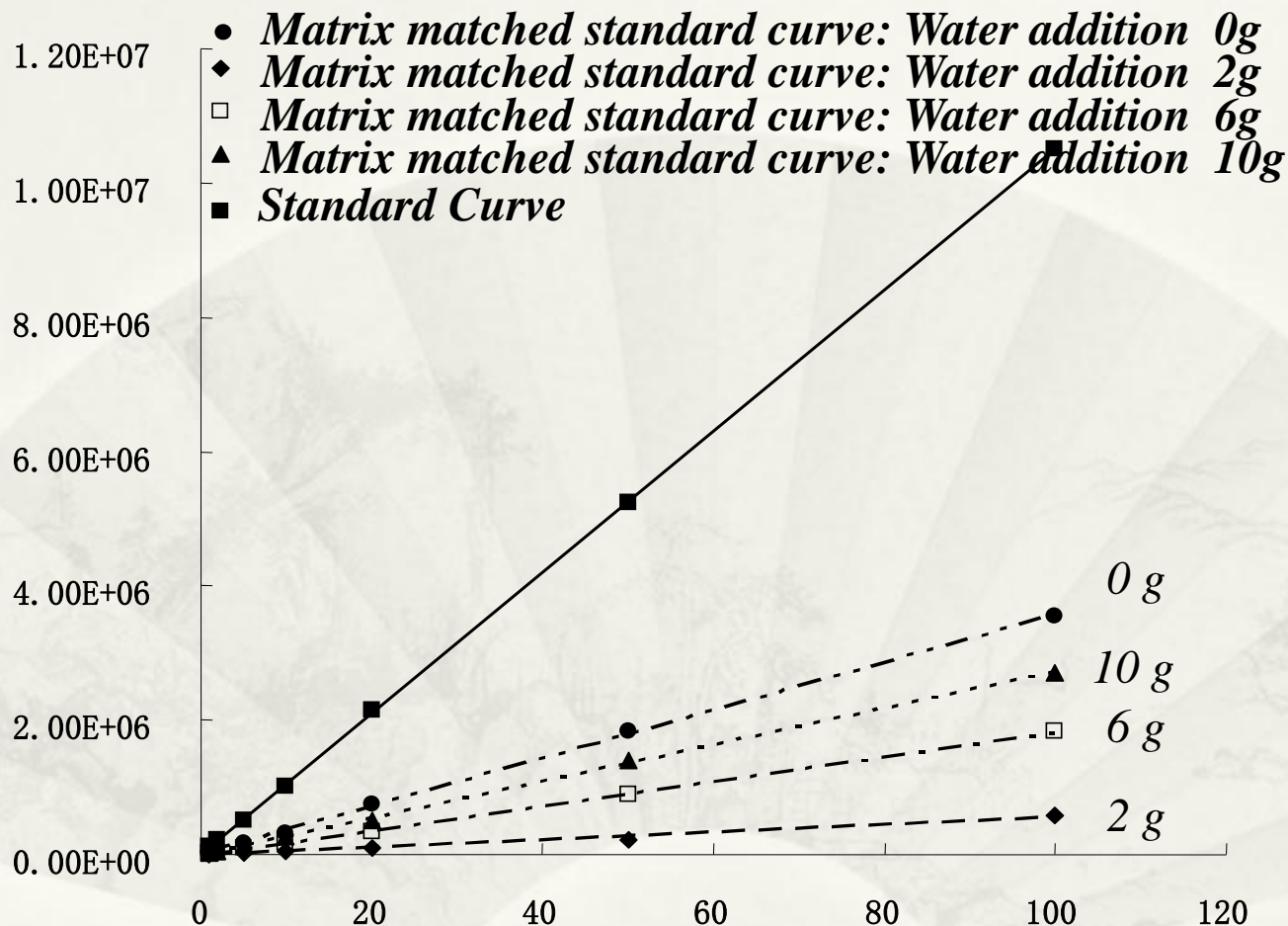*Clomazone*
Pymetrozine
Azoxystrobin
Thiamethoxam
Spirotetramat
Thiophanate-methyl
Methiocarb sulfoxide
Disulfoton sulfoxide
Demeton-S-methyl sulfone
Fenamiphos sulfone
Benalaxyl
Acetamiprid

Moisture content of the sample and matrix effects

- ● *Matrix matched standard curve: Water addition 0g*
- ◆ *Matrix matched standard curve: Water addition 2g*
- □ *Matrix matched standard curve: Water addition 6g*
- ▲ *Matrix matched standard curve: Water addition 10g*
- ■ *Standard Curve*

Standard curve and matrix matched standard curves with different water contents of Disulfoton sulfoxide
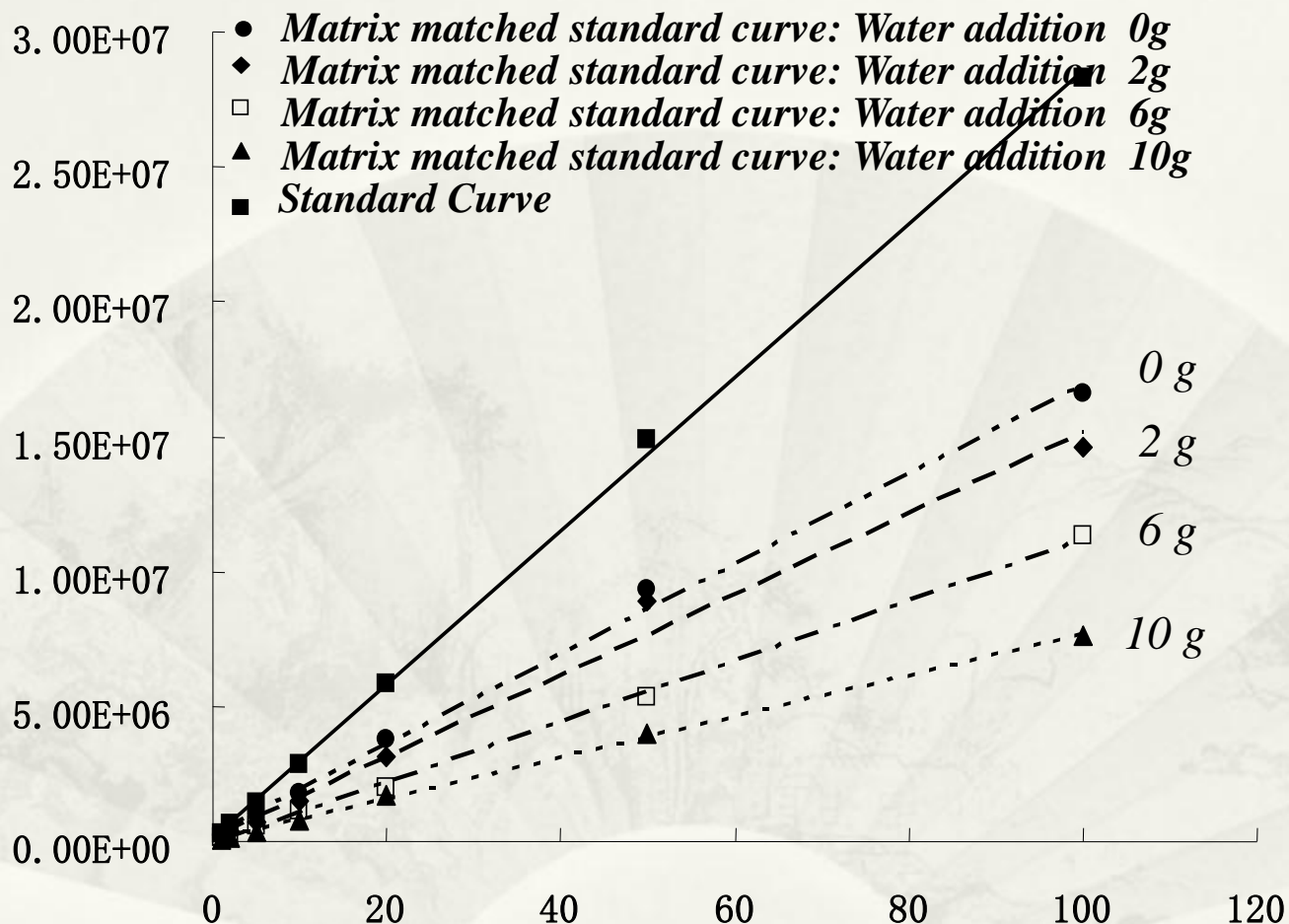
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Moisture content of the sample and matrix effects

- ● **Matrix matched standard curve: Water addition 0g**
- ◆ **Matrix matched standard curve: Water addition 2g**
- □ **Matrix matched standard curve: Water addition 6g**
- ▲ **Matrix matched standard curve: Water addition 10g**
- ■ **Standard Curve**

Standard curve and matrix matched standard curves with different water contents of Iprobenfos

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Moisture content of the sample and matrix effects

● Matrix matched standard curve: Water addition 0g
◆ Matrix matched standard curve: Water addition 2g
□ Matrix matched standard curve: Water addition 6g
▲ Matrix matched standard curve: Water addition 10g
■ Standard Curve

Standard curve and matrix matched standard curves with different water contents of Methiocarb sulfoxide

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Moisture content of the sample and matrix effects

Hypothesis

water addition + inorganic salts

polarity of extract solution

transfer of analytes with different polarities between inorganic and organic phase

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Summary

* Based on QuEChERS and studies mentioned before, a multi-pesticide residue analyzing method for 73 pesticides in tobacco by LC-MS/MS was built.

* Different tobacco types, dilution times in sample preparation and sample moisture contents should influence matrix effects.

* Extract efficiency of analyte may be influenced because of the polarities of extract solution and analyte. While the polarity of extract solution may be changed following the contents of water and inorganic salts

Thank you
for your attention!

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