GC-MS or LC-MS(/MS) - Which Technique is More Essential?

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CRL for Pesticide Residues using Single Residue Methods hosted at the

Chemisches und Veterinäruntersuchungsamt Stuttgart, Schaflandstr. 3/2, 70736 Fellbach, Germany

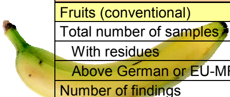
Introduction

LC and GC are indispensable tools in today's pesticide residue analysis. GC, initially in combination with selective detectors and later in combination with mass spectrometry (MS), has unquestionably been the main working horse in pesticide residue laboratories since the late 1960s. In the last decade, however, the booming LC-MS(/MS) technology has managed to also find its firm and indispensable place in the laboratories. With its high sensitivity, selectivity and robustness, LC/MS(/MS) has widely opened the door for the laboratories to significantly expand their scope of target pesticides. In fact, few innovations have had such a profound impact in pesticide residue analysis. Compared to GC-MS, LC-MS/MS instrumentation used to be by far more expensive but this gap has lately been narrowing substantially. LC-MS/MS has the advantage that practically all pesticides are amenable to the separation step in the one or the other way, so the detection step (in particular the ionization) is here the main bottleneck. In GC-MS it is mostly the chromatography part that causes the difficulties. The growing importance of LC-MS/MS is also reflected by the fact that the vast majority of recent pesticide-residue-related publications deal with this technique rather that with GC. Three new methods involving LC-MS/MS (EN 15055 for chlormequat; PrEN 15662 = QuEChERS-method; PrEN 15637 = "ChemElut-method") as well as a technical report with a compilation of LC-MS/MS parameters are being established as EN standards. Another recent trend is to modify classical multiresidue methods in order to ensure their amenability with LC-MS/MS.

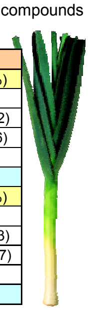
In the initial period, LC-MS/MS has been mainly regarded just as a complementary tool to GC that is predominantly applicable for non GC-amenable or "problematic" pesticides. However, when comparing the pesticide scope covered by GC with that of LC-MS/MS applications it becomes clear that the number of pesticides only amenable to LC-MS/MS is by far much greater than that of pesticides only amenable to GC applications. In addition, for the vast majority of pesticides covered by both techniques LC-MS/MS offers a much better sensitivity than GC-MS. So, clearly LC-MS/MS is today regarded as a more versatile and universal technique [1].

Dataset

In this poster we aim to demonstrate the broader scope of LC-MS/MS compared to GC applications based on our findings from the analysis of approx. 6200 fruit and vegetable samples between 2005 and 2007. The scope of pesticides and metabolites targeted started with ~330 compounds in 2005, and ended with ~540 in 2007.



	2005	2006	2007
Fruits (conventional)	No. (%)	No. (%)	No. (%)
Total number of samples	926	883	942
With residues	867 (94)	838 (95)	868 (92)
Above German or EU-MRL	79 (8.5)	68 (7.7)	53 (5.6)
Number of findings	4453	4711	4002
Number of different pesticides	165	170	153
Vegetables (conventional)	No. (%)	No. (%)	No. (%)
Total number of samples	791	866	899
With residues	631 (80)	736 (85)	742 (83)
Above German or EU-MRL	98 (12)	113 (13.1)	96 (10.7)
Number of findings	2544	3735	3139
Number of different pesticides	158	199	173

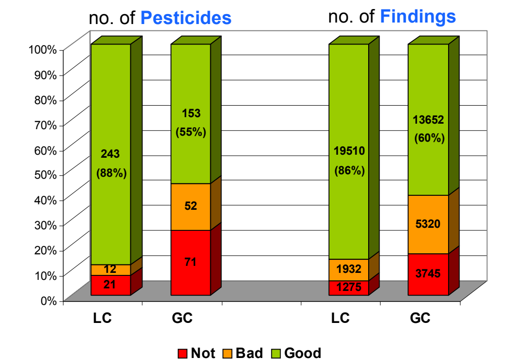


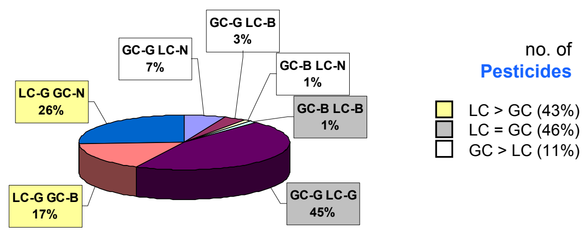
We reviewed the 22584 findings from 5307 conventional samples and the 563 findings from 904 organic samples and the pesticides found were classified into the following 7 groups based on own experience as well as information provided in [1,2]:

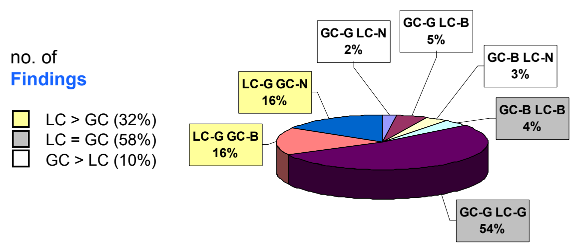
GC good LC not (GC-G LC-N)	**GC good LC bad** (GC-G LC-B)	**GC bad LC not** (GC-B LC-N)	**GC bad LC bad** (GC-B LC-B)	**GC good LC good** (GC-G LC-G)	**GC bad LC good** (LC-G GC-B)	**GC not LC good** (LC-G GC-N)
Endosulfan, sum	Procymidone	Captan/Folpet	Iprodione	Cyprodinil	Dimethoate, Omethoate	Carbendazim, sum
Brompropylate	Vinclozolin	Chlorothalonil	Dicloran	Fludioxonil	Triadimefon, Triadimenol	Imidacloprid
Chlorfenapyr	Fenitrothion	Dicofol	Oxyfluorfen	Chlorpyrifos	Imazalil	Spinosad
Tetradifon	Tolclofos-methyl			Tolylfluanid	Difenoconazole	Thiacloprid
Chlorthal-dimethyl	Acrinathrin			Myclobutanil	Dimethomorph	Fenbutatin oxide
...	...			...	...	...
18 pesticides	9 pesticides	3 pesticides	3 pesticides	126 pesticides	46 pesticides	71 pesticides

Evaluation based on Residue Findings

Out of the 276 pesticides detected in this period 255 (92%) were considered as LC-MS/MS-amenable, 205 (74%) as being GC-MS-amenable and 189 (67%) to both techniques. In other words 71 pesticides (26%) would have been missed if LC-MS/MS was not available compared to just 21 (8%) if GC-MS was not available in the laboratory.







Notes: Compounds included in summed residue definitions were only counted once. The option of using GC following derivatization was not taken into account.

Evaluation based on Toxicity

When just looking at the 50 toxically most critical of the pesticides found (based on ARfD and ADI values), 6 (12%) would have been missed in the absence of GC-MS compared to 14 (28%) in the absence of LC-MS/MS.

Conclusion

Based on these results, LC-MS/MS technology should be seriously considered when establishing or upgrading pesticide residue laboratories, as it covers by far more pesticides than GC, including most of the newly introduced as well as the most toxic ones.

References

1 Alder L., Greulich K., Kempe G. and Vieth B.; Mass Spectr. Reviews, 25 (2006) 838-8652

2 Amtliche Sammlung von Untersuchungsverfahren nach § 64 LFGB